

Biodegradability Enhancement of Polymer Polylactic Acid (PLA) by using Ultrasonic and Rheological Techniques

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Abstract: In the progressing world of today, there is a lot of use of polymers/plastics in different areas. Research and Development in the field of Polymer industries is expanding steadily. An advance method, Ultrasonic velocity measurement is a very fruitful and resourceful technique that can be adopted for the study of liquids, liquid mixtures and also for Polymer solution mixtures. In this study the acoustical parameters like adiabatic compressibility, acoustic impedance, free length, free energy and relaxation time has been calculated by the measurement of ultrasonic velocity, density and viscosity values at different temperatures (423.15K, 433.15K and 443.15K) and concentrations (0.002, 0.004 and 0.006) of starch blend polylactic acid. After calculating all these parameters, the results of variation and change in properties of polymer solution were observed Also the percentage of degradation through weight loss with time period were studied. All the changes were verified by SEM techniques conclude that the rate of biodegradation depends on polymer structures and environmental conditions like temperatures, pressure, humidity etc.

Keywords: Polymer properties, Acoustical parameters, Molecular interactions, Structural properties, Spectral studies.

Date of Submission: 03-08-2019

Date of acceptance: 14-08-2019

I. INTRODUCTION

During the last decades i.e. post Staudinger times within the 21st century there has been a rapid development of global economy and a great enhancement in the overall population of the world leading to a tremendous consumption of our natural resources [1]. At present the plastic industry is indeed witnessing a shift to more from all petroleum based industrial economy to one that encompasses a broader base of materials which include plant-derived products and fermentation by-products. Plastics and in general polymeric materials provide enhancement to our daily life but at the same time lead to worldwide pollution because to date, they have been designed with little consideration for their ultimate disposability or recyclability. The majority of synthetic polymers are not readily broken down in the environment (common plastics often decompose over hundreds of years). A major build up of these materials result within the environment are often scaring our landscapes, fouling of our beaches and posing a serious hazard to marine life. Polymer materials however derived from natural carbon compounds that can play an important role in helping alleviate many of the environmental cancers. These polymers are biodegradable and renewable and when compared to petroleum products they lead to little contamination [2].

Plastic materials have found wide application in every aspect of life. However, most conventional plastics such as polyethylene, polypropylene, polystyrene, poly (vinyl chloride) are non-biodegradable and their increasing accumulation in the environment has been a threat to the planet. To overcome these problems involved production of plastics with high degree of degradability.

Bio-plastics consist of either biodegradable plastic (i.e. plastics produced from fossil) or bio-based plastics (i.e. plastics synthesized from biomass or renewable resources). Here PHB, PLA and starch blends are produced from biomass or renewable resources and are thus biodegradable and when compared to petroleum, they lead to little contamination. Biodegradation is defined by Albertson as "an event which takes place through the action of enzyme and/or chemical decomposition associated with living organisms or their secretion products" or it may also be defined as the deterioration of its physical and chemical properties and a decrease of its molecular mass down to the formation of CO₂, H₂O and CH₄ and other low molecular weight products under the influence of microorganisms.

Biodegradable Plastics are environment friendly can be derived from renewable feed stocks, thereby reducing green house gas emissions. They offer a lot of advantages such as increased soil fertility, low accumulation of bulky plastic materials in the environment (which invariably will minimize injuries to wild animals), and reduction in the cost of waste management.

Categories: Biodegradable polymer can be divided into three categories

1. Natural biodegradable polymer
2. Synthetic biodegradable polymer
3. Biodegradable polymer blends.

Among the natural polymers, starch is of interest it is regenerated from carbon dioxide and water by photosynthesis in plants. In this paper, how the starch enhances the biodegradability of biodegradable polymer (PLA) is presented.

Structure and Properties of Starch:

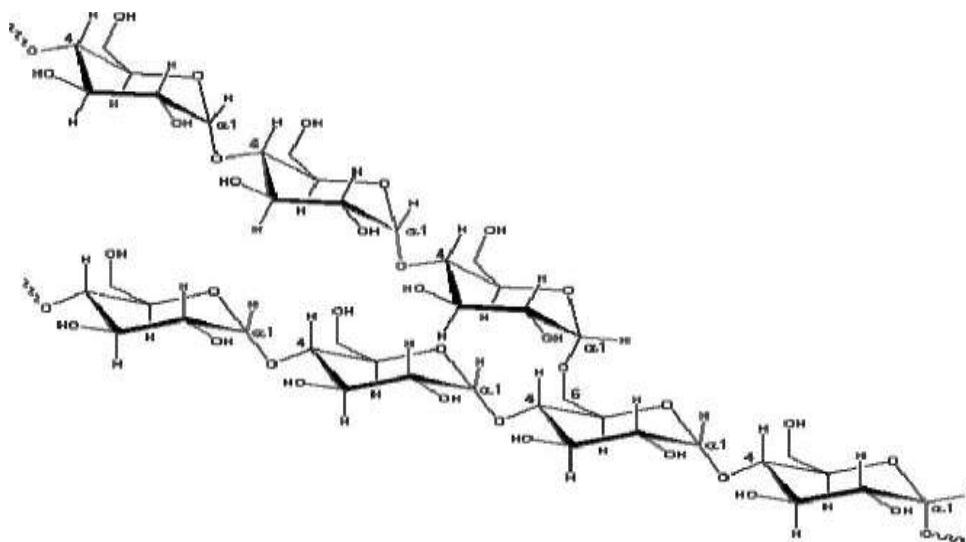
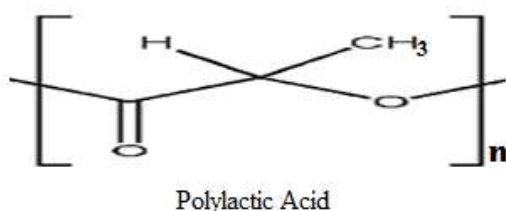


Fig.1: Structure of Starch

Starch is mainly composed of two homo-polymers of D-glucose, amylose, a mostly linear α -D(1, 4) glucose and branched amylopectin, having the same backbone structure as amylose but with many α -1,6-linked branch points (Fig.1). There is a lot of hydroxyl groups on starch chains, two secondary hydroxyl groups at C-2 and C-3 of each glucose residue, as well as one primary hydroxyl group at C-6 when it is not linked. Evidently, starch is hydrophilic. Owing to its hydrophilicity, the internal interaction and morphology of starch will be readily changed by water molecules. The hydrophilicity of starch can be used to improve the degradation rate of some degradable hydrophobic polymers. Starch is totally biodegradable in a wide variety of environment. It can be hydrolyzed into glucose by microorganism or enzymes and then metabolized into CO_2 and water it is with noting that CO_2 will recycle into starch again by plants and sunshine.

In this work, polymer taken is one of the most important biodegradable polyesters – Poly(lactic acid) with many excellent properties and has been widely applied in many fields, especially in biomedical one.

PLA possesses good biocompatibility and process ability, as well as high strength and modulus. Poly(lactic acid) (PLA) which was further blended with aqueous starch solution at different temperature (423.15K, 433.15K and 443.15K) and concentrations (0.002, 0.004 and 0.006M). But due to poor interfacial interactions (i.e. interactions between the faces of polymer matrix) between hydrophilic starch granules and hydrophobic PLA, mechanical properties are poor, which have been investigated by the help of Ultrasonic Interferometer. With Ultrasonic Techniques, the study of interfacial interactions between hydrophobic polymers and hydrophilic starch granules to improve the biodegradability of biodegradable polymers like Poly(lactic acid) (PLA) can be done. Interfacial interactions mainly depends on the temperature, concentration of starch and functional groups of polymer such as hydroxyl groups, halides etc.



Poly(lactic Acid)

Biodegradable polymers degrade as a result of natural biological processes, eliminating the need to create a disposal system which can cause harm to our environment. Biodegradation is the process of converting polymer material into harmless, simple, gaseous products by the action of enzymes, microorganisms and water. To improve the quality of production of polymeric solutions the thermo-physical and acoustical properties plays an important role [3,4]. In recent years, ultrasonic studies in liquid and polymeric solutions have been the subject of research. Ultrasonic studies on polymeric solutions explained that acoustical measurements are the best option to clarify the nature of molecular interaction between polymer and solvent (or other solution) according to many literature surveys[5,6]. Ultrasonic technique is used significantly in the field of polymer processing and chemical reaction between the mixture molecules.

First, starch based biodegradable polymer have been studied by Griffin (USA, 1977). The work is based on enhancement the biodegradability of the polymers by incorporating starch to a carbon – carbon backbone matrix. The starch granules were used to increase the surface area available for attack by microorganisms. Since polylactic acid is most common biodegradable polymer and widely used in the place of nondegradable polymers to resolve the problem of plastic pollution. In the area of research for polymer science, polylactic acid is a very valuable polymer which can be utilised in many directions of human needs and scientific uses [7]. There may be losses of about 98-99% from the environment by the attack of microbial activity on polymer matrix. The structural molecular interactions of polymer with the starch solution have been conducted as a subject of different concentration at different temperatures using ultrasonic technique [8, 9]. The molecular structure of polymer has been included some acoustical parameters such as adiabatic compressibility, acoustic impedance, relaxation time, free energy, intermolecular free length etc. to find out the strength of the interactions involved in the polymer mixture and also the types of the interactions whether it was a dipole-dipole, ion- dipole or hydrogen bonding etc.

In the present paper, the related properties of polylactic acid starch solution like structural morphology, electronic environment and structural interactions using ultrasonic velocity; rheological techniques and spectroscopic technique as SEM have been explained. Polylactic acids are three carbons membered thermoplastic with hydroxyl (-OH) and carboxyl (-COOH) groups at the end. PLA is partially crystalline material. It is produced from natural materials however, very little is known regarding the rheological behaviour of these materials. Rheological properties are useful in evaluating polymer resins for their suitability in processing operations and can be used to judge and predict the molecular orientations that are formed in these materials while in the molten stage during processing and when frozen into the final products. At different concentration, the thermo acoustical parameters has shown various curves and changes as based on thermal parameters of the polymer solution. These variations are induced by the different functional groups attached with the polymer chain [10].

II. Material And Experimental Techniques

Polylactic acid (PLA) was purchased from OTTO, Chennai, India. Starch used in the present work was of Cornstarch of Pharmaceutical ITEMS obtained from Chennai, India. The polymeric solution mixture was prepared by dissolving the polylactic acid in aqueous starch solution in the manner of weight/volume in the concentrations range of (0.002M) as primary solution and then prepared other concentrations (0.004 and 0.006M) by addition of starch step by step in primary solution. For the preparation of a clear transparent (homogenous) liquid mixture of polymeric solution heating mantle was used of Royal Scientific RSW 130 Heating Mantle. Ultrasonic velocity (u) was measured at 423.15, 433.15 and 443.15K using a single crystal ultrasonic interferometer at 2 MHz frequency (Model-83S) supplied by Mittal enterprises, New Delhi, that has an accuracy of 0.4 m/Sec at 25^oC. The temperature was kept constant, by constant temperature water bath with an accuracy of ± 0.1 K using equation-

$$U = n \times \lambda \quad (1)$$

The densities of these solutions were determined at different temperatures by magnetic float densitometer [11]. The densities of these polymeric solutions were determined by using Eq. 2.

$$\text{Density (d)} = (W+w+f.I) / (V+w/d_{pt}) \quad (2)$$

The terms involved in this equation have their usual meanings. The data of solution, i.e., weight, w used, current, I , passing in the circuit, ρ_{pt} , density of Pt wt and V , volume of float.

The viscosity (η) measurements were done through Ostwald's Viscometer. The viscometer is filled with reference liquid (distilled water) and then immersed in water bath. Using the time taken for the distilled water and mixture, the viscosity (η) of unknown polymeric solutions were determined by using Eq. 2.

$$\eta_s / \eta_w = \rho_s / \rho_w \times t_s / t_w \quad (3)$$

Where η_w , ρ_w and t_w are the viscosity, density and time flow of water respectively and η_s , ρ_s and t_s are the viscosity, density and time flow of unknown experimental solution respectively.

The SEM was collected for these samples with Scanning Electron Microscope of JSM-7900F Schottky Field Emission Scanning Electron Microscope. First of all the process is started with the measuring of melting point of the polymer (PLA), for this-The melting point of polymer (PLA) is measured with the help of melting point apparatus, comes out to be 145 degree centigrade. Three temperatures above the melting point were chosen as 150, 160, & 170 degree centigrade to precede the work. Starch solution of 0.002M concentration in 100ml of distilled water were prepared and known amount of polymer is added to this starch solution (0.002M) (25ml). For this the polymer (0.5gm) should be taken in 25 ml of starch solution. The experimental work was done at these above mentioned temperatures with three different concentrations (0.002, 0.004, & 0.006). For this the mixture of polymer with starch was heated at 423.15K and then it was cooled to room temperature, then all the thermo physical properties were studied. Whole process was repeated at 433.15K and 443.15K with same concentrations.

III. RESULT AND DISCUSSION

The acoustical parameters such as adiabatic compressibility (β_{ad}), acoustic impedance (z), relaxation time (τ), free energy (ΔG) etc have been computed and are given in Table 1. The structural and molecular interactions involved between poly lactic acid and starch solution with respect to change in concentration and temperature was explained with the help of Ultrasonic technique and SEM spectra studies. In the present paper, the viscosity (η) decreases with enhance in molar concentration but increase with the increase in temperature is given in Table 1. In all the cases such change may be due to strong force that is produced between polymer and the layers of the solution. It was found that the density of the polymer solution decreases with the addition of solute content because the number of polymer chain increases and added to the solution with increase the concentration of polymer solution. This behaviour is slightly abnormal and this decrease in density of the solution can be possible only due to involvement of much higher temperature.

Table.1: Experimental measured values of thermo-physical and acoustical parameters for polymeric solution (Polylactic acid + aq. starch solution) at different temperatures.

At 423.15K								
C (M)	ρ (Kgm ⁻³)	$\eta \times 10^{-3}$ (NSm ⁻²)	u (ms ⁻¹)	$\beta_{ad} \times 10^{-10}$ (kg ⁻¹ ms ²)	$z \times 10^3$ (kgm ⁻² s ⁻¹)	$\tau \times 10^{-10}$ (s)	$\Delta G \times 10^{-21}$ (gJmol ⁻¹)	$L_f \times 10^{-11}$ (m)
0.002	1005.8	1.0398	1461	4.6578	1469.47	6.4578	2.3065	3.2696
0.004	1005.7	0.9411	1511	4.3550	1519.61	5.4646	2.2766	3.1615
0.006	1005.6	0.8389	1567	4.0499	1575.77	4.5289	2.2430	3.0487
At 433.15K								
C (kgL ⁻¹)	ρ (Kgm ⁻³)	$\eta \times 10^{-3}$ (NSm ⁻²)	u (ms ⁻¹)	$\beta_{ad} \times 10^{-10}$ (kg ⁻¹ ms ²)	$z \times 10^3$ (kgm ⁻² s ⁻¹)	$\tau \times 10^{-10}$ (s)	$\Delta G \times 10^{-21}$ (gJmol ⁻¹)	$L_f \times 10^{-11}$ (m)
0.002	1006.2	1.5669	1496	4.4387	1505.27	9.3972	2.3735	3.1918
0.004	1006.0	1.3225	1569	4.0380	1578.41	7.1203	2.3239	3.0444
0.006	1005.9	1.1102	1635	3.7188	1644.64	5.1838	2.2672	2.9215
At 443.15K								
C (kgL ⁻¹)	ρ (Kgm ⁻³)	$\eta \times 10^{-3}$ (NSm ⁻²)	u (ms ⁻¹)	$\beta_{ad} \times 10^{-10}$ (kg ⁻¹ ms ²)	$z \times 10^3$ (kgm ⁻² s ⁻¹)	$\tau \times 10^{-10}$ (s)	$\Delta G \times 10^{-21}$ (gJmol ⁻¹)	$L_f \times 10^{-11}$ (m)
0.002	1007.0	2.0891	1539	4.1942	1549.31	11.6828	2.4054	3.1025
0.004	1006.3	1.9427	1620	3.7866	1630.20	9.8083	2.3856	2.9480
0.006	1006.1	1.7308	1704	3.4231	1714.39	7.8996	2.3182	2.8031

It was found that the ultrasonic velocity (u) of a polymer solution generally increases with concentration suggests strong solute-solvent interaction. However, on raising the temperature, there is an increase in ultrasonic velocity showing the abnormal behaviour that is opposite to the trend of normal solution mixture at normal temperature. From Fig.2, it was found that, adiabatic compressibility decreases with increase of polymer concentration; gives indication of closed packing of molecules or attractive molecular interaction occurred and shows weak ionic repulsion. Adiabatic compressibility is just reciprocal of ultrasonic velocity. According to Eyring and Kincaid [12], if sound velocity increases then molecular association takes place between solute and solvent, which are depicted in the present work.

At high concentration, the rotational hindrance of monomer unit occurred maximum, resulting the stiffness of polymer chains. Due to this molecular interaction may be influenced by the friction of the monomer unit. This trend shows for all the systems indicating the strengthening of intermolecular forces among polymeric molecules and suggests that segmental motion in onset.

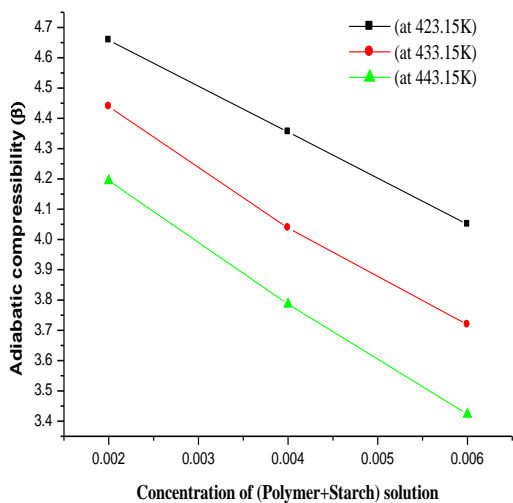


Fig.2: β vs C

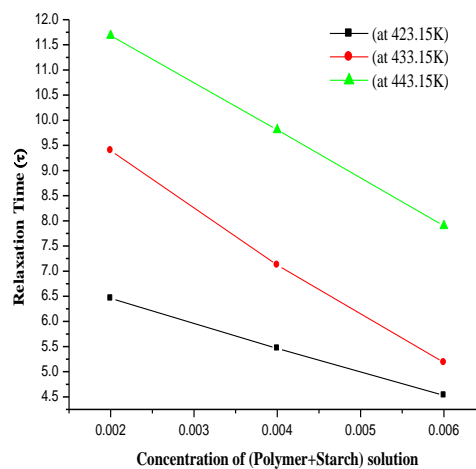


Fig.4: τ vs C

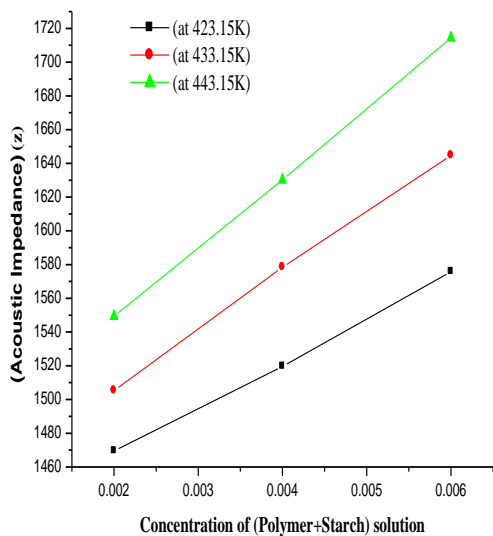


Fig.3: Z vs C

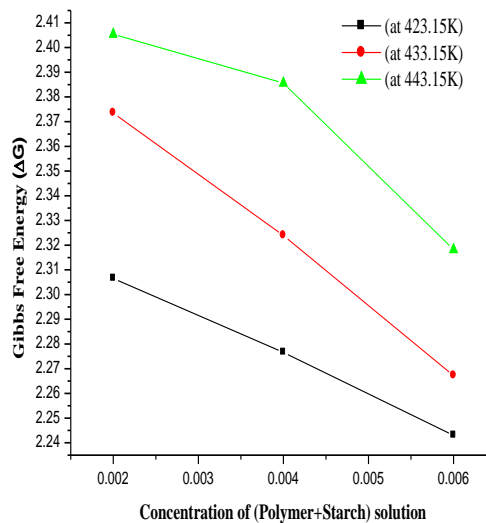


Fig.5: ΔG vs C

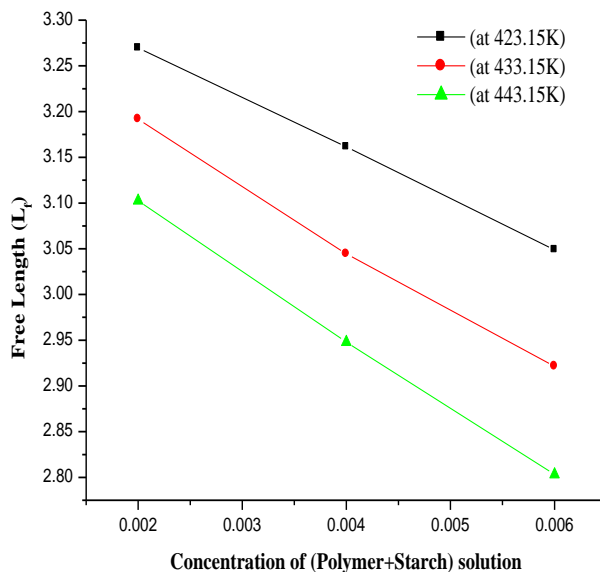


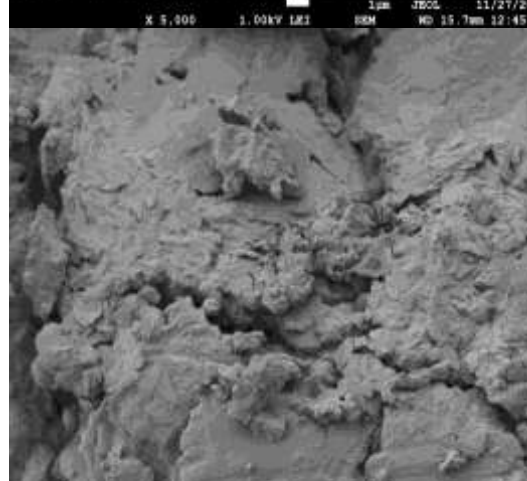
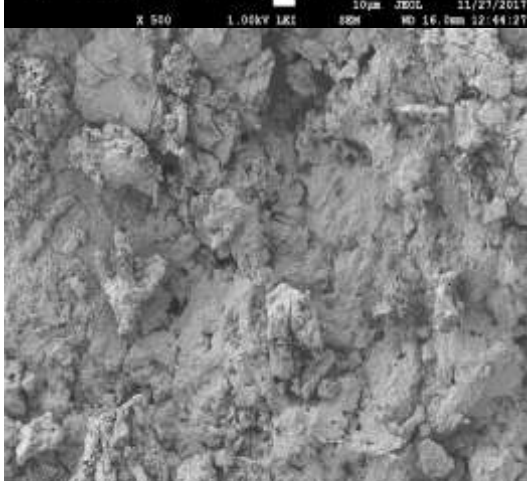
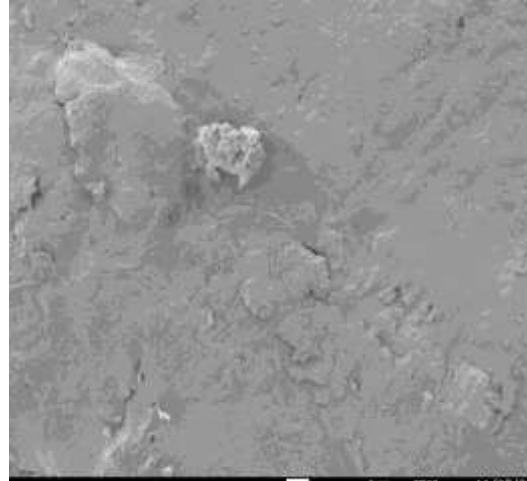
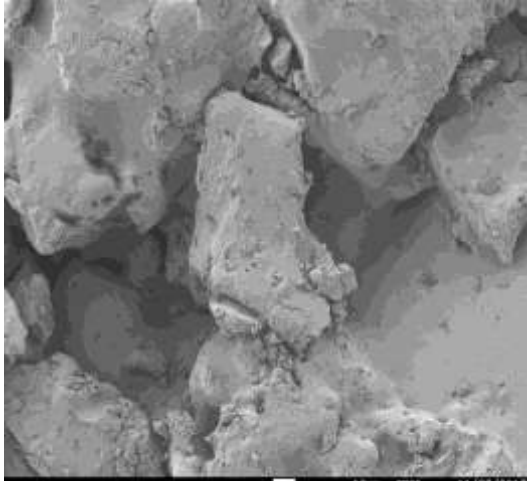
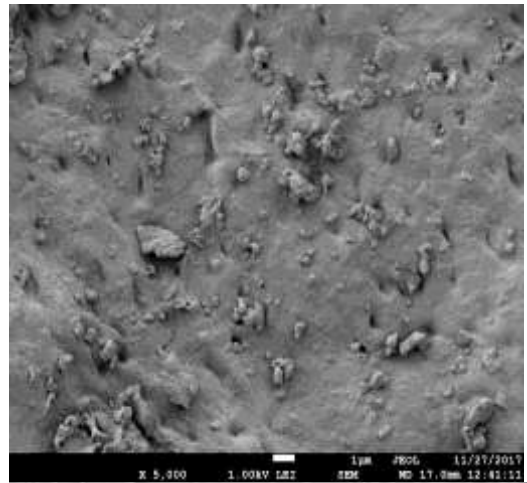
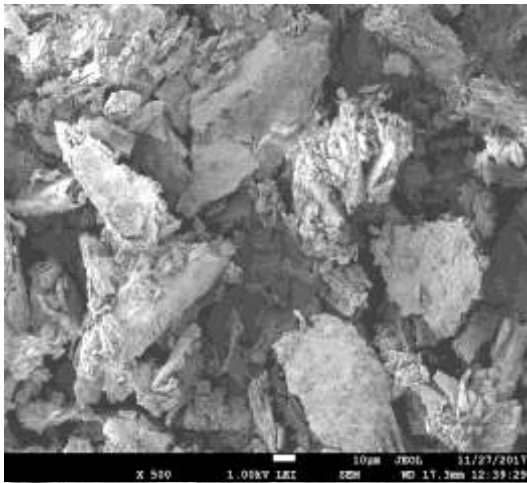
Fig.6: L_f vs C

The acoustic impedance is a measure of the resistance governed by the internal pressure and elastic properties of the medium, which depends on the structural changes of the polymeric solution. In the present investigation, the gradual increase in acoustic impedance with increasing concentration increases with rise of temperature shown in Fig. 3, predict strong intermolecular association occurred between polymeric and starch molecules. Above observations, also indicate the absence of complex formation and existence of solute-solute interaction. The result further supports the possibility of molecular interaction due to H-bonding between solute-solvent and solvent-solvent molecule due to the presence of (-OH) group in polymer (PLA). The increase in concentration is accompanied by an increase in relaxation time (τ), for all the systems shown in Fig.4, which indicates that viscous forces play a dominant role in the relaxation process. The molecular interaction causing association between polymeric and starch molecules are responsible for the increase in relaxation time. Such interactions give hardly the reason for the increase in ultrasonic velocity and indicate that degree of cooperation for relaxation of the molecule increases.

Free energy (ΔG) decreases with increase in concentration of polymeric solution as shown in Fig. 5. This trend of curves predicts that the thermo-physical properties of polymeric solution are affected by several types of molecular interactions, such as molecular reorganization, H-bonding etc. The change in free energy can be understood on the basis of hindrance of segmental motion of polymeric chain causes increase in free energy. Intermolecular Free length (L_f) also follows the same trend as that of adiabatic compressibility presented in Fig. 6, the decrease in the value of free length with increasing concentration and decrease in temperature indicates the presence of strong molecular interaction at higher concentration. At lower concentration range the polymeric molecules exhibit weak interaction due to dominant repulsive forces over attractive forces. The decreasing trends of intermolecular free length indicates that there is a significant interaction occurred between the molecules of polymer and starch molecules forming hydrogen bonding, shows decrease in the value of free length.

Sem Interpretation

Scanning electron microscopy (SEM) observations describe the structure and correlate with mechanical and rheological properties. In these slides the morphological changes in structure of polymer explained that some interactions play an important role in these mixtures. A Scanning Electron Microscope (SEM) scans a sample with a focused electron beam and delivers images with information about the sample's topography and composition. Scanning Electron Microscope (SEM) scans images of various concentrations of polymer + starch solutions at different resolutions are shown in Fig. 7.



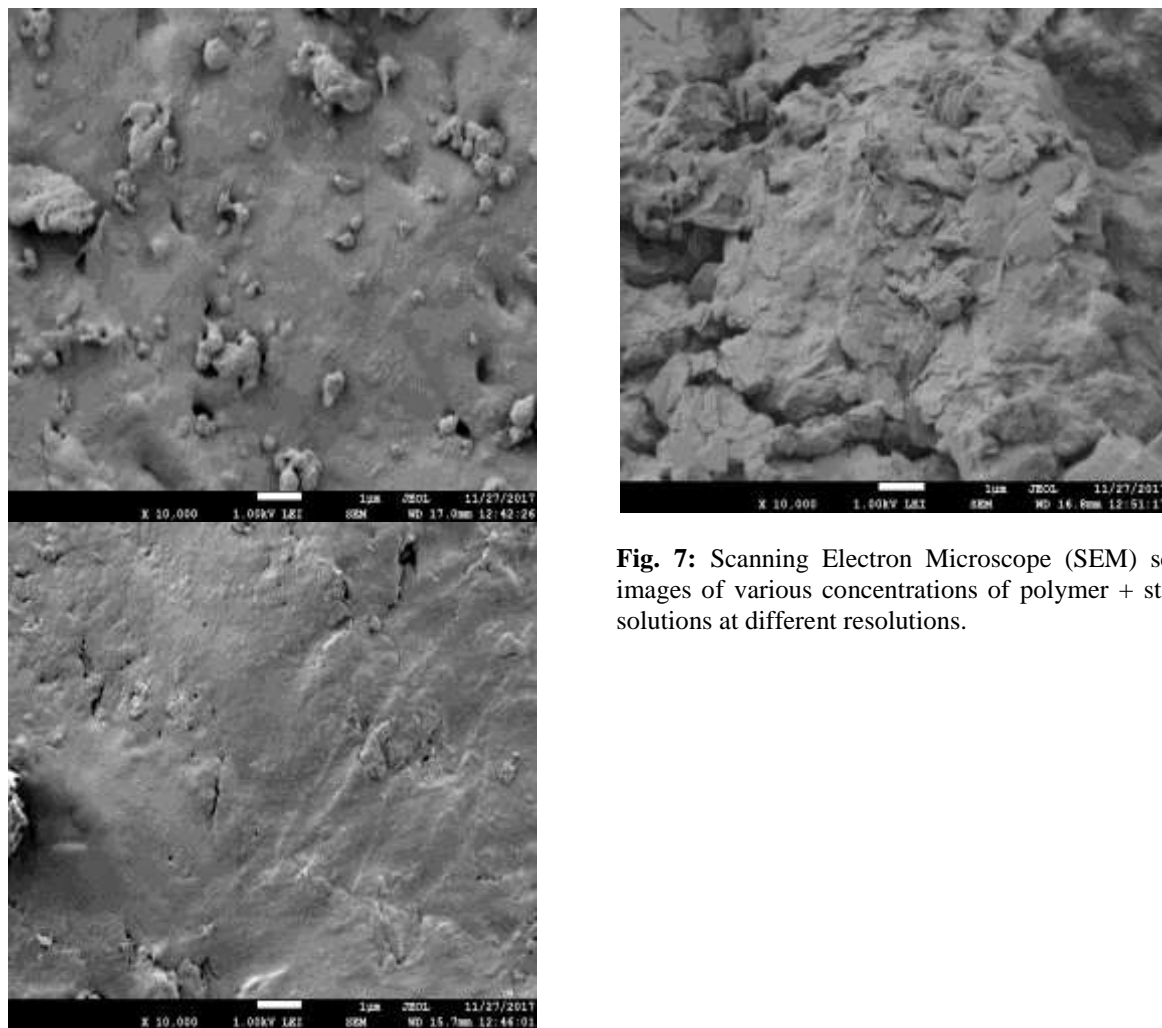


Fig. 7: Scanning Electron Microscope (SEM) scans images of various concentrations of polymer + starch solutions at different resolutions.

Table 2: Biodegradability degradation on the basis of Weight loss in percentage with Time Period

S.N.	Slide -A		Slide -B	
	Time interval(Hr.)	Wt. Loss (%)	Time interval (Hr.)	Wt. Loss (%)
1.	23.00	4.45	23.00	2.72
2.	24.00	8.20	24.00	7.30
3.	24.00	10.57	24.00	10.17
4.	24.00	14.88	24.00	12.18
5.	24.00	17.52	24.00	14.47
6.	24.20	19.75	24.20	16.47
7.	24.05	23.64	24.05	17.76
8.	24.30	27.12	24.30	19.34
9.	23.50	28.93	23.50	20.63
10.	24.00	30.88	24.00	21.77
11.	23.40	32.41	23.40	22.49

12.	23.40	34.49	23.40	22.78
13.	24.30	34.91	24.30	22.92
14.	24.20	35.46	24.20	23.21
15.	23.30	35.88	23.30	23.49
16.	24.10	36.16	24.10	24.07
17.	23.00	36.58	23.00	24.35
18.	24.05	36.99	24.05	24.78
19.	24.00	37.27	24.00	25.07

The change in weight of polymer with time period of approximately 24 hrs is in decreasing order shows that the attack of microbes due to the presence of starch increases day by day due to environmental conditions like humidity, temperature etc. are shown at different slides in Fig. 8.



Slide.1



Slide.4



Slide.2



Slide.5



Slide.3

Fig. 8 – Showing weight loss with the time interval for slides.

IV. CONCLUSION

Polymeric mixture of polylactic acid with aqueous starch solution of various concentrations were prepared and its thermo-physical and acoustical parameters were determined at different temperatures (423.15K, 433.15 and 443.15K). The SEM technique was also utilized for these solutions to clear the molecular structure. The experimental values, acoustical data showed that the solute-solute and solute-solvent interactions were favored but it also showed little abnormalities too. Due to association among polymeric chain of polylactic acid, density, viscosity and ultrasonic velocity found to increase with increase in concentration.

Acknowledgements

Indu Saxena thanks to Council of Science & Technology, U.P. (CST), Lucknow- India for the sanction of major research project no. CST/D-2278. The authors are thankful to CSTUP for providing financial assistance for the award of project fellowship and making the research possible. Also, the authors are thankful to the Head of Chemistry Department for providing the laboratory facility.

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