

## Development and characterization of biodegradable blending Starch/PVA Films theoretical and experimental comparison

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**Abstract.** In this work the biodegradable films by blending starch and PVA in desired proportions were developed by solution casting process[2]. The starch content was varied from 1 to 60 wt % of PVA. The effect of composition on various characteristics of the resulting blends were investigated. The starch incorporation increased the Glass transition temperature (T<sub>g</sub>). Because of starch, these films have attained more insulating properties by decreasing dielectric constant. The transmissibility and chemical resistance of the films decreased and vapour barriers properties of the films improved by the presence of starch. The swelling coefficient increased with the starch content, reached maximum for the film with 30wt% of starch, and then decreased. The formation of hydrogen bond in the films, which could improve the compatibility of the two components were investigated by FTIR spectroscopy. The mechanical properties such as tensile strength, tear strength, and percentage elongation decreased with the increase in the starch content[3]. However Young's modulus, density and hardness increased with the increase in the starch content and compared with theoretical model.

**Key words:** Bio degradable films, solution casting process, Mechanical properties ,starch, PVA.

### 1. Introduction

PVA is a versatile polymer with many industrial applications. The prominent properties of PVA are its Biodegradability in the environment and good mechanical properties. But the degradation duration is still higher for PVA. it is well suited for making blends with natural polymers since it is highly polar and can be manipulated in water solution[10]. However poor mechanical properties constituted one of the



major unresolved problems. Also plasticized starch alone swells and deforms on exposure to moisture.

## 2. Experimental

### 2.1. Materials used

The materials used in the work include; starch, PVA and distilled water. Soluble starch was obtained from Qualigens Fine Chemicals (Mumbai, India; amylase content = 21%). PVA was obtained from Nice Chemical Pvt. Lt., Kochi, Kerala. The properties of PVA were as follows;

1) Average molecular weight = 125,000g/mol.

2) Degree of hydrolysis = 99%

3) Ash content = 0.75%

The distilled water was taken from the Polymer Science and Technology Laboratory, NITC, Kerala. The pH of distilled water was 7.5.

### 2.2. Preparation

A series of PVA/ starch blends were processed into films by solution casting process. The starch content was varied from 0 to 60 wt % of PVA. 5gms of PVA was added to 50ml of hot distilled water at 90°C. Using a magnetic stirrer, the mixture was stirred at an rpm ranging from 500 to 1200 for about 1 hr to get the PVA solution. This solution was then poured into a glass mould of dimension 15cm\*15cm\*3cm (length\*breadth\*height). Mould was then placed in an oven at 50°C for 12 hrs. Figures 1 and 2 shows the magnetic stirrer and glass mold used for making films.

**Table 2.1** Composition of the films

S.No.	PVA amount(grams)	Scratch content(%)	Scratch content (grams)
1	5	0	0
2	5	10	0.5
3	5	20	1.5
4	5	30	2
5	5	40	2.5
6	5	50	3
7	5	60	3.5



**Figure 1.** Magnetic Stirrer



**Figure 2.** Glass Mould

### 3. Testing procedure

#### 3.1 Morphology

The morphological studies were conducted on the films using the “Optical Microscope”, MOTIC BA 300 and also by the SEM (Scanning Electron Microscope).

#### 3.2 Mechanical properties

##### 3.2.1 Tensile strength, Tear strength, Percentage elongation & Young's modulus.

The tensile test specimens were prepared by using a standard cutting die 80×12.5×4 mm which corresponds to BS 903 part A2-Type3. The test was conducted on an Instron Universal Testing Machine (UTM) at a crosshead speed of 50mm/min. The obtained value was an average of 3 specimens. Tensile strength, Tear strength, Percentage elongation and Young's modulus were evaluated

##### 3.2.2. Hardness

The measurement of hardness was carried out using a Shore durometer. The hardness number (Shore D) was obtained by taking the average.

#### 3.3 Electrical properties:

The dielectric constant and resistance offered by the samples were determined using the “Electrochemical Workstation”. Samples of area 2.5 cm\* 2.5 cm were cut from the films.

#### 3.4 Solvent resistance :

Solvent resistance test was conducted to study the swelling behavior of the blend films. Samples of area 2.5 cm \* 2.5 cm (breadth \* width) were cut from the films. The samples were dried by heating in an oven at 50°C for around two hours. The swelling coefficient ( $\alpha$ ), for each samples, was calculated by using the equation ; [15]

$$\alpha = \frac{(M_e - M_o)}{(M_o \cdot \rho_s)} \text{ Where, } M_e = \text{Equilibrium weight, } M_o = \text{Initial weight}$$

$$\rho_s = \text{Density of solvent (Benzene, 0.8786 g/cm}^3\text{)}$$

### 3.5 Chemical resistance:

The chemical resistance test was conducted to study the effect of acids and alkalies on the blend films. Samples of area 2.5 cm \* 2.5 cm (breadth \* width) were cut from the films. The samples were dried by heating in an oven at 500C for around two hours. The samples were then immersed in 100ml of NaOH (Sodium Hydroxide) and HNO<sub>3</sub>(Nitric Acid) respectively for 1hour [15].

### 3.6 Transmission analysis

The transmission analysis of the films was conducted by using the UV spectrometer. The transmission spectrum obtained for each film was analyzed.

### 3.7 Permeability

The permeability study was conducted to valuate the vapour barrier property of the films. Methanol, which is having a low boiling point, was used for the study.



**Figure 3.** Permeability beaker



**Figure 4.** Permeability study Test set up

The entire system was then placed on an accurate weight measuring device

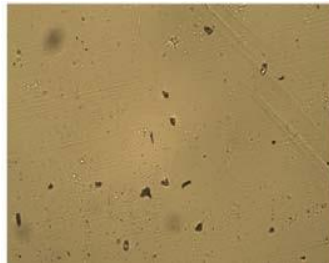
### 3.8 FTIR (Fourier Transformed Infrared) Spectroscopy:

The test examples were placed into transparent disks for analysis by FTIR spectroscopy.

## 4. Results and discussion

### 4.1.MORPHOLOGY

From the morphological study using the Optical microscope and SEM, it was revealed that a uniform distribution of starch particles was obtained in the film containing 30 wt % of starch. Agglomerates of starch particles were observed in the films with 40, 50 ad 60 wt % of starch. Figure 4.1 shows the Optical microscope images of various blend films. From the above images, it is clear that there is a good interaction between the filler materials and the matrix at lower



Pure PVA film



PVA + starch (10 wt %) film



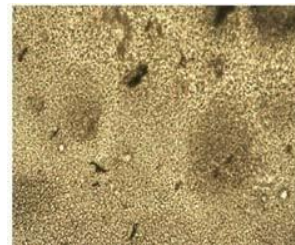
PVA + starch (20 wt %) film



PVA+ starch (30 wt %) film



PVA+ starch (40 wt %) film

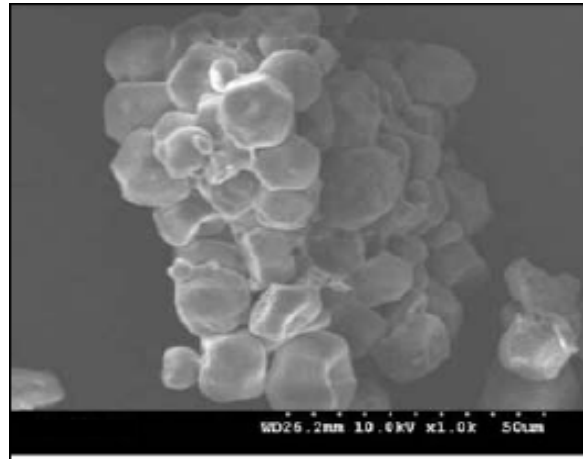


PVA+ starch (50 wt %) film



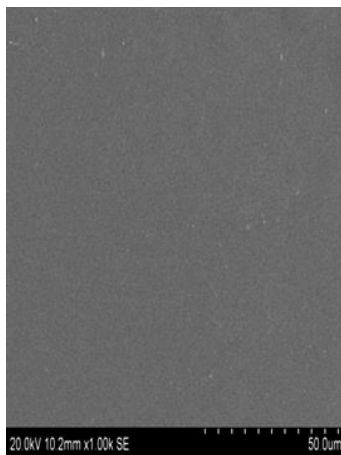
PVA+ starch (60 wt %) film

**Figure 5.** Optical microscope images of the blend films.



**Figure 6.** SEM image of the starch agglomerate

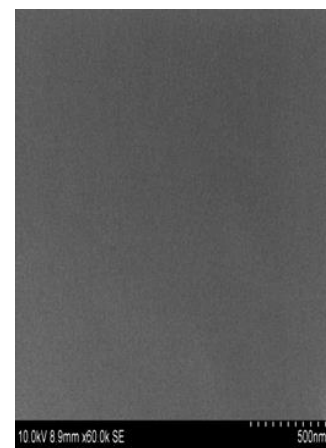
Figure 6. shows the SEM image of the agglomerates in the film with 40 wt% starch Figure 7 shows the SEM images of the various films. Since polymers are not good conductors of electron, their morphology cannot be properly studied using SEM. That is why a good image showing the distribution of the starch particles is not obtained for the films with 0, 10, 20, 30 wt % of starch. But agglomerates can be seen in the films with 40, 50, 60 wt % of starch. The size of the agglomerates was found to increase from 396 nm to 496  $\mu\text{m}$  as shown in figure 6.



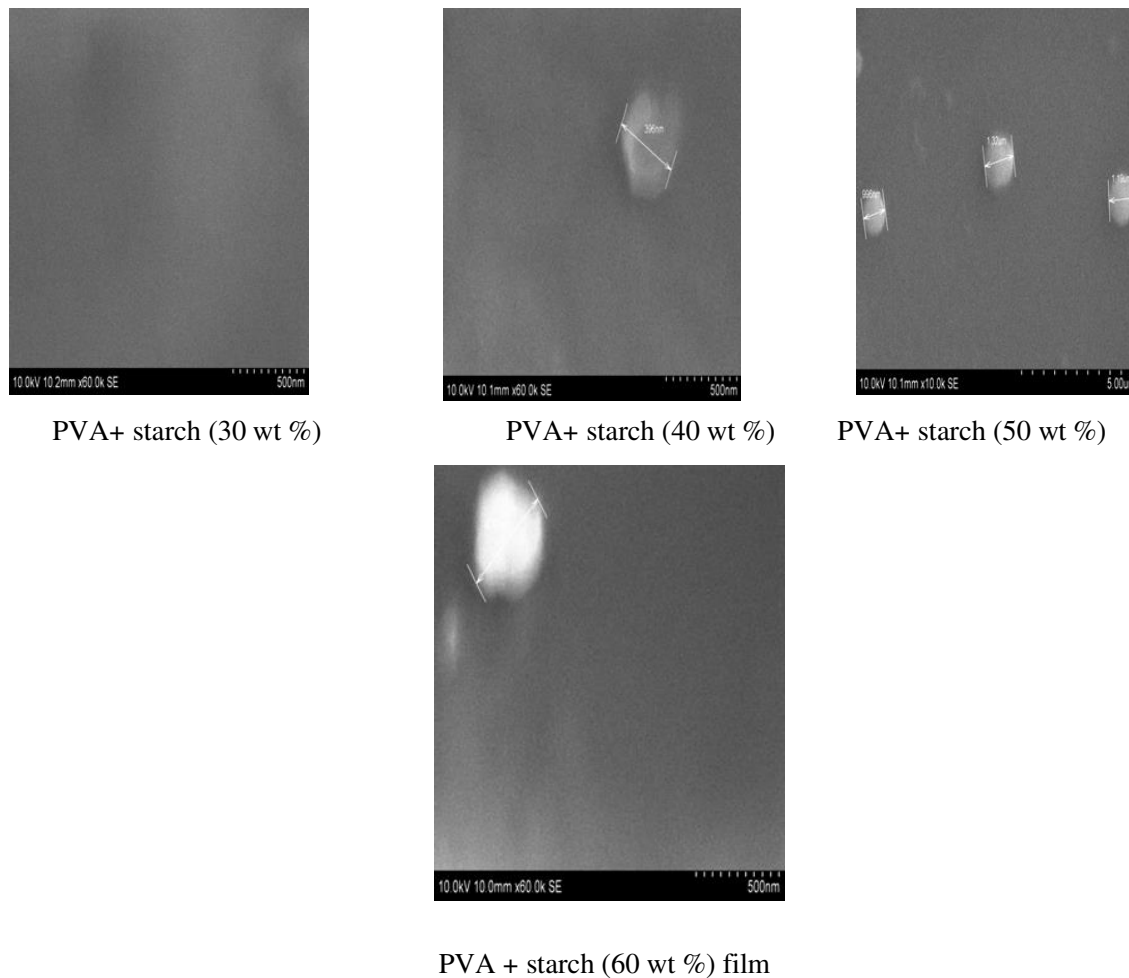
Pure PVA film



PVA+ starch (10 wt %)



PVA+ starch (20 wt %)



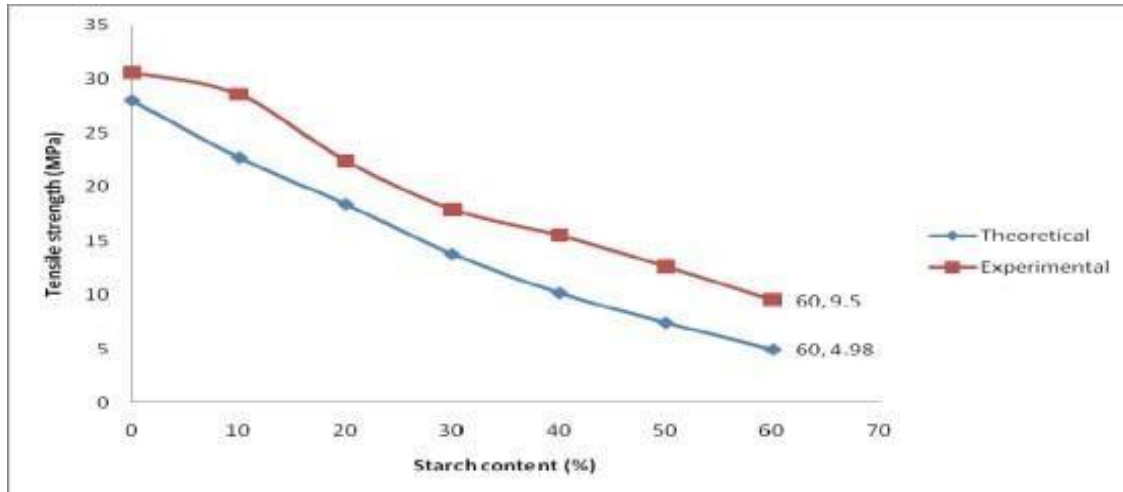
**Figure 7.** SEM images of the various blend films

#### 4.2 MECHANICAL PROPERTIES

**4.2.1 Tensile strength** The tensile strength decreases with increase in the starch content. As the starch content increased, the effective cross sectional area of the PVA continuous phase was reduced, resulting in decreased strength.

##### *Comparison with a theoretical model*

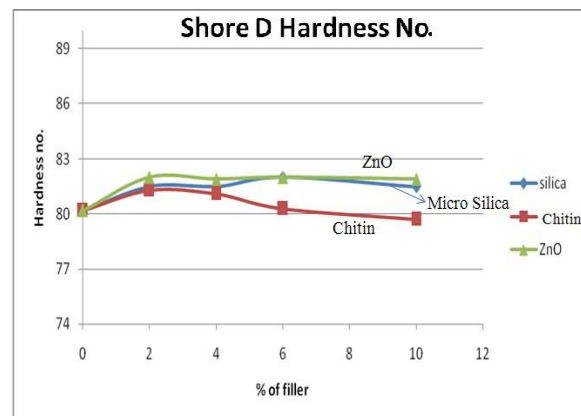
Nicolais and Narkis developed a geometrical model for the tensile strength of a blend ( $\sigma_b$ ), [16]. The expression is given by;  $\sigma_b = \sigma_0(1 - 1.21\phi^{2/3})$ , where  $\sigma_0$  - Tensile strength of the matrix.  $\phi$  -> Weight fraction of the filler material.



**Figure 8.** Comparison between the experimental and theoretical Values of the tensile strength

At 1 and 2 wt% of nano silica, the tensile strength was found to be maximum. It was increased by nearly 46%. With further addition of nano silica, the tensile strength was found to be constant at around 30 MPa.

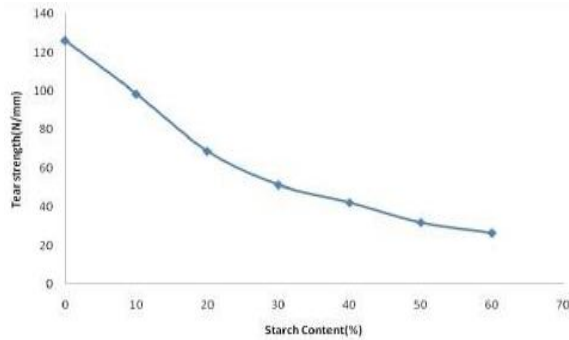
#### 4.2.2 HARDNESS PROPERTIES.



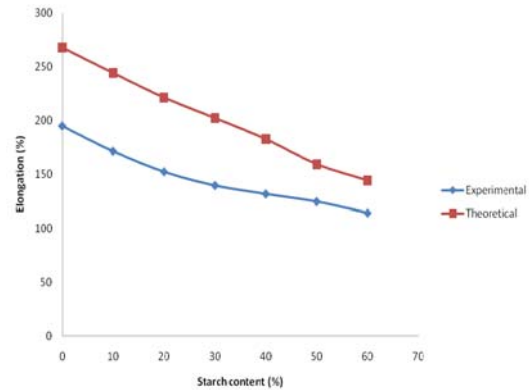
**Figure 9.** Variation of hardness with the content of micro silica, ZnO and chitin powder

The hardness was found to be increased slightly with the addition of micro silica and ZnO and it was almost constant at higher contents of micro silica and ZnO whereas, with the addition of chitin powder, the hardness decreased Gradually.[9]

**4.2.3. Percentage elongation:** Percentage elongation decreases with increase in the starch content. The decrease in the percentage elongation is due to the fact that the Young's modulus of the blend film increases with starch content.



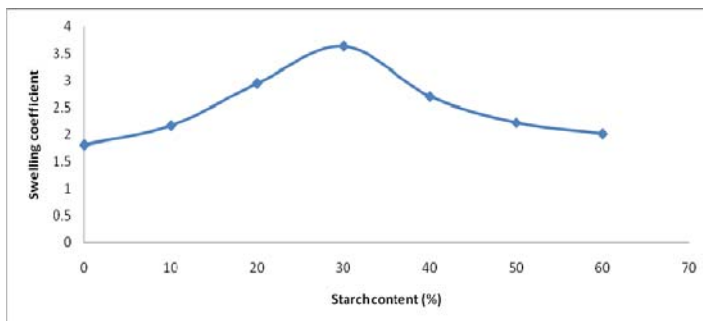
**Figure 10.** Variation in tear strength of the blends



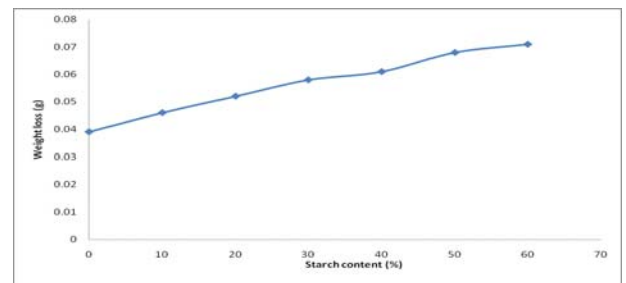
**Figure 11.** comparison between experimental and theoretical values of percentage of elongation

**Comparison with a theoretical model:** Nielson developed a geometrical model for the percentage elongation of a blend ( $C_b$ ) [16]. The expression is given by;  $C_b = C_0(1 - \Phi^{1/3})$  where  $C_0$  - Percentage elongation of the matrix.  $\Phi$  - Weight fraction of the filler material.

#### 4.3 Solvent resistance test and Chemical resistance test:



**Figure 12.** Variation in the swelling coefficient



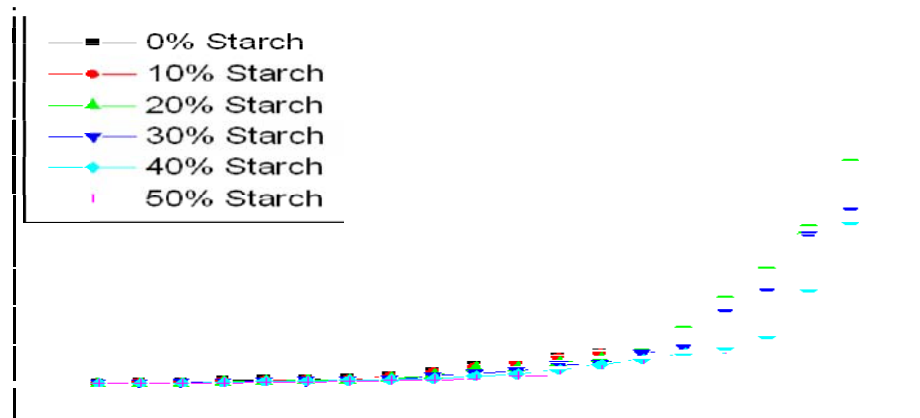
**Figure 13.** Variation in weight loss of the blend films immersed in Sodium hydroxide

From the figure, it is clear that the swelling coefficient increases with increase in the starch content upto 30 wt % and then decreases with further increase in the starch content. Starch is highly reactive with benzene. The presence of starch in the blends made the reaction between the blends and benzene possible. Benzene was penetrated in the blends, which increased the value of the swelling coefficient. In films with starch content more than 30 wt %, agglomerates of starch were found. The variation in weight loss of the samples immersed in Sodium hydroxide (NaOH) and Nitric acid (HNO<sub>3</sub>) is shown graphically in figure

4.9 respectively. From the figures, it is clear that the weight loss increases with the increase in the starch content.

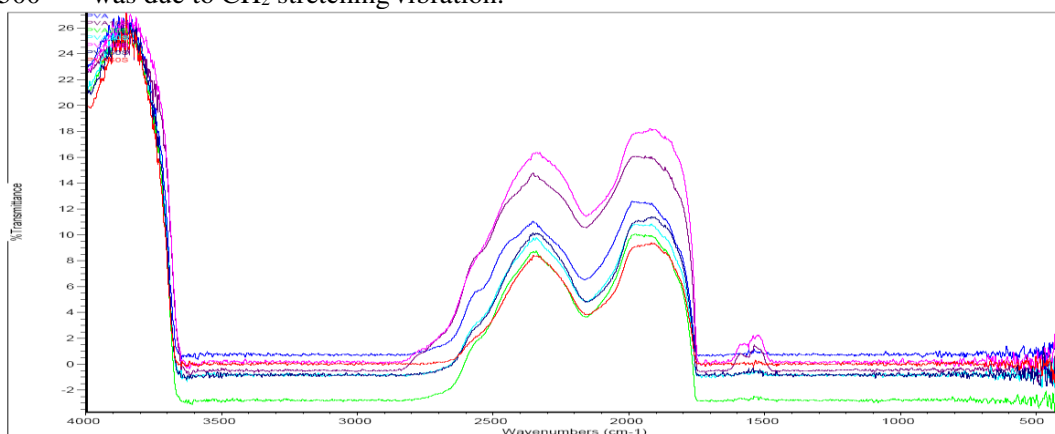
#### 4.4. Permeability

From the figure, it is clear that, for a particular film, the vapour permeability increases with time. But with the increase in the starch content, the methanol vapour permeability decreases[8].



**Figure 14.** Permeability test

**4.5. FTIR SPECTROSCOPY :** The peak at  $1663\text{ cm}^{-1}$  arises due to the presence of water in the films. Since the films were prepared by the solution casting process, some water molecules will be present in the films. The broad peak in the region  $3500\text{--}4000\text{ cm}^{-1}$  was due to O-H stretching vibrations. A small but sharp peak is evident at  $1722\text{ cm}^{-1}$ [16]. This was attributed to the carbonyl functional groups arising from the residual acetate groups that remain after the manufacture of PVA[12]. The broad but sharp peak in the region  $2100\text{--}2500\text{ cm}^{-1}$  was due to  $\text{CH}_2$  stretching vibration.

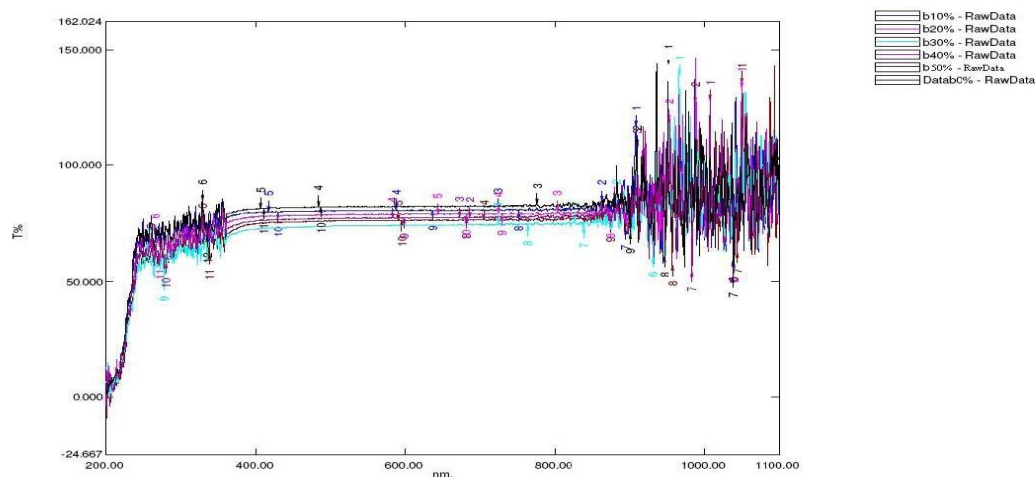


**Figure 15.** FTIR spectrum of the blend films

#### 4.6. TRANSMISSION ANALYSIS

##### Overlay Spectrum Graph Report

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**Figure 16.** transmissibility to the visible radiations

From the figure.16, it is clear that pure PVA films offered better transmissibility to the visible radiations[5]. Almost 80% of the incident visible radiations were transmitted by the pure PVA film. With the increase in the starch content, the transmissibility was decreased and the film with 30 wt % starch showed the least.

#### 5. Conclusions:

From the morphological study using the Optical microscope and SEM (Scanning Electron Microscope), it was revealed that a uniform distribution of the starch particles was obtained in the film with between 0% to 30 wt % of starch. Further increase in starch content caused agglomeration. starch content and the resistance offered by the films increased with the starch content. This concludes that the film has attained more insulating properties due to the presence of the starch. From the solvent resistance test, it was found out that the swelling coefficient increased with the starch content, reached a maximum for the film with 30 wt % of starch, and then decreased. The FTIR Spectroscopy revealed the formation hydrogen bond in the films.

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