

**MAJOR PROJECT (PART-2)**

**On**

**STUDIES OF PRINTABILITY ON BIODEGRADABLE FILM**



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**IN**

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**Under the guidance of:**

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**(Roll No: 2010/PST/09)**



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**CERTIFICATE**

This is to certify that **Mr. Naveen Arya** has carried out his major project entitled “STUDIES OF PRINTABILITY ON BIODEGRADABLE FILM” under my supervision and guidance during the session 2012-2013. To the best of my knowledge and belief, this work has not been submitted to any other university or institutions for the award of any degree or diploma.

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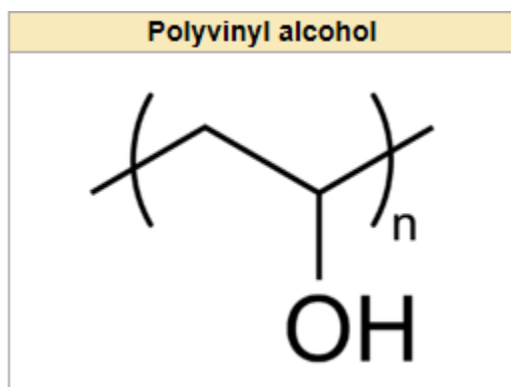
## **ABSTRACT**

Biodegradable film made from PVA was synthesized in the lab. The biodegradability of the same film tested during soil burial test showed only 11-15 % degradation in 55 days under atmospheric condition. While manufacturing film plasticizers like glycerin & PEG was added, it was concluded during characterization that plasticizer could largely reduce the melting point of PVA and increase the thermal stability of PVA. The increase in the difference between the melting point and the thermal decomposition temperature enables the thermal processing of PVA in melt extrusion. The FTIR studies show that the plasticizer could effectively destroy the hydrogen bonding of PVA, this is because that the plasticizer glycerin could form strong interaction with the hydroxyl group of PVA. Synthesized films were given surface treatment & coating (like PVDC, Acrylic & 2% Borax) to test the printability which reduces when PEG is added. Initial results clearly shows that corona treatment provide better results compare to plasma, finally it is clear that in PVA film treated with plasma & Corona & coated with borox 2% solution gave better results in this study.

## 1.0 Introduction

### 1.1 Biodegradable Polymers (PVA):

Polyvinyl alcohol (PVA) has excellent property like film forming, emulsifying and adhesive. It is resistant to oil, grease and solvents, odorless and nontoxic. It has high tensile strength and flexibility, as well as high oxygen and aroma barrier properties. However these properties are dependent on humidity, in other words, with higher humidity more water is absorbed. The water, which acts as a plasticizer, will then reduce its tensile strength, but increase its elongation and tear strength. PVA is fully degradable and dissolves easily in water. PVA has a melting point of 230°C and 180–190°C (356-374 degrees Fahrenheit) for the fully hydrolyzed and partially hydrolyzed grades, respectively. It can undergo pyrolysis at high temperatures above 200 °C.



PVA is a water-soluble polymer which is produced on a large scale commercially. PVA has been used in the shape of fibers, films, hydrogels, and glues. PVA has been processed mainly from an aqueous solution even though the melt processing is more economically favored, because melting point ( $T_m$ , typically 230°C) and the decomposition temperature of PVA are closed to each other, the thermal degradation also undergoes simultaneously during melting. PVA is a semicrystalline polymer in which high physical interactions between polymer chains exist, due to the hydrogen bonding between hydroxyl groups. It is this hydrogen bonding which also controls the thermal properties of PVA, making  $T_m$  (melting point) of PVA much higher in comparison with polyethylene ( $T_m$  117-135-°C). The thermal properties of PVA films are mainly dependent on & can be tailored by changing the intensity of the hydrogen bonding. Also thermal property of PVA can be modified by adding the plasticizer (like glycerol or PEG, Polyethylene glycol). The plasticizer can form stable hydrogen bonds with PVA chain and therefore reduce the inter- or intramolecular interactions between PVA chains. The widely used plasticizers for PVA are high boiling water soluble organic compounds containing hydroxyl groups, such as ethylene glycol and low molecular weight poly(ethylene glycol). The plasticizing effects of these plasticizers are limited due to the partial evaporation and thermal decomposition of the plasticizer. The research of new and high efficiency plasticizer for PVA is meaningful.

According to the results before, the functional part of these plasticizers is hydroxyl group. The “C=O” and “-NH<sub>2</sub>” groups could form more stable hydrogen bonding with the hydroxyl groups and were more effective in breaking the hydrogen bonding between the PVA hydroxyl groups. PVA is an atactic material but exhibits crystallinity as the hydroxyl groups are small enough to fit into the lattice without disrupting it. PVA is close to incompressible. The Poisson's ratio has been measured to between 0.42 and 0.48.

### **PVA/Starch Blends:**

The addition of PVA into the starch films to improve their properties (such as mechanical properties, moisture sensitivity) has been reported. Shorgen et al. (1998)<sup>1</sup> reported that the factors that most limit the use of starch in biopolymer material applications are brittleness and loss of strength at low humidity and poor resistance to water. PVA, starch could improve strength and flexibility. However, the desired strength, flexibility, or stiffness can be tailored by formulating with different PVA levels, PVA types, better level of solids and cross-linking agents. Liu et al. (1999)<sup>1-a</sup> found that incorporation of PVA into starch could enhance the mechanical properties. However, improvement in the mechanical properties is limited, mainly due to the poor interface adhesion between the fibrous PVA structure and the starch matrix. Chen et al. (2008) investigated the effect of PVA on the properties of starch films. It was found that the tensile strength, elongation at break of starch films increased with the addition of PVA. Because both starch and PVA are polar substances having hydroxyl groups (-OH) in their chemical structure, these highly polar hydroxyl groups tend to form inter molecular and intra-molecular hydrogen bonds which improve the integrity of starch-PVA films. On the other hand, the solubility parameters of starch and PVA modeling complexes have been found to be close to each other, which confirmed that starch and PVA are compatible blends. In addition, the vibration frequency analysis of these molecular complexes has shown that the hydroxyl group shifted to lower wave numbers due to formation of hydrogen bonds between starch and PVA.<sup>2</sup>

PVA is a technological potential material; it is produced through the hydrolysis of polyvinyl acetate. It is found to be 53% syndiotactic. Isotactic PVA has a high melting point (T<sub>m</sub> = 230°C) compared to polyethylene (T<sub>m</sub> = 117-135°C) as a result of the high level of hydrogen bonding in the crystals.

PVA is well suited to be blended with natural polymers since it is highly polar and can also be manipulated in water solution. PVA is blended with corn starch as the starch is available in abundance at low price. Particularly, plant materials derived from renewable crops by-product or their industrially processed wastes offer a good source of fiber for applications. Research done by Sreedar *et. al.*, 2005 reported that incorporation of PVA into starch had changed the thermomechanical properties of the material and thus modified the polymer structure at both molecular and morphological levels. Starch possesses similar function as PVA which is biocompatible and consumable by microorganism. When PVA and starch are blended together, the presence of hydroxyl groups (-OH) tend to form strong hydrogen bonding among the molecules and subsequently lead to synergistic stability and better system integrity. Both PVA and starch disperse homogeneously in solution cast film under the scanning electron microscopy. Starch is the major carbohydrate in plant tubes and seed endosperm, where it is found as granules. Each granule contains several millions amylopectin molecules accompanied by much larger number of smaller amylose molecules. The largest source of starch is corn and rice.

Generally corn starch consists of 20-30% amylose and 70-80% amylopectin. Both polymers have  $\alpha$ -D-glucose units in 4C1 conformation.<sup>3</sup>

### **1.1.1 Type and content of plasticizers**

A plasticizer is incorporated into rigid material which increase flexibility, workability, and dispensability, as glass transition temperature ( $T_g$ ) is reduced and increasing chain lubricity, plasticizers could also improve processing and extrusion characteristics. They could also reduce the minimum required processing temperature, reduce the plastic's hardness and improve low temperature flexibility.

Generally, two types of plasticizers are distinguished. Internal plasticization is a result of modifications to the chemical structure of polymer. External plasticization is obtained by adding an agent which modifies the structure and energy within the three-dimensional arrangement of the film polymer (Banker, 1966). It is the second method which, on the basis of the type of materials and the technology used, is mainly used for biodegradable packaging. The addition of a plasticizer to a film produces a film which is less likely to break and is more flexible and stronger.

The intensity of the hydrogen bonding between the plasticizer and PVA is crucial for the plasticization efficiency. Both UE ( Urea/ethanolamine) and GL (glycerol) can form hydrogen bonding with PVA molecule.

Basically, the plasticizers should be generally compatible to the structure of the polymer and the permeability is present within the solvent-polymer system and under the conditions used. The compatibility of plasticizer with the polymer increases inter-molecular reactions. It is important to note that the formulation of the whole film system (polymer, solvent, plasticizer, and other additives) has a direct effect on the nature and characteristics of the film produced. As a result, the polymer and the plasticizer must not only be compatible, but must also have similar solubility in the solvent used. A soluble plasticizer will generally be sought for the development of soluble coating and an insoluble plasticizer (or a dispersible one) for an insoluble coating or for a slow solubilization. The plasticizer should not be volatile (or not only very slightly volatile) and its degree of retention by the film should be high. Other properties, such as its chemical stability, hygroscopicity, color, flavor, and so on, are also more or less important depending on the type of film under consideration. In addition, the content of plasticizer necessarily varies from 10-60% (dry basis) according to the nature and type of film and the method of application. The plasticizers that are most usually used in the field of rice starch films are mono-, di-, and oligosaccharides, polyols and lipids and its derivatives. The molecular size, configuration and total number of functional groups of the plasticizer as well as its compatibility with the polymer, could affect the interactions between the plasticizer and the polymer (Yang & Paulson, 2000).<sup>1</sup>

<sup>1</sup>Bourtoom & Chinnan (2008) determined plasticizer effect on the properties of biodegradable blend film from rice starch-chitosan. The results of these studies demonstrated that sorbitol plasticized films provided the films with highest mechanical resistance, but the poorest film flexibility. In contrast, glycerol and polyethylene glycol plasticized films exhibited flexible



structure; however, the mechanical resistance was low, while inversely affecting the water vapor permeability.

The effectiveness of glycerol in biodegradable blend films from rice starch-chitosan is most likely due to its small size which allows it to be more readily inserted between the polymer chains. It consequently exerts more influence on the mechanical properties than the larger polyethylene glycol molecule. In addition, at an equal percentage of concentration, the total number of glycerol molecules in the film solution is greater than that of the higher molecular weight polyethylene glycol. Therefore glycerol has more functional groups (-OH) than polyethylene glycol which should promote the plasticizer-polymers interactions in the films. As a result of the glycerol, plasticized films provided the films with higher water vapor permeability than polyethylene glycol, and sorbitol should be the result of the high hydrophilicity of the glycerol molecule, which is favorable to the adsorption of water molecules and could also contribute to the increase in the film water vapor permeability. In addition, at high glycerol concentration, glycerol could cluster with itself to open the polymer structure, enhancing the permeability of the film to moisture (Lieberman & Gilbert, 1973)<sup>1</sup>. An increase in inter chain spacing due to the inclusion of glycerol molecules between the polymer chain may promote water vapor diffusivity through the film and hence accelerate the water vapor transmission (Yang & Paulson, 2000).

<sup>1</sup>Dai et al. (2010) reported that type and content of plasticizer affected the properties of corn starch films. Increasing the plasticizer content resulted in increasing water vapor permeability of the resulting film. These results would be related to structural modifications of the starch network brought about by the plasticizer concomitant with the hydrophilic character of plasticizer, which favored the absorption and desorption of water molecules. Plasticizers reduced intra- and inter-molecular forces in starch. In addition, plasticizers could extend, dilute and soften the structure effectively; then the starch chain mobility would be increased.

### **1.1.2 Effect of atmospheric moisture in the PVA film:**

Water also acts as a plasticizer in hydrophilic films; the plasticizing effect of water is based on the weakening of hydrogen bonds and the dipole–dipole intra and intermolecular interactions due to shielding of these attracting forces by the water molecules. As a consequence, free volume increases which affects their mechanical properties. Stading et al (2001)<sup>1</sup> studied the effect of relative humidity on amylose and amylopectin film properties. They found that when the relative humidity of surrounding films increase this yielded increasing water content and oxygen permeability. However, the storage modulus and glass transition temperature ( $T_g$ ) showed an inverse effect. The change in surrounding relative humidity affected the water content of the films. When the water content in the films increase this provides an increasing mobility of molecule in the network allows swelling with resulting heterogeneous network structure. Hence, sharply decreased storage modulus and glass transition temperature and increased the oxygen permeability of the resulting films.

## 1.2 Raw Materials for Printing ink & formulations<sup>4</sup>.

The raw materials for ink production are pigments, binders, solvents and additives .

**Pigments**- colour the ink and make it opaque.

**Resins**- bind the ink together into a film and bind it to the surface

**Solvents**- make the ink flow so that it can be transferred to the printing surface

**Additives**- alter the physical properties of the ink to suit different situations

**Pigments:** A pigment is essentially any particulate solid - coloured, black, white or fluorescent - that alters the appearance of an object by the selective absorption and/or scattering of light. Pigments are considered to be the chief constituent of ink and contribute about 50 per cent of its cost. It occurs as a colloidal suspension in ink and retains a crystal or particulate structure throughout the colouring or printing process. Colour Index System number is generally used to identify the organic pigments in modern inks. It reflects the colour shade or hue, and structural and chronological details (order of synthesis) of the pigment. For example the well-known blue pigment copper phthalocyanine blue is PB 15. As the particle size reduces, the colour intensity (strength) of a pigment increases and the opacity peaks around a particle size of 0.3µm. Pigments colour the ink and provide gloss, abrasiveness and resistance to light, heat, solvents. Special pigments such as extenders and opacifiers are also used. Extenders are transparent pigments that make the colours of other pigments appear less intense, and opacifiers are white pigments, which make the paint opaque so that the surface below the paint cannot be seen.

**Resins:** Resins are primarily binders that bind the other ingredients of ink together so that it forms a film. They also bind the ink to paper. They also contribute gloss, resistance to heat, chemicals and water. More than one resin is typically used in an ink formulation. The Common resins used in ink formulations :

Acrylics, Ketones, Epoxides, Polyvinylbutyral, Alkyds Maleics Fumarics, Polyamides, Cellulose derivatives Formaldehydes Hydrocarbons Shellac Rubber resins Phenolics Isocyanate free polyurethanes

**Solvents:** These are used to keep the ink in liquid form from the period when it is applied to the printing plate or cylinder until when it has been transferred to the surface to be printed. At this point the solvent separates from the ink to allow the image to dry and bind to the surface. Some printing processes such as gravure and flexographic require a solvent that evaporates rapidly.

### Printing ink solvents

<b>Solvent</b>	<b>Boiling point (°C)</b>
Ethyl acetate	77
Isopropanol	82.5
n-propyl acetate	101.6
Cyclohexanone	155.6
Butoxyethanol	171-172
Aromatic distillates	240-290
Butyrolactone	89 (Boiling point at 12 torr)

High boiling point ( $T_b=240^{\circ}\text{C} - 320^{\circ}\text{C}$ ) hydrocarbons are chosen as solvents for lithographic inks as the solvents used must be viscous and hydrophobic. Screen printing inks need to have solvents with moderately high boiling points.

### Formulations of Gravura ink for paper :

Contents (function)	Amount (%w/w)
C.I.pigment red 57:1(red pigment)	10.00
alcohol soluble nitrocellulose (resin)	20.00
ketone resin (resin)	10.00
dioctyl phthalate (plasticiser)	2.00
polyethylene wax (prevents damage to the film against rubbing)	1.00
ethanol (low b.p. solvent)	30.00
n-propyl acetate (low b.p. solvent)	20.00
ethoxy propanol (low b.p. solvent)	7.00

**Additives:** Additives are used to alter the final properties of the formulation. These include:

- (i) Plasticisers, which enhance the flexibility of the printed film; e.g., Dibutyl phthalate
- (ii) Wax, which promotes rub resistance; e.g., Carnuba-an exudate from the leaves of *Copernicia prunifera* consisting of esters of hydroxylated unsaturated fatty acids with at least twelve carbon atoms in the acid chain
- (iii) Drier, which catalyses the oxidation reaction of inks that dry by oxidation; e.g., Salts or soaps of cobalt, manganese or zirconium
- (iv) Chelating agent, which increases the viscosity of the ink (aluminium chelate) and promotes adhesion (titanium chelate)
- (v) Antioxidant, which delays the onset of oxidation polymerization by reacting with free radicals formed during the autooxidation thus preventing them from reacting further; e.g., eugenol
- (vi) Surfactants, which improve wetting of either the pigment or substrate. They act as stabilizing agents for pigment dispersion
- (vii) Alkali, which controls the viscosity/solubility of acrylic resins in water based inks, e.g. monoethanolamine
- (viii) Defoamer, which reduces the surface tension in water based inks so that stable bubbles cannot exist; e.g., hydrocarbon emulsions

(ix) Humectants retard premature drying

(x) pH modifiers (usually amine derivatives) and biocides and bacteriostats

### **1.3 Biodegradable Polymer:**

Polymers which can be degraded by environment in a reasonable amount of time are supposed to be called biodegradable polymers. European Union norm EN13432 defines a compostable material as: one possessing biodegradability (i.e. converted into carbon dioxide under microbial action), disintegrability (i.e. fragmentation and loss of visibility in the final compost), and an absence of negative effects in the final compost (e.g. a low level of heavy metals).<sup>5</sup>

The implications of polymer biodegradation is:

- Molecular weight decreases
- Crystallinity is destroyed
- Physical properties (e.g. mechanical strength) diminish.

Biodegradable plastics are plastics that can be biologically broken down, in a reasonable amount of time, into their base compounds. They may be composed of:

- "Bioplastics", whose components are derived from renewable raw materials
- Traditional petroleum-based plastics containing additives which allow them to disintegrate
- A combination of the two

#### **1.3.1 Types of biodegradable film:**

Polythene or polyethylene film naturally biodegrade, but it can take many decades to be degraded. There are two methods to resolve this problem. One is to modify the carbon chain of polyethylene with an additive to improve its degradability and then its biodegradability; the other is to make a film with similar properties to polyethylene from a biodegradable substance such as starch. The latter are however much more expensive.

#### **Starch based or biobased (hydrodegradable) film:**

This type is made from corn (maize), potatoes or wheat. This form of biodegradable film meets the ASTM standard (American Standard for Testing Materials) and European Norm EN13432 for compostability as it degrades at least 90% within 90 days or less at 140 ° F. However, actual products made with this type of film may not meet those standards.

Few examples of polymers made from starch:

- Polycaprolactone (PCL)

- Polyvinyl alcohol (PVA)
- Polylactic acid (PLA)

The heat, moisture and aeration in an industrial composting plant are required for this type of film to biodegrade, so it will not therefore readily degrade if littered in the environment.

Pros & cons of starch based film/bag

Pros

- It is "compostable" under industrial conditions.
- Reduced fossil fuel content (depending on loading of filler.)

Cons

- Much too expensive for use everyday
- Source of starch can be problematic (competition against food use, rainforests being cleared to grow crops for bioplastics)
- Fossil fuels are burned and CO<sub>2</sub> produced in the agricultural production process.
- Poorer mechanical strength than additive based example – filling a starch bag with wet leaves and placing it curbside can result in the bottom falling out when a haulier picks it up.
- Often not strong enough for use in high-speed machines
- Degradation in a sealed landfill takes at least 6 months.
- Emits CO<sub>2</sub> in aerobic conditions and methane under anaerobic conditions
- Limited Shelf life. Conditions must be respected for stockage.
- If mixed with other plastics for recycling, the recycling process is compromised.

Typical applications:

Carrier bag, refusal sacks, vegetable bags, food films, agricultural films, mailing films. However, these applications are still very limited compared to those of petroleum based plastic films.

### **1.3.2 Additive based**

#### **Oxodegradable**

The additives consist of transition metals that theoretically foster oxidation and chain scission in plastics when exposed to heat, air and/or light, these metals include cobalt, manganese, magnesium, iron and zinc. The theory behind chain scission is that it is supposed to shorten the polymer chains to the point where they can be consumed by microorganisms found in the disposal environment and used as a food source.

Biodegradable films are made by blending an additive to provide an oxidative and then a biological mechanism to degrade them. These films typically take 6 months to 2 years for degradation in the environment if adequate exposure to oxygen is provided. Degradation is a two stage process; first the plastic is converted by reaction with oxygen (light, heat and/or stress accelerates the process but is not essential) to low molecular-weight fragments that water can wet, and then these smaller oxidized molecules are biodegraded, i.e. converted into carbon dioxide, water and biomass by microorganisms. Commercial competitors and their trade associations allege that the process of biodegradation stops at a certain point, leaving fragments, but they have never established why or at what point. This is similar to the breakdown of woody plant material where lignin is broken down and forms a humus component improving the soil quality.

Recently, Guar –gum/ Polyvinyl alcohol (GG/ PVA ) blend films were prepared by using Guar – gum , polyvinyl alcohol (PVA ) and Citric acid ( CA ) as additive and gluteraldehyde as crosslinking agent for the mixing process . The additives , drying temperature , and the influence of crosslinker of films on the properties of the films were investigated . The mechanical properties tensile strength , elongation at break ( % E ) and thermal properties includes thermogravimetric analysis , degree of swelling ( DS ) of GG / PVA films were examined by using CA as additives .when the film was dried at low temperature , physical properties of the films were clearly improved because the hydrogen bonding was activated at low temperature. <sup>6</sup>

Gupta et. Al. recently reported Biodegradable Packaging Film Derived from Potato Starch & LDPE Grafted with Maleic Anhydride : There is a paradigm shift from non renewal resources to renewable resources in view of problems of disposal of plastic products after their life cycle. This paper deals with the approach, preparation and product properties of polymer prepared by using polysaccharide based biodegradable polymer. Basic material has been prepared by mixing LDPE, LDPE-g-mA (LDPE grafted with (0.5%) maleic anhydride (1:1)) containing a polar group in the LDPE backbone. Prepared basic material has been compounded in twin screw extruder with 0, 2.5, 5.0, 7.5, 10.0, 12.5 & 15% of Potato Starch. Thereafter, after conditioning blown film samples were prepared using extrusion film blowing technique, under temperature profile ranging from 120 to 160 °C. Packaging films have been prepared with maximum 15% potato starch contents and have been characterized by FTIR, DSC, TGA, and XRD techniques to ascertain its impact on some structural and thermal properties like thermal stability, flexibility, crystallinity, crystal size etc. <sup>7</sup>

## **1.4 Environmental concerns; benefits <sup>8</sup>**

Over 270 million tons of plastic are manufactured annually around the world, according to the Society of Plastics Engineers Of those 270 million tons, 26 million are manufactured in the United States. The EPA reported in 2003 that only 5.8% of those 26 million tons of plastic waste are recycled, although this is increasing rapidly.

Much of the reason for disappointing plastics recycling goals is that conventional plastics are often commingled with organic wastes (food scraps, wet paper, and liquids), making it difficult and impractical to recycle the underlying polymer without expensive cleaning and sanitizing procedures.

On the other hand, composting of these mixed organics (food scraps, yard trimmings, and wet, non-recyclable paper) is a potential strategy for recovering large quantities of waste and dramatically increases community recycling goals. Food scraps and wet, non-recyclable paper comprises 50 million tons of municipal solid waste. Biodegradable plastics can replace the non-degradable plastics in these waste streams, making municipal composting a significant tool to divert large amounts of otherwise nonrecoverable waste from landfills <sup>9</sup>.

Compostable plastic combine the utility of plastics (lightweight, resistance, relative low cost) with the ability to completely and fully compost in an industrial compost facility. Rather than worrying about recycling a relatively small quantity of commingled plastics, proponents argue that certified biodegradable plastics can be readily commingled with other organic wastes, thereby enabling composting of a much larger position of nonrecoverable solid waste. Commercial composting for all mixed organics then becomes commercially viable and economically sustainable. More municipalities can divert significant quantities of waste from overburdened landfills since the entire waste stream is now biodegradable and therefore easier to process.

The use of biodegradable plastics, therefore, is seen as enabling the complete recovery of large quantities of municipal solid waste (via aerobic composting) that have heretofore been unrecoverable by other means except land filling or incineration.

## **2.0 Objective & Purpose of Study:**

1. To synthesize biodegradable film based from PVA.
2. To enhance printability in these films.
3. To investigate the best suitable biodegradable films which will have better printability?



## **3.0 Experimental part**

### **3.1 Materials**

PVA used in this study was supplied by Kuraray ( PVA 220 K partially hydrolyzed, 27-33 mPa's viscosity, Viscosity is measured at 4% aqueous solution at 20<sup>0</sup>C determined by Brookfield, 25 gm ), Water ( 100 gm ), Glycerin ( regular, 2.5 gm ) & Poly ethylene Glycol ( from IGL MW 4000, 1.25 gm ) taken.

### **3.2 Instrumentation:**

#### **Fourier -Transform Infrared (FT-IR) Spectroscopy -**

The FTIR spectra were recorded on Thermo- Nicolet 380 Spectrophotometer using ATR assembly the spectra were taken of PVA granule ( mixed in potassium bromide in 1:100 ratio & after grinding pallet is made ) & films. The spectra were obtained from 4000cm<sup>-1</sup> to 500 cm<sup>-1</sup>

#### **Thermogravimetric ( TG )analysis-**

Thermogravimetry analyses were carried out by Instrument TA-250, about 10mg sample was positioned in silica pans and the samples were heated at 10<sup>o</sup> C / minute from ambient Temp to 600<sup>o</sup>C . Thermal analysis was performed under the nitrogen flow.

#### **Scanning Electron Microscopy Study .-**

The surface Morphology of the Film samples were investigated with HITACHI S 3700N using a Voltage of 15KV by Coating with Au.

#### **Differential Scanning Calorimetry**

The melting point (T<sub>m</sub>) was measured by a differential scanning calorimeter (NETZSCH DSC 204). Slices of the plasticized PVA films & granules with total weight of 5-7 mg were weighted and sealed in an aluminum pan. The pans were heated from 30 to 320<sup>o</sup>C at a rate of 10<sup>o</sup>C/min under a flow of Nitrogen. T<sub>m</sub> was determined as onset temperature of the melting endotherm.

## **3.3 Preparation of PVA based biodegradable films.**

The formulation of film based on PVA may require one of the following methods.

- 1) Casting, which is a process consisting of drying a solution or a gel is a simple method for producing films with controlled thickness. In this method, used for food coatings as well as for non-food applications, the gelled state is usually preferred to set hot solutions on a surface upon cooling.
- 2) Extrusion or the thermo pressing process is a process used to create objects of a fixed cross sectional profile. A material is pushed or drawn through a die of the desired cross section. The two main advantages of this process over other manufacturing processes are its ability to create very complex cross sections and work materials that are brittle, because the material only encounters compressive and shear stresses. It also gives finished parts an excellent surface finish.

### **Preparation of PVA based film:**

PVA films were prepared by the casting method for this experiment. First, a calculated amount of PVA ( from Kuraray 220 K partially hydrolyzed, 27-33 mPa's viscosity, Viscosity is measured at 4% aqueous solution at 20<sup>0</sup>C determined by Brookfield, 25 gm ), Water ( 100 gm ), Glycerin ( regular, 2.5 gm ) & Poly ethylene Glycol ( from IGL MW 4000, 1.25 gm ) taken.

- 1) Glycerin & PEG is first mixed in the cold water so that both can easily go into PVA molecule with water. To this solution PVA was added.
- 2) Above mixture was slowly heated to about 80 <sup>0</sup>C with stirring until a homogeneous solution was formed. Water was added to compensate for any moisture loss that may have occurred during the heating process.
- 3) The film-forming solutions were casted onto the petridish and dried at 50<sup>0</sup>C for 12 h to completely eliminate water. Dried films were put in polyethylene bags and stored at room temperature for 1 week before testing.

### **3.4 Soil burial Test: Checking biodegradability**



Figure 1.

Tests based upon this methodology evaluate in-service soil contact exposure. The material is buried in soil beds prepared in the laboratory using standard sieved soil. The soil beds are normally conditioned for up to four weeks prior to use and may be supplemented with organic fertilizer to encourage an active microbial flora. The soil beds containing the samples are incubated at ambient temperature ( from 11<sup>th</sup> March,13 to 6<sup>th</sup> May,.2013, temperature was recorded 30-14 <sup>0</sup> C & 41-28 <sup>0</sup>C respectively) for 55 days.

We took two sample one is square in shape ( 12.5 \* 14 cm, Initial weight : 0.9449 gm ) & other circular ( ID : 9 cm & OD 17 cm, Initial weight was 1.2650 gm.

After 55 days sample were weighed after carefully removing soil from sample.

Weight of square sample recorded 0.7958 gm & weight of circular sample recorder 1.1161 gm.

Finally weight lost due to biodegradation was recorded 0.1491 gm for square sample & 0.1489 gm for circular sample, therefore percentage degradation recorded as 15 & 11%.

Although weight loss look lessor as compare to previous study, this may be due to less microorganism in those conditions.

Percentage moisture in soil checked for both days.

### **Materials**

- Oven with 100 –110 °C temperature
- A balance of precision of  $\pm 0.001$  g.
- Small Petridish.
- Auger or tool to collect soil samples

### **Procedure**

1. Weigh Petridish & record this weight : 46.48 gm & tare it.
2. Place a soil sample of about 5.0036 g in the Petridish.
3. Place the sample in the oven 105°C, and dry for 24 hours or over night.
4. Weigh the dry soil + petridish : 51.1179 gm ( deduct petridish previous weight, therefore we have weight of dry soil as 4.6379 ).

Percentage moisture was calculated & recorded on first day ( i.e.11.03.13 ) : 7.308 %

Same procedure repeated after 55 days to see the difference in moisture before & after burial of samples.

Percentage moisture was calculated & recorded on last day ( i.e.06.05.13 ) : 1.46 %

## **3.5 Surface Treatment (Corona )**

Corona treatment system is a very effective way to increase the surface tension of virtually any material. Surface treatment is required for plastic films/fabrics whose normal surface tension is not sufficiently high to permit good wetting by flexo graphic inks.

**Corona treatment** (sometimes referred to as air plasma) is a surface modification technique that uses a low temperature corona discharge plasma to impart changes in the properties of a surface. The corona plasma is generated by the application of high voltage to sharp electrode tips which forms plasma at the ends of the sharp tips. A linear array of electrodes is often used to create a

curtain of corona plasma. Materials such as plastics, cloth, or paper may be passed through the corona plasma curtain in order to change the surface energy of the material. All materials have an inherent surface energy (dyne level). Surface treatment systems are available for virtually any surface format including dimensional objects, sheets and roll goods that are handled in a web format. Corona treatment is a widely used surface treatment method in the plastic film, extrusion, and converting industries.

Many plastics, such as polyethylene and polypropylene, have chemically inert and nonporous surfaces with low surface tensions causing them to be non-receptive to bonding with printing inks, coatings, and adhesives. Although results are invisible to the naked eye, surface treating modifies surfaces to improve adhesion.

Polyethylene, polypropylene, nylon, vinyl, PVC, PET, metalized surfaces, foils, paper, and paperboard stocks are commonly treated by this method. It is safe, economical, and delivers high line speed throughput. Corona treatment is also suitable for the treatment of injection and blow molded parts, and is capable of treating multiple surfaces and difficult parts with a single pass.

Corona discharge equipment consists of a high-frequency power generator, a high-voltage transformer, a stationary electrode, and a treater ground roll. Standard utility electrical power is converted into higher frequency power which is then supplied to the treater station. The treater station applies this power through ceramic or metal electrodes over an air gap onto the material's surface.

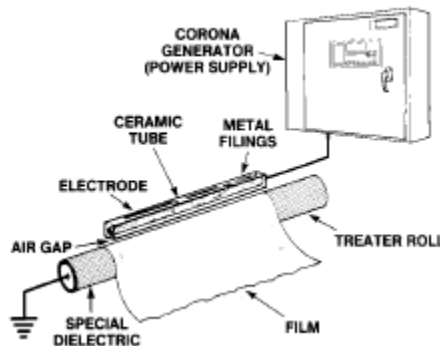


Figure 2

### What Is Corona Treating system ? <sup>10</sup>

A corona treating system is designed to increase the surface energy of plastic films, foils and paper in order to allow improved wettability and adhesion of inks, coatings and adhesives. As a result, the materials treated will demonstrate improved printing and coating quality, and stronger lamination strength.

The system consists of two major components:

1. the power supply, and
2. the treater station.

The power supply accepts standard 50/60 Hz utility electrical power and converts it into single phase, higher frequency (nominally 10 to 30 kHz) power that is supplied to the treater station. The treater station applies this power to the surface of the material, through an air gap, via a pair of electrodes, one at high potential and the other, usually a roll which supports the material, at ground potential. Only the side of the material facing the high potential electrode should show an increase in surface tension.

A corona treating system in its simplest form can be portrayed as a capacitor (see Figure ).

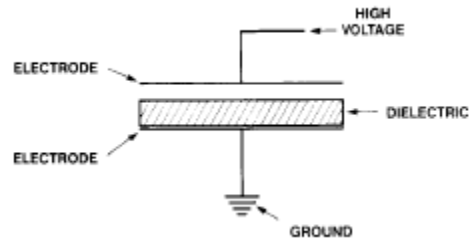


Figure 3. (Capacitor)

Voltage is applied to the top plate which, in the case of a corona treating system, would be the electrode. The dielectric portion of the capacitor would be made up of some type of roll covering, air, and substrate in the corona treating system. The final component, or bottom plate, would take the form of an electrically grounded roll. In the corona treating system, the voltage buildup ionizes the air in the air gap, creating a corona which will increase the surface tension of the substrate passing over the electrically grounded roll.

## PLASMA <sup>11</sup>

Plasma Treatment cleans, etches and functionalizes plastic and metal surfaces to improve adhesion.



Figure 4

Plasma surface treatment is a process that raises the surface energy of many materials so as to improve the bonding characteristics. One form of plasma treatment is also commonly known as a corona treatment, which was invented by Danish engineer Verner Eisby in the 1950s. In many cases this process is the standard treatment for materials such as: plastic polymers, papers, films, glass, and even metals.

Plasma technology is inclusive of many different purposes for surface treatment such as: cleaning, coating, printing, painting, and adhesive bonding. Plasma technology has come to encompass so many different applications that it is now one of the top methods in surface treatment, especially in industries which rely heavily on packaging. There are numerous industrial and packaging solutions created all the time due to the wide versatility in which plasma treatments can be applied. This technology is even heavily used in the automobile and aircraft industries. Plasma treatment also yields very high quality products in basically every applicable field while still being an environmentally friendly process. There is no doubt that plasma treatment is one of the top contenders in surface treatment methods, but which form of plasma treatment is the best? Some of the types, benefits, and shortcomings of different forms of plasma treatment will be explored to determine if any particular treatment types pose significant benefits in comparison to the others.

Plasma is a fairly simple concept which refers to the fourth chemical state of matter. When enough energy is added to each state it changes in sequence from solid to liquid and from liquid to gas. Once in the gas phase if additional energy is forced into the system, then the gas becomes ionized and reaches the plasma state. When the plasma comes into contact with the material surface it transfers the additional energy from the plasma to allow for subsequent reactions to take place on the material surface. The altered surface properties on most materials are ideal for printing, painting, or adhesive bonding; which are used in some form in almost every industry whether plasma treatment is used or not.

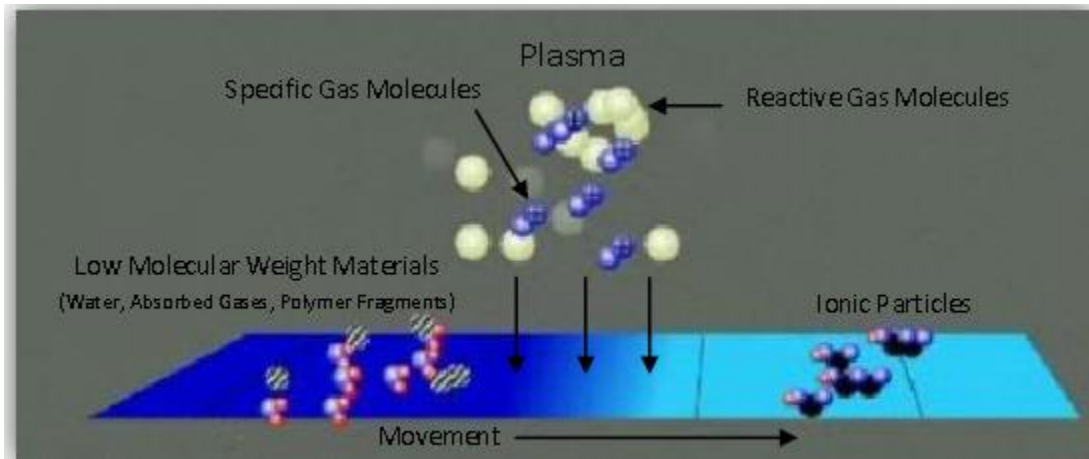


Figure 5

## Difference in Corona & Plasma :

Although there are numerous theories explaining the principles behind the process of corona treating, the most commonly accepted theory appears to be the theory of high-speed oxidation. This theory states that the energy of the high-charged electrical corona breaks the molecular bonds on the surface of the non-polar substrate. The broken bonds then recombine with the free radicals in the corona environment to form additional polar groups on the film surface. These polar groups have a strong chemical affinity to the polar inks and adhesives, which results in improved adhesion. Similarly, the polar surface results in an increased surface energy that correlates with improved wettability.

Plasma or "modified atmospheric" treating is very similar to traditional corona treating with the exception that gases are injected into the corona discharge to modify the reaction with the substrate. Some materials are less reactive to a traditional corona and require this special treatment. Additionally, semi-conductive gases such as helium can be utilized to lower the operating voltage at the corona to meet other particular application requirements.

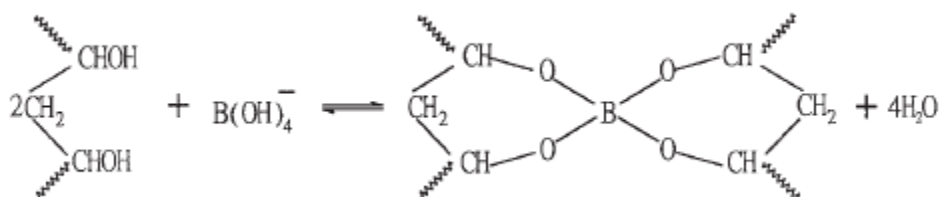
Corona treatment is still the most popular means of achieving better adhesion and will continue to be the dominant choice for years to come. Why? Because corona treatment is still the most economical and practical means of promoting adhesion.

We have done both corona & plasma treatment over PVA film to check the printability.

## 3.6 Surface coating

### 3.6.1 Borox ( 2% Coating ) <sup>12</sup>

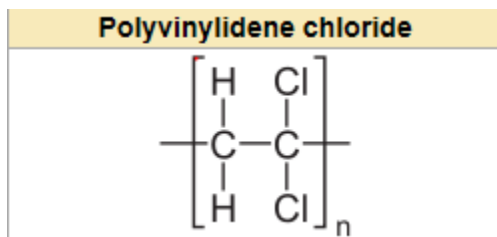
PVA crosslinked films were obtained by coating a layer of 2 wt % borax solution on the surface of PVA films, and the redundant water was absorbed by filter paper. Surface crosslinking is another efficient treatment method because it can further break the intra- and intermolecular interactions of PVA and improve the mechanical properties of the films, as well as affect the states of water in the films. Borax is the commonly used crosslinking reagent of PVA, and it can crosslink PVA in several seconds.<sup>1,31-33</sup> The crosslinking reaction is as follows:



After being coated by a 2 wt % borax solution, a layer of net structures forms on the surface of the films, which will inhibit the evaporation of water; therefore, it needs more energy for water to evaporate.

### 3.6.2 Polyvinylidene chloride coating

Polyvinylidene chloride (PVDC) is a homopolymer of vinylidene chloride



It is a remarkable barrier against water, oxygen and aromas. It has a superior chemical resistance to alkalis and acids, is insoluble in oil and organic solvents, has very low moisture regain and is impervious to mold, bacteria, and insects. But it is soluble in polar solvents. It has good thermal stability, but above 125 °C decomposes to produce HCl.

Polyvinylidene chloride is applied as a water-based coating to other plastic films such as biaxially-oriented polypropylene (BOPP) and polyester (PET). This coating increases the barrier properties of the film, reducing the permeability of the film to oxygen and flavours and thus extending the shelf life of the food inside the package. Coated films have superior barrier properties, heat sealability and printability, consequently they are often used to package goods to extend their shelf life and prevent tampering.

PVDC coated films provides transparent quality that are required in “see-through” food packaging.

We have done PVDC coating over Plasma & Corona treated film manually with steel scale.

### 3.6.3 Acrylic coating

Acrylic coating facilitate printability, sealability and seal integrity of the film. Acrylic coated films are used as overwraps due to their low sealing point, which also offers high aroma barrier with excellent printability and good finishing appearance.

<sup>13</sup>A prime coated oriented polyester film material is disclosed wherein the primer coating consists essentially of a crosslinked copolymer containing at least about 50% by weight of acrylic and/or methacrylic monomers and from about 1% to 15% by weight of a comonomer capable of inter-molecular crosslinking upon the application of heat, and from 0 to about 49% by weight of one or more halogen-free mono-ethylenically unsaturated monomers copolymerizable therewith.



The priming layer may be applied to the polyester film at any suitable stage during manufacture of the film, i.e., before or during the stretching operations, and is crosslinked after application by means of heat. The resultant primed polyester film is found to provide excellent adhesion to many organic solvent based coatings subsequently applied thereto, and to be reclaimable when reprocessed during the manufacture of polyester film without giving rise to significant or intolerable discoloration or degradation of the film.

We have done Vinyl coating over Plasma & Corona treated film manually with steel scale.

### **3.7 Printing over different films**

We had taken ink based on PU, wherein solvent has 70 % alcohol ( ethanol IPA ) & 30 % ethyl acetate.

Vinyl Resin is a high molecular weight, hydroxyl-functional, partiallyhydrolyzed vinyl chloride/vinyl acetate resin. VAGH Solution Vinyl Resin is crosslinkable with amino resins and polyisocyanates and is also compatible with a wide variety of resins including alkyds and acrylics. This resin has good adhesion to vinyl, cellulosic and treated polyester and PE substrates. UCAR VAGH Resin has a high Tg which imparts good sandability in vinyl/alkyd/urea wood sealers. It is cited in FDA regulations for use in food contact applications and is also heat-sealable.

Both inks ( PU & Vinyl based ) were coated manually over nine surface ( as per table 1), therefore we have now 9 surface, tape test is conducted to see which surface has better adhesion or printability.

### 3.8 Tape test: for comparing printability

As per below table we have 9 surface to see the printability in PVA films.

Table I. Prepared Films

No.	Name	Description
1	PVA	PVA at 20 % wt %
2	PVA-Plasma	PVA Plasma treated film
3	PVA- Crona	PVA Crona treated
4	PVA-Plasma (PVDC)	PVA Plasma treated film with coating of PVDC
5	PVA-Plasma (Acrylic)	PVA Plasma treated film with coating of Acrylic
6	PVA-Plasma (Borox)	PVA Plasma treated film with coating 2% Borox Solution
7	PVA-Corona (Acrylic)	PVA Corona treated film with coating of Acrylic
8	PVA-Corona (PVDC)	PVA Corona treated film with coating of PVDC
9	PVA-Corona (Borox)	PVA Corona treated film with coating 2% borox solution.

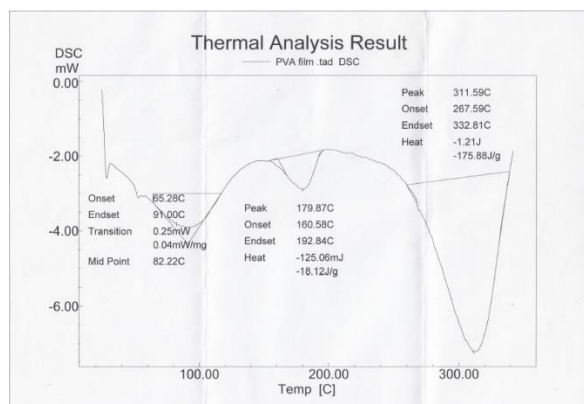
## 4.0 Result & Discussion:

### 4.1 Characterization

#### 4.1.1 Differential Scanning Calorimetry (DSC) analysis:

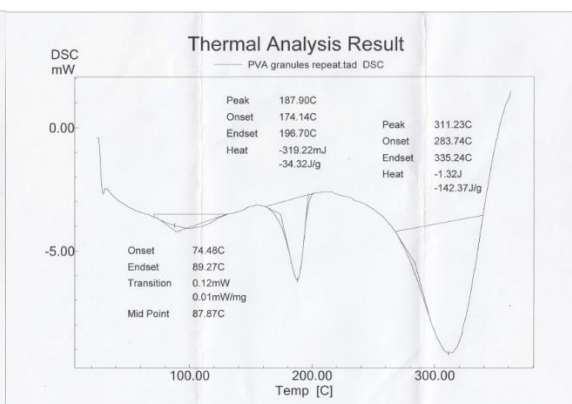
T<sub>m</sub> values of pure PVA and plasticized PVA were measured using DSC starting from room temperature to 320 °C at 10<sup>0</sup>C per minute of heating rate. The obtained thermograms of plasticized PVA and pure PVA are shown in Fig. 6 & 7. and the onset temperature of the endotherm is taken as T<sub>m</sub>. T<sub>m</sub> values of pure PVA is recorded 283 °C and plasticized PVA is recorded as 267 °C.

Previous studies have shown that most of the plasticizers can reduce the T<sub>m</sub> of PVA, such as glycerol, ethylene glycol, and compound containing amide group. The decrease of T<sub>m</sub> may be attributed to the decrease in the average crystallite size and the degree of crystallinity. With a lower degree of the crystallinity, the segmental mobility of PVA increased and thus the T<sub>m</sub> decreased.



**Figure 6 PVA Film ( Plasticized)**

**$T_m : 267\text{ }^\circ\text{C}$**



**Figure 7 Pure PVA**

**$T_m : 283\text{ }^\circ\text{C}$**

The  $T_g$  was determined ( $\approx 67^\circ\text{C}$ ) as the midpoint temperature by standard extrapolation of the linear part of DSC curves.

## 4.1.2 Fourier Transform Spectroscopy:

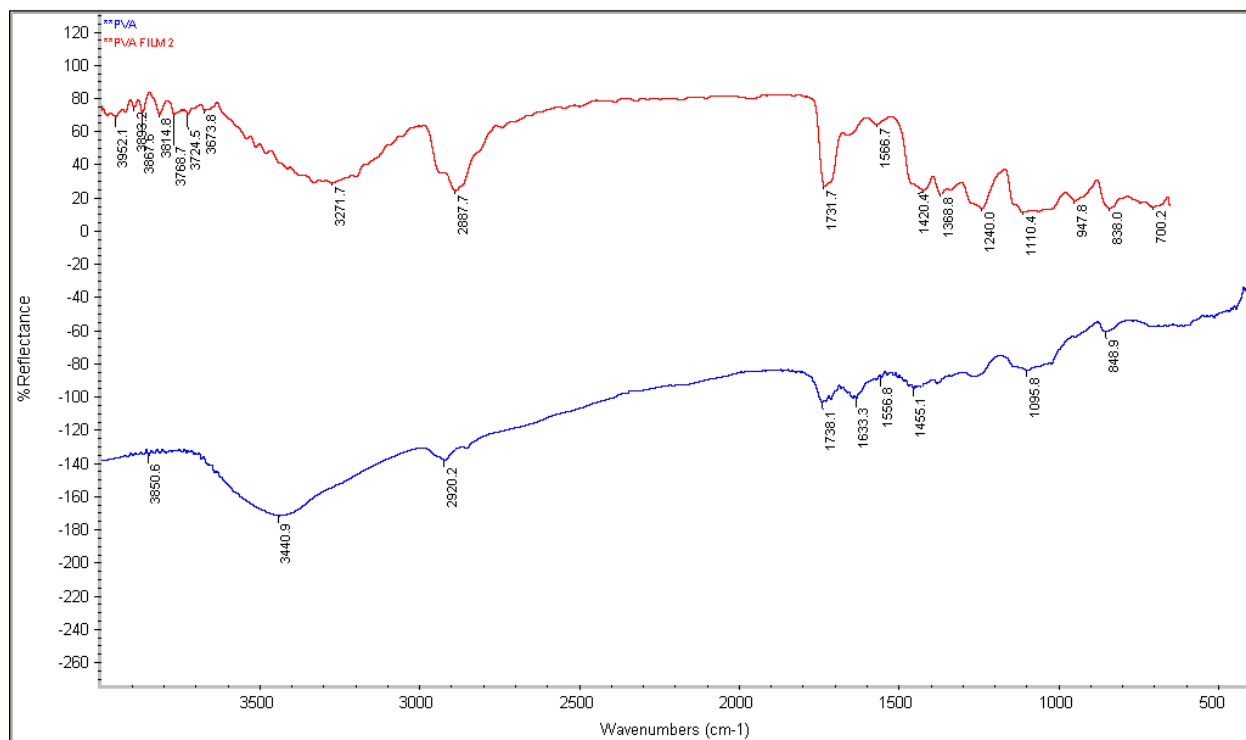


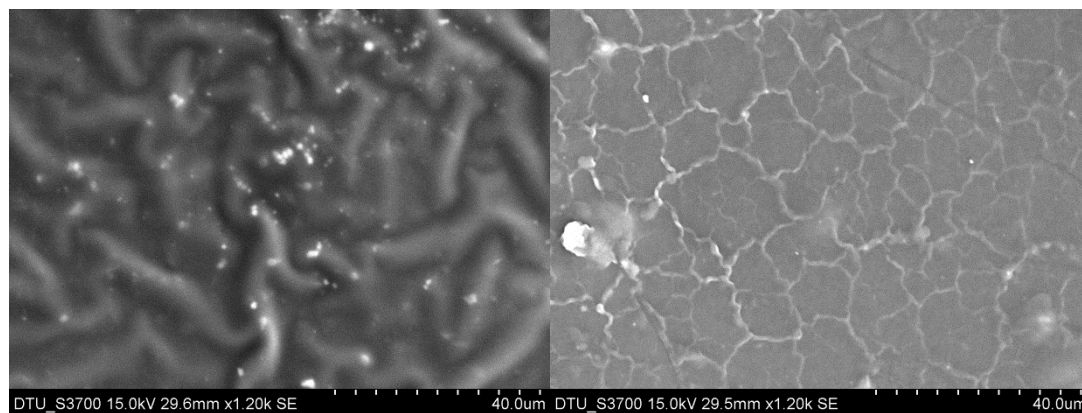
Figure 8

The basic rationale of the plasticization of PVA is that the plasticizer can form stable hydrogen bonding with PVA molecules. The most commonly used investigation of hydrogen bonding is in the infrared region. PVA molecule is generally associated with the intermolecular and intramolecular hydrogen bonding and there is no absorption band of free “-OH” at 3600  $\text{cm}^{-1}$ . The absorption band of “-OH” engaged in the hydrogen bonding at 3440  $\text{cm}^{-1}$  is obviously shown in Fig. 8.

FTIR spectrum of PVA is represented in Figure by blue line & plasticized PVA Film by red line. The important peaks are characterized below. A broad peak between 3440–2920  $\text{cm}^{-1}$  is due to the OH stretching of PVA. The C-H symmetric and antisymmetric stretching vibrations are observed at 3000 and 2020  $\text{cm}^{-1}$  respectively. A peak at 1738  $\text{cm}^{-1}$  is corresponding to the carbonyl stretching of vinyl acetate in PVA. C-H out of plane bending vibration is observed at 848  $\text{cm}^{-1}$ .

### 4.1.3 Scanning Electron Microscope

Micrograph analysis is very important to observe the physical structure of the blend film. The microcosmic morphology of the plasticized PVA films was examined by scanning electron microscope and the photographs were shown in below Figure 4.



Corona treated

Plasma



Reference- Untreated

Figure 9

As per above photographs it is clear that after corona as well as plasma treatment, the surface of the films became very rough which could be helpful in enhancing the printability on synthesized biodegradable films. Indentation were more in Corona as compare to Plasma, therefore corona treated film can provide better room for ink molecule, thus increases printability.

#### 4.1.4 Thermogravimetric Analysis (TGA)

TGA has been used extensively in the study of polymeric systems. This analytical technique used to determine materials thermal stability and its fraction of volatile components by monitoring the weight loss of the sample in a chosen atmosphere as a function of temperature. Figure shows the TGA experimental results of PVA resin & film blends. The samples were measured in the temperature range from 30°C to 600°C with a constant rate of 10°C/min under nitrogen atmosphere. Figure shows that the weight loss of the sample decreases as the temperature increases. This shows that degradation of the sample occurred in the system. The first stage presents the loss of weakly physisorbed water while second stage exhibits the decomposition of side chain of PVA. The third stage shows the decomposition of main chain of PVA. A typical weight loss occurred at about 100°C due to moisture escape during the melting.

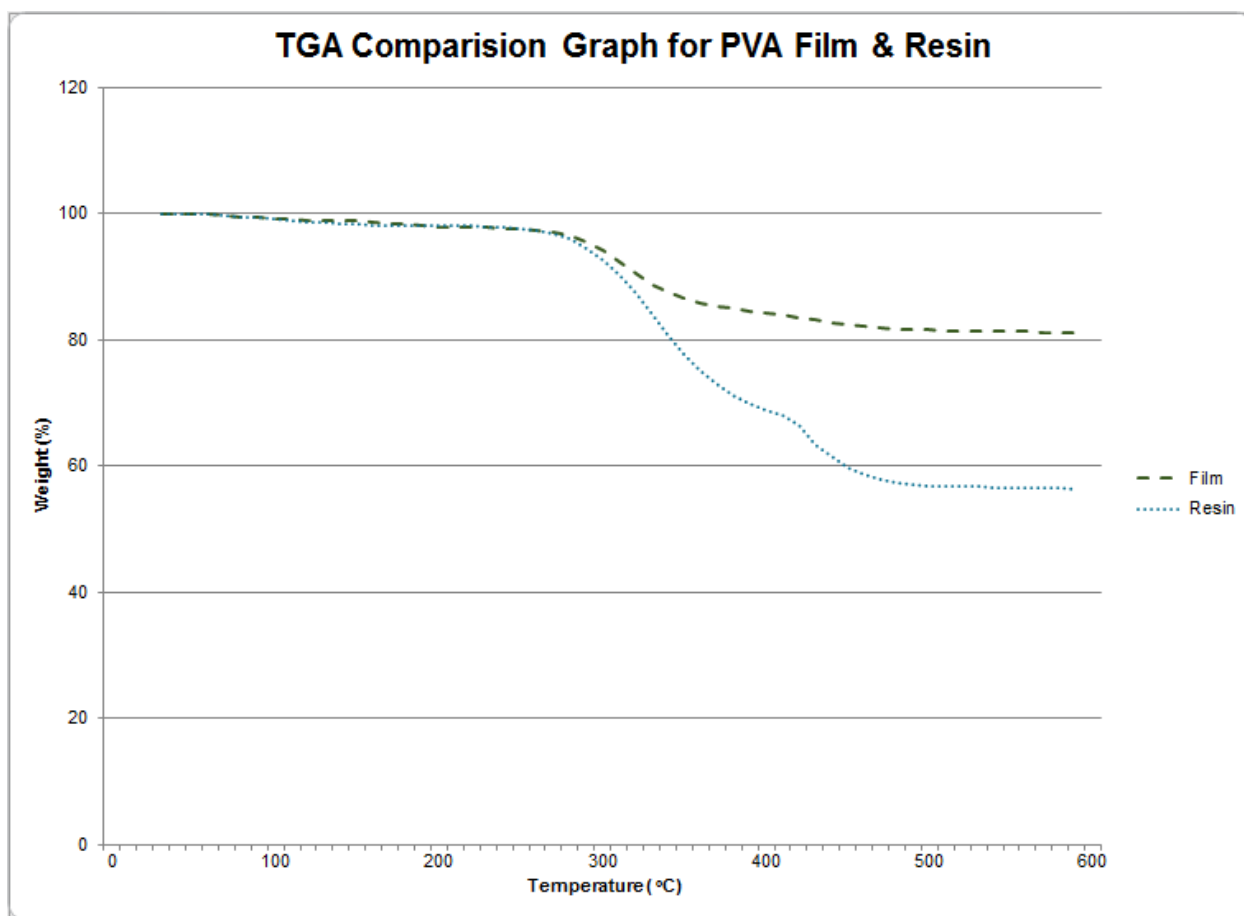


Figure 10

Another important factor in the thermal processing of PVA is the thermal stability of PVA. In this study the thermal stability of pure PVA and plasticized PVA ( Film ) was studied by TGA. The measurements were carried out from room temperature to 600°C. The TGA traces were shown in above figure. The mass loss below 200°C could be mainly ascribed to the loss of water.

Pure PVA starts the thermal decomposition process almost at the same temperature with  $T_m$ . With the addition of the plasticizer, the initial decomposition temperature of PVA sharply moves to a higher temperature. The difference between  $T_m$  and the decomposition temperature was much enlarged. It is obvious that by the addition of the plasticizer, the thermal processing window of PVA was obtained, which is useful in processing.

The increase of the thermal stability of plasticized PVA when compared with pure PVA suggests the strong interaction between the hydroxyl groups of PVA and the plasticizer. Previous studies<sup>14</sup> proved that the thermal degradation of PVA is initiated by the elimination of side groups from the main chain and follows a two-step mechanism.

The first degradation step of PVA is the elimination of the hydroxyl and acetate side groups. For fully hydrolysis PVA, the ratio of acetate side groups is very small. These indicate that at least hydroxyl groups take part in the thermal degradation of PVA and the stability of hydroxyl group is crucial for the stabilization of PVA. The plasticizer (Glycerin) could form strong interaction with the hydroxyl groups of PVA and thus the thermal stability of PVA was improved.

## 4.2 Printability Test:

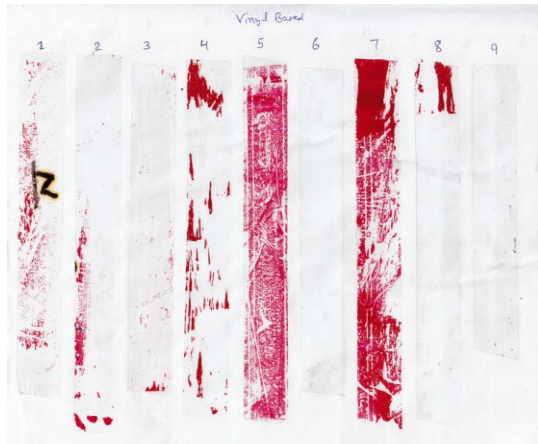
Table 2

S.no.	Type of film	PU Based Ink			Vinyl Based Ink		
		Fully Transfer	Partial Transfer	Not Transferred	Fully Transfer	Partial Transfer	Not Transferred
1	Normal PVA		2			2	
2	Normal-Plasma		4			2	
3	Normal-Corona		3			1	
4	Normal-Plasma with PVDC	Failed				4	
5	Normal-Plasma with Acrylic		1		Failed		
6	Normal-Plasma with Borox			Passed			Passed
7	Normal-Corona with Acrylic		1		Failed		
8	Normal-Corona with PVDC	Failed				1	
9	Normal-Corona with Borox			Passed			Passed

Scale for Partial transfer: 1 is less & 5 is more transfer of ink

From above table it is clear that in PVA film treated with plasma & Corona & coated with borox 2% solution produced better results in the present study.





**Tape test with Vinyl based Ink**



**Tape test with PU based Ink**

Figure 11

## **5.0 Conclusion:**

Biodegradable film made from PVA shows potential for use as packaging material. However, compared to the common thermoplastics, biodegradable films based on PVA still reveal some disadvantages, such as water dissolving & low printability due to PEG which is to be added during melt processing to avoid stickiness in the film which also act as plasticizer. This constraint has led to the development of the improved properties of biodegradable film made from PVA. Surface treatment ( like Plasma and Corona ) & coating ( like PVDC, Acrylic & 2% Borox ) in combination is done, initial results clearly shows that corona treatment provide better results compare to plasma. Finally, it is clear that in PVA film treated with Plasma and Corona & surface coating with borox 2% solution produced better results. However, the potential application, in terms of properties and limitations on the use of facilities, should be taken into account when selecting techniques for improvement.

The plasticizer could largely reduce the melting point of PVA and increase the thermal stability of PVA. The increase in the difference between the melting point and the thermal decomposition temperature enables the thermal processing of PVA. The FT-IR studies show that the plasticizer could effectively destroy the hydrogen bonding of PVA, this is because that the plasticizer glycerin could form strong interaction with the hydroxyl group of PVA.

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