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Shock Wave Treated PVA Films as Alternative Bio Degradable Polymer for Packaging Industry

Thirumalesh[1,3,*], S.P. Raju[4], H.M. Sosmashekharappa[2,†]

[1] *Department of Studies in Physics, Mangalore University, Mangalagangotri – 574 199, Karnataka, India*
[2] *Center for Application of Radioisotopes and Radiation Technology (CARRT), Mangalore University, Mangalagangotri – 574 199, Karnataka, India*
[3] *Departement of Physics, R L Jalappa Institute of Technology, Doddaballapur – 561203, Karnataka, India*
[4]*Departement of Physics, Malnad College of Engineering, Hassan – 573202, Karnataka, India*

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Poly Vinyl Alcohol is being an environmental friendly and having very good mechanical properties, the hydrophilic property of it makes it un-usable for packaging industry as an alternative to environmental hazardous petro chemical based polymers. To increase its water resistant property an indigenous shock wave treatment is tested and it is found that the hydrophilic property reduces significantly. The Poly Vinyl Alcohol films of around 0.25 mm thickness is bombarded with 0, 50, 100 and 150 shock wave impulses, with time gap of around 15 seconds of having Mach number around 1.7 to 1.8. The shock waves are produced with the help of a shock tube which can produce shockwaves with Mach number upto 2. The water resistant property is studied by film dissolve time method and by contact angle measurement. The morphological changes due to shock loading is studied by UV-VIS, EDAX, FTIR methods and the SEM images confirm the structural changes. The reduction in hydrophilic property promises the future of PVA films as biodegradable packaging material.

Keywords: Shock waves, Shock wave interactions, Poly Vinyl Alcohol, PVA.

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1. INTRODUCTION

Shock waves [1] and blast waves are a sort of wave that carries the disruption created by sudden bursting in any medium. The immediate effect of shock waves results in an abrupt increase in pressure, enthalpy and temperature on the surface of the medium on which the wave front of the shockwave impacts [2]. Shock tubes or shock tunnels are used in production of shockwaves in the laboratory in a controlled way [3-6]. In general, a shock tube will consist of two parts. Namely, a driver section(pre-shock side), a driven section(post-shock side), and a thin diaphragm separates the two regions. The pressure in the driver section is increased with the help of a pump by compressing the driving medium. Therefore, the diaphragm breaks down and produces a shockwave in the downstream of driven section. The velocity of the shockwave generated will be more than the velocity of sound in that medium. This supersonic velocity is measured in a unit called Mach number. Mach number is the unit of speed defined as the ratio of object velocity in a medium to the ambient sound velocity. So, Mach-1 corresponds to, the sound velocity in a medium and more reflects multiples of the sound velocity. Appropriate sensors are mounted on the shock tube to assess the shockwave movement and to measure strength of rupture pressure which creates the wave. The present work focuses primarily on the treatment of Poly vinyl alcohol (PVA) films by shockwave in pursuit of increase in the hydrophobic nature.

Poly vinyl alcohol (PVA) is a bio-degradable and water-soluble polymer, in which the hydroxyl(OH) groups hooked up to carbon atoms of methane groups on carbon chain backbone. Such hydroxyl groups forms the origin of bonding between hydrogen atoms and thus responsible for polymer formation[7]. PVA's impressive chemical and physical properties are water-soluble, non-toxic, environmental friendly, good mechanical strength and strong dielectric strength etc. Also, these properties can be further enhanced or tuned by adding compatible dopants [8-11] and we can find good number of attempts in modifying PVA properties with irradiation methods [12-15]. Consequently, PVA has numerous applications in various fields. In pursuit of changes in chemical and physical properties, the analysis discussed here is another approach used for processing PVA. The electrical property changes of PVA films due to shockwave impacts is studied and published elsewhere [16].

2. EXPERIMENTAL TECHNIQUES

2.1 PVA Films Preparation

PVA in semi crystalline powder form of 99.9% pure was obtained from SD Fine Chemicals Ltd., Mumbai, India. 4wt% PVA solution is prepared in 60 °C hot distilled water with continuous stirring for about 5-6 hours. The prepared PVA solution is distributed to 2inch diameter petri dishes and is dried under hot air oven at 50 °C for about 24-30 Hrs to get thin films of PVA samples.

2.2 Shock Tube Setup

The shock tube used for this study is designed and

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[*] thirumalesh.dbp@gmail.com
[†] carrtmu@gmail.com

developed in-house. This is a low pressure manually operated shock-tube type, and has the ability to generate shockwaves of Mach number upto 2. The actual photograph of the shock tube used is given in Fig. 1. The method of construction of the shock tube, its working, calibration and results obtained are discussed in detail and submitted for publication in a reputed journal [6].

The shock tube specifications are as follows. The driving section of the tube is around 400 mm long and the driven section is 500 mm long. The inner and outer diameter of the tube is 20mm and 38 mm respectively. The material of the tube is 316 grade stainless steel. The driving and driven sections of the tube are separated by a diaphragm which is placed in an arrangement having a handle to join and separate the two sections. The diaphragm can be replaced every time in this arrangement easily.

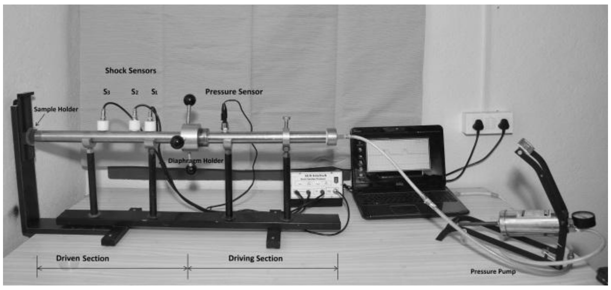


Fig. 1 – Actual photograph of the shock tube setup used in this study

2.3 Shock Wave Treatment

The petri dishes containing the PVA films are placed inside the sample holder attached to the open end of the driven section of the shock tube with a gap of around 10mm between the sample and the shock tube. A leg pump used to inflate the tires of vehicles is used to create a pressure in the driving section. A paper diaphragm of thickness 90GSM can produce shockwaves around 1.7 to 1.8 Mach numbers. The Mach number of the shock wave generated can be found by measuring the time delay between the signals plotted on the computer screen by a ‘shock tube data analyzer’ software specifically developed for this device and by knowing the distance between the sensors. This process is repeated to generate shock waves continuously by replacing the diaphragms. The time interval between the successive shockwave impacts is maintained as not more than 15 seconds. The PVA samples were bombarded with 0, 25, 50, 100 and 150 shock waves impacts.

2.4 Characterization

The PVA samples which are exposed to shock waves are characterized for physical and chemical property changes. The Fourier Transform Infrared Spectrophotometer (FTIR) method was used to know the chemical composition changes over a wave number range of 4000-1500 cm $^{-1}$. For optical characterization of the PVA samples, the Ultraviolet-Visible (UV-Viz) absorption spectrometer analysis was carried out in the wavelength range of 200-500 nm. To know the surface morphology of the samples, FESEM - Field Emission Scanning Electron Microscopic method was used. The EDAX studies were conducted to identify the PVA samples elemental composition. The contact angle measurement was done to study the hydrophilic nature of the samples and an indigenous test was carried out to quantify the water solubility nature for the use of PVA as a packaging material.

3. RESULTS AND DISCUSSION

3.1 UV-Vis Absorption Spectrum Studies

From the UV-Vis spectral analysis (Fig. 2), it is observed that, the wavelength corresponding to the maximum absorption shifting towards longer wavelength side as the number of shock waves impact increases from zero to 150 numbers. This could be observed in the careful study of the readings corresponding to the spectrum in the marked region. This clearly exhibit as the higher delocalization in electron confinements of the PVA samples in response to shockwaves. This tendency is checked by examining the wavelengths referring to the maximum absorbance value for different curves. This reorganization of PVA molecules increases the delocalization of polymer bonds due to the shock waves. The improvement in delocalization decreases the energy difference between the occupied uppermost molecular orbital and the unoccupied lowermost antibonding orbital [17].

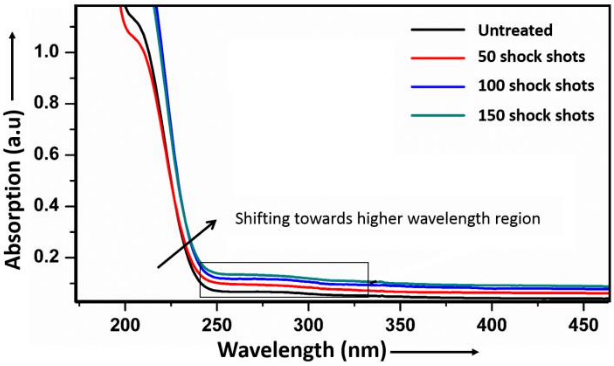


Fig. 2 – UV – Vis spectra of shock treated and untreated PVA samples

Therefore, the energy required to jump between these levels becomes less and thus the wavelength of absorption becomes longer. Therefore, the absorption shift to longer wavelengths as the delocalisation in the PVA molecules rises.

3.2 FTIR Studies

Changes in the main peaks of FTIR spectra (Fig. 3), suggest the effective changes in PVA functional groups by shockwaves. In the FTIR spectra it is observed that, the peak corresponding to the O-H group situated at 3300 cm^{-1} is reduced after shockwave treatment when compared with the pure samples. The decrease in Hydrogen bonding signifies that, the molecules of PVA becoming less polar [17]. This implies that, the solubility of these molecules becomes less in a polar solvent like water.

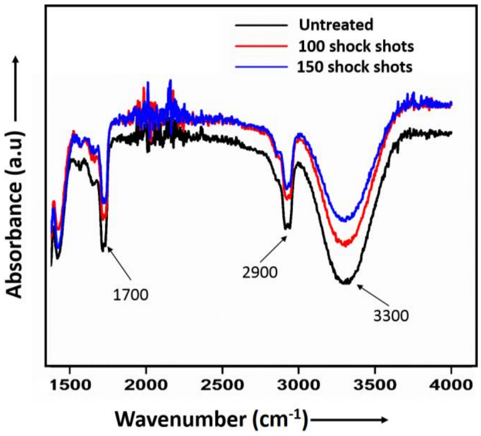


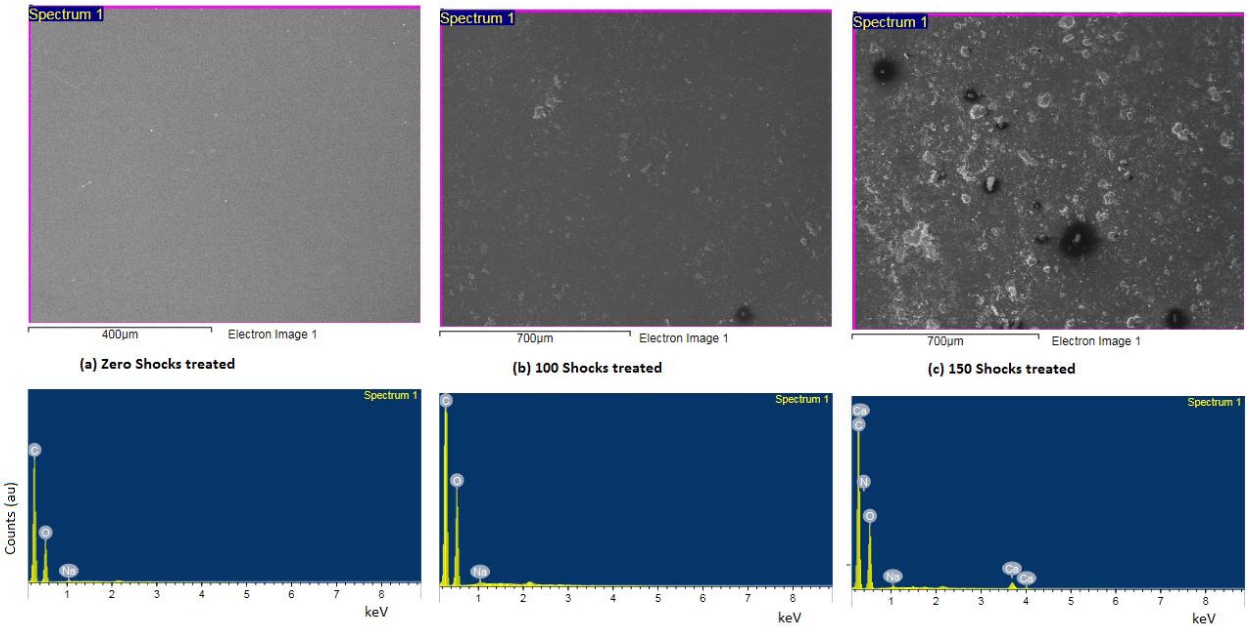
Fig. 3 – FTIR spectra of shock wave treated PVA films

This directly supports the claim of less water solubility of PVA films after treating with shockwaves. Decrease in the width of important Corban related peaks present at 2900 and 1700 for C-H asymmetric stretching and C=O stretching respectively on comparison with treated and untreated samples clearly confirms the carbonization of the samples due to shockwaves effect.

3.3 FESEM and EDAX Studies

SEM images (Fig. 4) for treated samples (B & D) comparing with untreated sample (A) clearly show that the surface of them is sensitive towards shock waves. EDAX spectra given in the same Figure corresponding to A, B & C clearly shows the modification in the samples surface chemistry with respect to the variation in the elemental composition.

Shockwaves interaction with PVA breaks the long polymers molecules and contributes towards the cross-link between them. Such break-up and cross-linking of molecules results in an improvement in carbon content per unit volume. The increase in the carbon concentration peak for the shockwave treated samples in the EDAX spectra is a strong evidence of this observation.



(a) Zero Shocks treated

(b) 100 Shocks treated

(c) 150 Shocks treated

Fig. 4 – SEM images and EDAX spectra of untreated and shock-wave treated samples

3.4 Water Solubility Test

An indigenous technique was used to test the observation received with the FTIR and UV-Vis spectral studies about the hydrophobic or less water solubility of PVA after shock wave treatment. The test was performed for PVA samples of 0.4 mm thick films of same number of shock wave treatments. The sample films were folded to conical shape and placed in a glass funnel which is kept on a conical flask (Fig. 5). A stop clock was turned ON when 1ml of water is poured into it. The time taken for the water to drop into the conical flask after dissolving through the PVA films was recorded. As to support the expectation, the time taken by the water drop to dissolve through the shock wave treated sample was more compared to untreated PVA sample. The test was repeated with the same number of shocks for two more samples and the similar results were found. The average water dissolve time recorded is given in Table 1. Thus, the tabulated values supported the claim that, the PVA samples were become less water soluble after shock-waves treatment.

Fig. 5 – Water solubility test for PVA films

Table 1 – Water solubility test values for various shock treated PVA films

Number of Shock treatment	Time taken by 1 ml water to dissolve through PVA films in seconds
0 (pristine PVA)	102
50 shocks	537
100 shocks	483
150 shocks	499

3.5 Contact Angle Measurement

Contact angle of water for pristine PVA and shock treated PVA samples were measured in order to investigate the hydrophilic or hydrophobic nature of the surfaces of the materials. The material wettability is known to be high for low water contact angles (< 90°) and low wettability for high contact angles (> 90°) [11, 18]. Low water contact angles, in other words, may mean higher hydrophilic nature and high contact angles may mean higher hydrophobic nature of material surfaces.

In good agreement with the previous results, the neat PVA had a very low water contact angle of 24.8° [11]. Whereas, there is a remarkable increased water contact angle for the shock treated PVA films. The hydrophilic level of shock treated films was slightly modified as the number of shock wave impacts increases, as shown in Table 2. The contact angle measurement photographs for untreated samples and shock wave treated samples are given in Fig. 6.

Table 2 – Water contact angle values for various shock treated PVA films

Number of Shock treatment	**Water contact angle**
0 (pristine PVA)	24.8
50 shocks	110.5
100 shocks	95.4
150 shocks	100.7

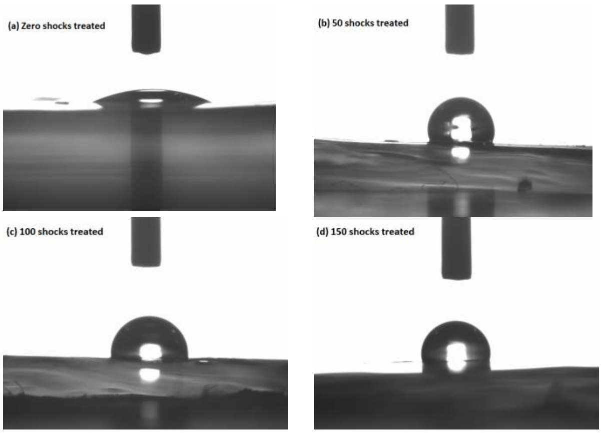


Fig. 6 – Contact angle measurement photographs of the untreated and shock treated PVA films

4. CONCLUSIONS

It is evidenced from the above studies that an increase in water contact angle by 85° and large increase in the water solubility time, in comparison with that of pure PVA films. Thus, the shock treated samples shifted from hydrophilic nature to the hydrophobic. This improvement for PVA films could be associated with the decreased hydroxyl groups in the PVA and increase in carbon content as evidenced by FTIR and EDAX studies. This remarkable shift from hydrophilic to hydrophobic nature of shock treated PVA films promises the future of PVA for the biodegradable environmental friendly polymer as packaging material.

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REFERENCES

1. W. Payman, W.C.F. Shepperd, *Proc. Roy. Soc.* **A186**, 293 (1946).
2. C.S. Kumar, K. Takayama, K.P.J. Reddy, *Shock waves made simple* (Wiley India: 2014).
3. R.J. Stalker, *AIAA Journal* **5** No 12, 2160 (1967).
4. R. Morgan, *Free piston driven expansion tubes: A Handbook of Shock waves*, 603 (Ed. G. Ben-Dor) (Academic Press: New York: 2001).
5. K.P.J. Reddy, N. Sharath, *Curr. Sci.* **104** No 2, 172 (2013)
6. Thirumalesh, S.P. Raju, K Swaroop, H.M. Somashekharappa, *Engg. Reports* (2020).
7. B.P. Balaji, M.V. Madhu, A.K. Sharma, V.V. Rao, *Ionics* **13**, 441 (2007).
8. M. Abdul-Aziz, *Physica B: Condens. Matter.* **406** No 6-7, 1300 (2011).
9. K.G. Vijaya, R. Chandramani, *J. Appl. Sci. Res.* **4** No 11, 1603 (2008).
10. R.F. Bhajantri, V. Ravindrachary, A. Harisha, Vincent Crasta, Suresh P. Nayak, Boja Poojary, *Polymer* **47**, 3591 (2006).
11. Z.W. Abdullah, Y. Dong, *Front. Mater.* **6**, 58 (2019).
12. A. Harisha, V. Ravindrachary, R.F. Bhajantri, Ismayil, Ganesh Sanjeev, Boja Poojary, Dhanadeep Dutta, P.K. Pujarid, *Polym. Degrad. Stabil.* **93**, 1554 (2008).
13. T. Sheelaa, R.F. Bhajantria, V. Ravindrachary, S.G. Rathod, P.K. Pujari, B. Poojary, R. Somashekard, *Radiat. Phys. Chem.* **103**, 45 (2014).
14. Shreedatta H, Ravindrachary V, Praveena SD, Guruswamy B, Sagar RN, Sanjeev G, *AIP Conf. Proc.* **1942**, 110043 (2018).
15. B.K. Mahantesha, V. Ravindrachary, R. Padmakumari et al, *J. Phys: Conf. Ser.* **1172**, 012030 (2019).
16. Thirumalesh, S.P. Raju, Swaroop K., H.M. Somashekharappa, *Mater. Res. Express* **7**, 015344 (2020).
17. W. Kemp, *Organic Spectroscopy* (Palgrave: London: 1991).
18. S G Deshmukh, V. Kheraj, K.J. Karande, A.K. Panchal, R.S. Deshmukh, *Mater. Res. Express* **6**, 084013 (2019).