Study on effects of shockwave treatment on PVA films in view of electrical property changes

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Abstract
The shock wave impact effects have been studied on PVA (Poly Vinyl Alcohol), thin films in view of morphological and electrical property changes. The PVA films of thickness around 0.25 mm are subjected to shock waves impact of Mach number around 1.7 to 1.8. The samples are subjected to 0, 25, 50, 100 and 150 numbers of shocks, in a time interval of around 15 s between the shocks. The shock waves are generated with an in-house developed shock tube capable of producing shock waves of Mach number up to 2. The films are further characterized with FTIR, UV–visible spectral analysis for chemical and physical changes and the EDAX, SEM image analysis further confirmed the effects. The trend in the I–V characteristics and the impedance data obtained clearly shows the significant increase in the conductivity of PVA films. Thus, shock wave impact method proves to be another method of treatment of materials and the results obtained promises about the possible electrical applications of PVA films.

1. Introduction

Polyvinyl alcohol (PVA) is a water-soluble biopolymer, with carbon chain backbone and hydroxyl (OH) groups attached to methane carbons. These OH groups are the source of hydrogen bonding and therefore responsible for the formation of polymer [1]. PVA has many interesting physical and chemical properties such as good mechanical strength, water soluble, nontoxic, biodegradable, high dielectric constant etc Therefore, PVA finds many applications in diverse fields. With different kinds of additives or dopants further these properties can be improved or fine-tuned [2–5]. Also, there are fair number of irradiation techniques applied to modify the properties of PVA films [6–9]. The work presented here is another method used to process PVA in view of physical and electrical properties changes.

The work is focused mainly on the shockwave [10] treatment of PVA films. Shock waves or blast waves are a kind of waves which carry the disturbance produced in a medium due to sudden burst in the medium. The effect of shock waves is instantaneous and can cause sudden increase in the temperature, pressure and enthalpy on the surface of the material/medium where the shock wave-front incidents or travels. Shock waves can be produced in laboratory in controlled manner with the help of shock tubes or shock tunnels [10–14]. Generally a shock tube will be consisting of a driver section, a driven section and a thin diaphragm separating the two. When a high pressure is created by any means of compression of the medium in the driver section, the diaphragm ruptures by producing a shock wave in the driven section. The shock produced will move with a supersonic speed which is measured in terms of Mach numbers. Mach number is the ratio of the speed of the object in a medium to the speed of the sound in the medium. Thus Mach 1 refers to the speed of sound in a medium and more will
represent multiples of the speed of the sound. Suitable sensors are attached with shock tube to measure the rupture pressure and the movement of shock wave.

2. Experimental methods

2.1. Sample preparation

The sample films are prepared using 99.9% pure PVA of semi-crystalline powder which was procured from SD Fine Chemicals Ltd, Mumbai. The PVA granules were taken without further purification and the films were prepared using casting evaporation technique. The PVA granules weighing 4 gm was added to 100 ml double distilled water at 50 °C temperature with constant mechanical stirring. The stirring was continued until the PVA gets dissolved in water completely to obtain a clear solution of 4 wt% PVA. The clear solution of PVA is poured into number of glass petri dishes of size 2 inches diameter. Further the samples are dried in hot oven at 50°C until the films get completely dried. A fully dried PVA films were taken directly for shockwave treatment and other characterization.

2.2. Shock tube

The work presented here is carried out with the help of an in-house developed shock tube capable of producing shock waves up to shock Mach number 2. The design, construction and calibration of the device is submitted for publication elsewhere [14]. The photograph of the device used is shown in the figure 1.

The shock tube is made up of 316 grade stainless steel tube having 20 mm inner and 38 mm outer diameter. The driving section is around 400 mm length and driven section is around 500 mm length. Both the driver and driven sections are joined with a threaded cup arrangement system with a handle to load the diaphragm between the sections easily. The system consisting of three shock sensors $S_1$, $S_2$ and $S_3$. Out of which the first sensor ($S_1$) acts as trigger, which give signal to the processor to grab the shock movement data through the other two sensors ($S_2$ and $S_3$). So, when a shock wave propagates through these sensors, we get two peaks plotted on the output window of the software tool developed specifically for this shock tube. From this, we can measure the time delay between the peaks which is nothing but the time taken by the shock wave to travel between these sensors. As the distance between the sensors $S_2$ and $S_3$ is 10 cm fixed, we can calculate the speed of the shockwave and there by the Mach number.

This system is a low pressure operated compared to a large shock tunnels (input pressure of the gas is less than 500 psi or 35 bar) but good enough to produce shock waves of Mach number up to 2.

2.3. Shock wave treatment

PVA films prepared on petri dishes were fixed against a rigid wall in the direction of the axis of the shock wave tube at a distance of around 1 cm from the opening end of the driven section for the shock wave treatment. Shock waves of Mach numbers around 1.7 to 1.8 is generated by the burst of an art paper (90 GSM) diaphragm placed between the driver and driven section, due to the pressure created by a pressure pump attached to the driving section of the shock tube. The process of shock wave generation is repeated by replacing the diaphragm every time. The time between the shocks is maintained around 15 s. The samples were treated with shock waves...
of 0, 25, 50, 100 and 150 impacts. The PVA films were peeled off carefully from the petri-dishes after the treatment with shock wave for further studies/characterization.

2.4. Characterization

The shockwave treated samples were characterized for its physical, chemical and electrical properties. The functional groups involved in the PVA films were identified using Fourier Transform Infrared Spectrophotometer (FTIR) over a wavenumber range 4000–400 cm\(^{-1}\). The Ultraviolet-Visible (UV-Viz) absorption spectrometer analysis were studied within the wavelength range of 190–800 nm for optical characterization of the PVA samples. The Field Emission Scanning Electron Microscopy (FESEM) was used to study the surface morphology of the shock-treated and untreated samples. The EDAX studies were carried out to study the elemental composition of the PVA samples. The DC conductivity properties of the shock-treated PVA samples were studied using at room temperature. And the AC conductivity studies were carried out for a frequency range from 40 Hz to 5 MHz.

3. Results and discussion

3.1. FTIR studies

FTIR spectroscopy was used to assess the functional groups involved in the PVA treated with shockwaves. Figure 2 shows the FTIR spectra of pure and shock wave treated PVA films. Alterations in the important peaks of FTIR spectra clearly support the successful modification in PVA functional groups by shock waves. The spectrum shows some dominating peaks related to the hydroxyl and acetate groups. A broad band observed between \(\sim 3600\) to \(\sim 3200\) cm\(^{-1}\) which is associated with O–H stretching from intermolecular and intra-molecular hydrogen bonding. There is a reduction in the O–H stretching peak after shockwaves treatment comparing with the pristine PVA samples situated at 3300 cm\(^{-1}\). This reduction in hydrogen bonding indicates that the molecules becoming less polar. This means that molecules are less soluble in a polar solvent such as water which indirectly supporting that the material becoming less water soluble after shock waves treatment [5]. The sharp vibrational peak at \(\sim 2900\) and 1700 cm\(^{-1}\) is attributed to the C–H asymmetric stretch from alkyl groups and C=O stretching respectively.

3.1.1. Water solubility test

The inference obtained with the FTIR analysis about the less water solubility was tested with an easy direct measurement technique. The test was carried out for samples of (a) untreated and (b) treated (100 shocks) PVA films against shock waves. These (a) and (b) PVA samples were folded to a cone shape and mounted on a glass conical flask. They were poured with 5 ml of water in to it and a stop clock was switched on simultaneously and waited for the first water drop to fall inside the conical flask. As expected, the water drop from the sample (b) fell down into the conical flask with delayed time of 15–17 s comparing with the case (a) for untreated PVA sample of 8 to 9 s. The test was repeated for two more samples with same number of shocks and found the similar results. Hence, supported the claim on shifting of the PVA samples to less water solubility after the treatment with shock waves.
3.2. UV–vis absorption studies

The careful observation of UV-Vis spectra (figure 3) inside the marked/zoomed area revealed that, the wavelength of absorption spectrum shifted towards higher wavelength regions from untreated PVA sample to higher number shockwaves treated samples. This trend is confirmed by examining the wavelengths corresponding to the highest absorbance value for different colored curves employed to indicate untreated and treated with different shock numbers within the marked area. And found that, there is an appreciable wavelength shift even after considering the error limit of the instrument. This can be attributed as follows. The treatment of PVA samples with shock waves brings systematic modification to its host atomic/molecular environment for electron confinement. These modifications would be mainly of two types named as (a) chain session and (b) crosslinking. Breaking of long polymer molecules after shock wave treatments is clearly depicted in the SEM images given in the manuscript. The rearrangement/breaking/cross linking of PVA molecules due to the shock waves, increases the delocalization in the polymer bonds. This increase in delocalization lowers the energy gap between the highest occupied molecular orbital and the lowest unoccupied anti-bonding orbital. It needs less energy to make the jump and so a longer wavelength of light is absorbed. Thus, as the absorptions move to longer wavelengths the amount of delocalization in the molecule increases [15]. This clearly says that the electron confinement of the samples was modified to exhibit higher delocalization as a response for shockwaves. This could be evidenced from the I-V characteristics of the samples.

3.3. SEM and EDX studies

The surface morphology of the shockwave treated PVA films were studied with FESEM analysis. Figures 4(a)–(c) the surface morphology of the PVA films treated with 0, 100 and 150 shots of shockwaves. Broadly it can be observed that the shockwave treated samples with 100 and 150 shots have changed their morphology after the treatment. The untreated sample show a stable plane surface morhology of the PVA films with no distortions or cracks. The interaction of shockwaves with polymers breaks the long chain molecules and lead for cross linking of them. Such breaking and cross linking of molecules lead to increase of carbon elements per unit volume. This hypothesis is clearly confirmed in the EDX spectra as well. The increment of carbon concentration is evidenced from the increase of carbon peak for the modified samples (B and C).

3.4. Current—voltage characteristics

DC conductivity studies supports the aspects on delocalization of electrons discussed in the UV–vis results after shockwaves treatments. The DC conductivity of treated samples were continuously increased as shown in the figure 5 comparing with the untreated samples due to increase of such delocalization process of electron. Fundamentally, PVA is an insulating material and non-conducting polymer. The untreated samples of them would exhibit lower electrical conductivity for alternating or direct current. However, treated samples showed increase in the rate of current for the same voltage values when DC was applied as shown in the figure 5. This is a clear indication that the sample is being modified to favor the situation to decrease the resistivity values thereby increasing its conductivity. The only possible way of such increment of conductivity trend of an insulating material is due to change in its path of charge conducting environment. This conductivity is due to carbonization of the material due to shock wave treatment where breakage of some bonds of the polymer chain pull number of carbon atoms towards each other which would facilitate for conduction. However, this is not the
only possible way which has leaded the PVA to exhibit such increment in the conductivity trend. There may be some debris of polymers created with some charge on them when shock waves hit the polymer samples. These debris or free radicals move with respect to their opposite polarity when direct current is applied to partially contribute to reduce the higher resistive region.

3.5. Impedence studies
The further evidence on the increase in conductivity was obtained from the impedence analysis for the AC voltages. Cole-Cole plot of the treated samples in the range of 40 Hz to 5 MHz frequency sweeping, is given in the figure 6. Decriment in the half circle of the plots for treated samples with respect to untreated PVA samples indicates the increase of the over all conductivity of the samples.

4. Conclusions
The work presented illustrates the effect of shockwave impact on the PVA films. It is clear from the observations that the shockwave treatment on PVA films has significantly altered the physical and chemical properties of the

**Figure 4.** SEM images and EDX spectra for untreated (A) and treated samples (B & C) with shockwave.

**Figure 5.** Current and Voltage curves for untreated and treated samples with shockwave shots.
material. The FTIR studies shows the reduction in the O-H groups of the PVA molecules which lead to the reduction in the water solubility of the material and the UV–vis spectroscopic analysis confirms the significant shift in the absorption wavelength due to the chain session and delocalisation of main PVA chains. The FESEM analyses confirm the changes in the surface morphology. Further, it is noticed from the IV characteristics and impedance analysis that there is an increase of around 3 times in the overall conductivity of the samples after the shockwave treatment. This confirms that shockwave treatment can be used as a tool for processing of materials and with increasing in conductivity of PVA films promises about the potential applications in the electrical field.

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Figure 6. Cole—Cole plots for untreated and treated samples with shockwaves.