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Study of Degradation rate for PLA with Starch Blended Polymer through Molecular Interactions Using Acoustical Parameter

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Abstract : The enormous use of synthetic polymers, for the food packaging area, has a big influence on our environment, and as a substitute, more ecological materials are being required. Poly(lactic) acid (PLA) and starch have been extensively studied as potential replacements for non degradable petrochemical polymers based on their availability, adequate food contact properties and competitive cost.

In this paper observation gone through the additional acoustic parameters such as Wada's constant, Internal pressure, Surface tension, Relative association and Attenuation with respect to temperature variation (423.15, 433.15 and 443.15K) and various concentration. When the whole parameters have been computed the study of molecular interaction through these parameters furnished as according to this paper work. After all the process had done the result shows that what kind of changes occur in the molecular & structural properties of polymer mixture that can support the biodegradability of it.

Keywords **- Poly(lactic) acid; starch; films; blends; food packaging; mechanical properties; acoustical properties**

I. INTRODUCTION

In Polymer field, the use of Polylactic acid (PLA) is very fruitful for scientific research and combination of Starch is very useful for ecological purpose.

However, both polymers have their some encumbrance for packaging uses and need to be modifying to the food packaging requirements. Especially starch is very water absorbing and its film properties are highly reliant on the moisture content, having relatively less mechanical resistance. PLA films are very fragile and offer low resistance to oxygen interpenetration.

With the help of their blending, some sufficient properties are provided for the food-packaging field based on their complementary characteristics. The properties of some blends/combinations have been discussed in comparison with those of pure polymer films.

In the previous work Polylactic acid was mixed with the aq. starch solution in different concentration and temperature to find out maximum molecular interaction to get enhanced biodegradability.

A specific concern is the field of packaging, which produces great amounts of non-degradable plastic waste accumulated in critical areas around the planet, causing severe problems and representing high recycling cost [1].

Polymer (Europe ranks second, along with North America, in the global production of plastic materials with 18.5% of the worldwide annual production (322 million tons in total in 2015). In Europe, the packaging sector is the largest one in the plastics industry, since it represents 40% of the total plastic demand, which rises to 49 million tons [2].

Bioplastics are classified into three types of criterion, based on their route and biodegradable nature: biobased nondegradable bioplastics (e.g., polyethylene terephthalate), biobased biodegradable bioplastics (e.g., PLA, starch, other polysaccharides or proteins) or fossil-based biodegradable bioplastics (e.g., polycaprolactone (PCL))

Crystallinity degree greatly affects the mechanical performance of the material, PLA exhibits many advantages; it is biodegradable, renewable and biocompatible [3,4].

PLA-Starch blends without compatibilizers by using the butyl-etherification of waxy and high amylose starches to increase their hydrophobicity and compatibility with PLA. Although the polymer thermal stability decreased, the modified blend exhibited an improved mechanical performance, while SEM micrographs showed a more homogeneous structure with this starch modification. Additionally, this study demonstrated that the amylose/amylopectin content of starch plays an important role in the tensile properties of the starch-PLA blend films [5]

The starch granules were used to increase the surface area available for attack by microorganisms.

Material :

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 [6].

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 250C The temperature was kept constant, by constant temperature water bath with an accuracy of ± 0.1K

The SEM was collected for these samples with Scanning Electron Microscope of JSM-7900F Schottky Field Emission Scanning Electron Microscope.

Equations :

The ultrasonic velocity can be measured using equation-

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

The densities of these solutions were determined at different temperatures by magnetic float densitometer [7].

The densities of these polymeric solutions were determined by using Eq. 2.

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

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, ρpt, density of Pt wt and V, volume of float.

The viscosity (η) measurements were done through Ostwald's Viscometer.

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

Where ηw, ρw and tw are the viscosity, density and time flow of water respectively and ηs, ρs and ts are the viscosity, density and time flow of unknown experimental solution respectively.

Method :

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 preceded 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. The SEM technique was also utilized for these solutions to clear the molecular structure in the previous part of paper [6].

II. RESULTS AND DISCUSSION

The acoustical parameters such as Wada's constant (W), Surface tension (σ), Adsorption Attenuation (a/f^2), internal pressure (π_i) and Relative association (R_a) have been evaluated and are given in Table 1. The structural and molecular interactions involved between polylactic acid and starch solution with respect to change in concentration and temperature had been explained with the help of Ultrasonic technique and SEM spectra studies in the previous paper. Ultrasonic velocity in a liquid system depends on the structural and molecular properties. In the increase of temperature, ultrasonic velocity in a liquid system is responsive to external pressure. This shows that computed internal pressure is sensitive to all the physicochemical characteristics of the liquid system [8].

Table 2.1: Experimental measured values of thermo-physical and acoustical parameters for polymeric solution (Polylactic acid + aq.starch solution) at different temperatures.

(At 423.15±0.1)K								
C (M)	**ρ** (Kgm^{-3})	**η× 10^{-3}** (NSm^{-2})	**u** (ms^{-1})	**W** (m^3mol)	**σ × 10^4** ($kg^{-1}mol^{-1}m^4s^2$)	**a/f^2×10^{-12}** (σ)	**π_i** (atm)	**R_a**
0.002	1005.8	1.0398	1461	74.3180	3.5385	9.5328	103.8445	1.0219
0.004	1005.7	0.9411	1511	73.6151	3.7214	6.8249	97.1353	0.9880
0.006	1005.6	0.8389	1567	72.8624	3.9298	4.6883	90.0498	0.9526

(At 433.15±0.1)K								
C (M)	**ρ** (Kgm^{-3})	**η× 10^{-3}** (NSm^{-2})	**u** (ms^{-1})	**W** (m^3mol)	**σ × 10^4** ($kg^{-1}mol^{-1}m^4s^2$)	**$a/f^2\times10^{-12}$** (σ)	**π_i** (atm)	**R_a**
0.002	1006.2	1.5669	1496	73.7788	3.6679	20.6348	128.9837	0.9984
0.004	1006.0	1.3225	1569	72.8029	3.9388	12.1485	115.6946	0.9518
0.006	1005.9	1.1102	1635	71.9586	4.1896	7.2599	103.8325	0.9133
(At 443.15±0.1)K								
C (M)	**ρ** (Kgm^{-3})	**η× 10^{-3}** (NSm^{-2})	**u** (ms^{-1})	**W** (m^3mol)	**σ × 10^4** ($kg^{-1}mol^{-1}m^4s^2$)	**$a/f^2\times10^{-12}$** (σ)	**π_i** (atm)	**R_a**
0.002	1007.0	2.0891	1539	73.1259	3.8303	34.2885	150.3082	0.9713
0.004	1006.3	1.9427	1620	72.1158	4.1337	24.1474	141.2105	0.9221
0.006	1006.1	1.7308	1704	71.0977	4.4585	15.6556	129.9428	0.8765

Wada's constant (W) is independent of external temperature and pressure. In the study of sound velocity in liquids, another constant had been suggested by Wada. Wada constant is also pronounced as molar adiabatic compressibility. It may be considered for involved interaction.

Internal pressure (π_i) is the fundamental property of liquid, which provides an excellent basis for examining the solution phenomena and studying the various properties of the liquid state. It is the measure of change in internal energy of liquid solution as it undergoes a very small isothermal change. It is a measure of cohesive or binding forces between the solute and solvent interactions. The internal pressure is the resultant of the force of attraction and the force of repulsion between the molecules in a liquid [9].

Relative association (R_a) is the measure of extent of association of components in the medium. It is a property of understanding the molecular interaction in liquid mixture and solutions. The relative association depends on either of breaking up of the solvent molecules on addition of solute to it or the solvation of ions that are present. R_a decreases which is due to the breaking up of solvent molecules on the addition of solute whereas if it increases which show solvation of ions. These variations in R_a suggest the specific molecular interactions among the components. The interactions may be solute-solute, solvent-solvent, solute-solvent type due to formation of H-bond. The increasing trend of R_a may be due to strong H-bonding happening in the solution because of presence of $–CH_2$ group. This increasing trend of relative association value shows stronger interaction between solute and solvent [10].

Surface Tension (σ) is the energy or work required to increase the surface area of a liquid due to intermolecular forces. Since these intermolecular forces vary depending on the nature of the liquid (water or gasoline) or solutes in the liquid (surfactants like detergent) each solution exhibits different surface tension properties.

Water has a surface tension of 0.07275 J/m^2 at 20 C. In comparison, organic liquids like benzene & alcohol have lower surface energy (or surface area) for instance gold is a solid, water is a liquid & nitrogen is a gas.

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 behavior is slightly abnormal and this decrease in density of the solution can be possible only due to involvement of much higher temperature.

In figure.1, the Wada's constant is explained as the compactness of the polymer system. The values of Wada's constant decreases with increase in concentration shown in Table.1 explained the less compactness of the molecule and hence molecular interactions become nonlinear. This situation may explain as less compactness i.e; less expense of energy and the degradation process triggered fast.

For the strong solute solvent interaction, the condition of ultrasonic velocity (u) should increases with increasing concentration [11]. However, on raising the temperature, there is an increase in ultrasonic velocity showing the abnormal behavior that is opposite to the trend of normal solution mixture at normal temperature. From Fig.2, it was found that, Surface tension increases with increase of solution concentration; gives indication of closed packing of molecules or attractive molecular interaction occurred and shows weak ionic repulsion.

Surface tension is visible in other common phenomena, especially when surfactants are used to decrease it:

- Soap bubbles have very large surface areas with very little mass. Bubbles in pure water are unstable. The addition of surfactants, however, can have a stabilizing effect on the bubbles (Marangoni effect). Note that surfactants actually reduce the surface tension of water by a factor of three or more.
- Emulsions are a type of colloid in which surface tension plays a role. Tiny fragments of oil suspended in pure water will spontaneously assemble themselves into much larger masses. However, the presence of a surfactant provides a decrease in surface tension, which permits stability of minute droplets of oil in the bulk of water (or vice versa).

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.

Figures and Tables

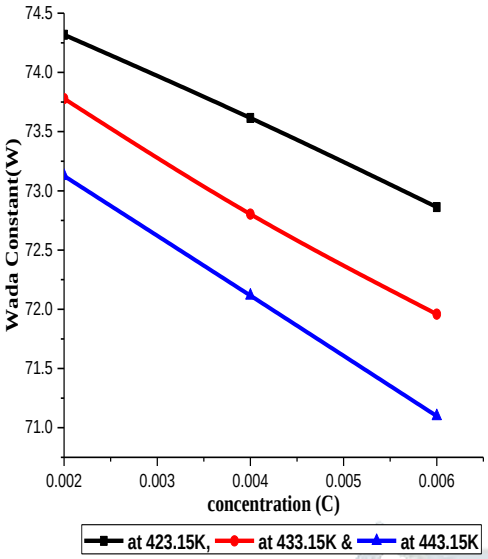

Fig. 1: Graph plotted between W vs C

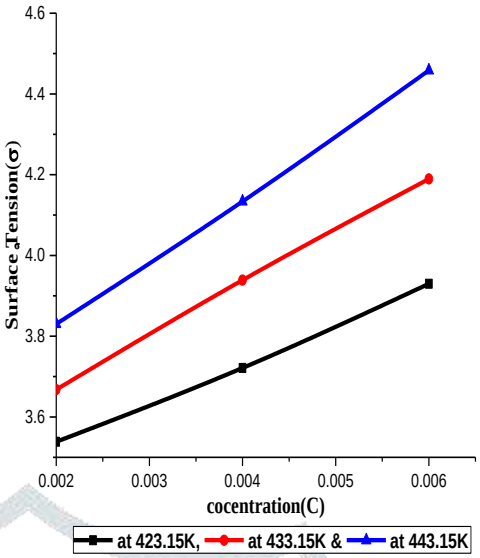

Fig. 2: Graph plotted between σ vs C

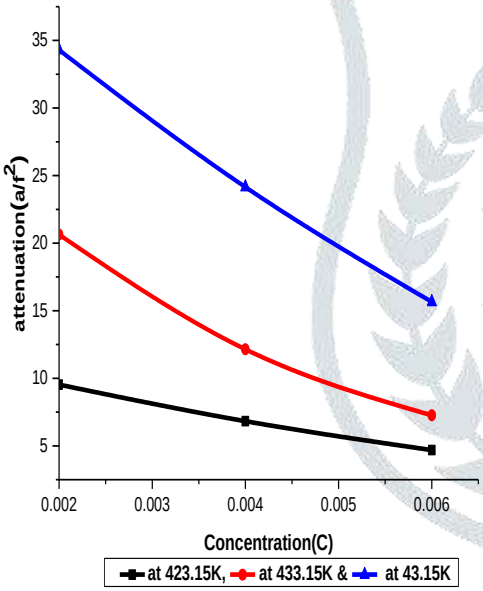

Fig. 3: Graph plotted between a/f^2 vs C

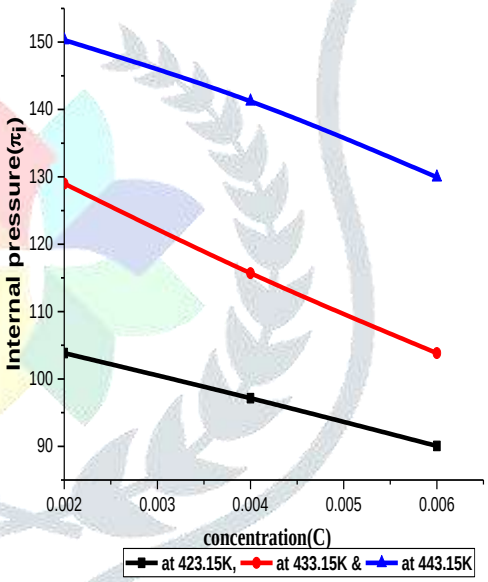

Fig. 4: Graph plotted between π_i vs C

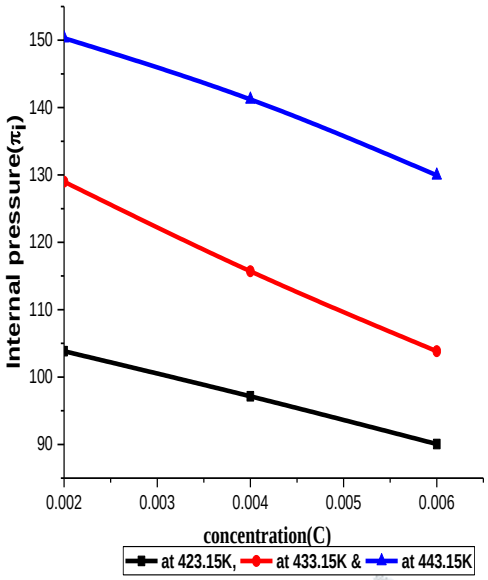

Fig. 5: Graph plotted between Ra vs C

The adsorption attenuation (a/f^2), 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 decrease in attenuation 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) [13].

The increase in concentration is accompanied by a decrease in internal pressure (π_i), for all the systems shown in Fig.4, in the calculation of internal pressure, 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 thus the pressure created by the molecules of polymeric solution get decreases.

Relative association (R_a) decreases with increase in concentration of polymeric solution as shown in Fig. 5. This trend of curves predicts that several types of molecular interactions, such as molecular reorganization, H-bonding etc., affect the thermo-physical properties of polymeric solution. The association between the polymeric molecules (starch + PLA) slowly diminished due to higher temperature and concentration randomness of the molecules increases so that association cannot take place.

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 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 nonlinear with increase in concentration.

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