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Preparation of Chitosan-Polyvinyl Alcohol Blends and Studies on Thermal and Mechanical Properties

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Abstract

Chitosan is a biopolymer, which is an amino polysaccharide derived from the N-deacetylation of chitin. It is a natural polymer because of the presence of degradable enzyme Chitinase. Chitosan is blended with synthetic polymer PVA with formaldehyde enhances the thermal stability. Thermogravimetric analysis was conducted to measure the weight loss of the above mentioned blend systems at a heating rate $10^{\circ}\text{Cmin}^{-1}$ in nitrogen atmosphere. It is evident that formaldehyde is acting as a cross linker for Chitosan-PVA blend which have high thermal degradation or high thermal stability when compared with Chitosan-PVA-glycerol and Chitosan-PVA blends. The presence of cross linking agents like formaldehyde decreases the solubility to certain extent, and also increases the thermal stability due to the presence of aldehyde (-CHO-) group in the formaldehyde, forming cross links with amine(-NH₂-) group present in the Chitosan. This reaction is based on the Schiff's base mechanism. Various compositions of Chitosan-PVA blends have been studied for its thermal and mechanical properties. The mean tensile strength and percentage elongation of Chitosan-PVA blends decreases with decrease in PVA content. But on addition of glycerol on to the blends of Chitosan-PVA, the percentage elongations increase and mean tensile strength decreases.

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1. Introduction

Biopolymers are abundantly available from its natural sources of extraction. A few major group of biological composition includes polysaccharides, proteins, lipids and others¹. Among them polysaccharides like cellulose, chitin and Chitosan are commonly applied. Chitin and Chitosan are the second most available biopolymer after cellulose. They are sourced mainly from exoskeleton of crustaceans such as shrimp also available from other sources such as fungi and some insect's wing. It is well known having common properties of poly saccharides such as biocompatibility, biodegradability, non-toxicity and antimicrobial as well as hydrophilicity. This made Chitosan is a very useful compound in wide range of applications in medical, pharmaceutical, chemical, agriculture and environmental fields. Chitin and Chitosan is naturally abundant polymer and renewable polymers have excellent properties like non toxicity, biodegradability, and adsorption. The reaction of Chitosan is considerably more versatile than cellulose due to the presence of NH₂ group. Natural polymers have attracted an increasing attention over the past two decades, mainly due to their abundance and low cost. The high sensitivity to moisture is one of the limitations to the application of Chitosan film in packaging applications².

Chitin and Chitosan are amorphous solid biopolymers that are almost insoluble in water. Chitosan is soluble in Organic acids like 1% acetic acid, formic acid, adipic acid, formic acid, lactic acid, malic acid, prop ionic acid or succinic acid. Solubility in mineral acids is limited. It is soluble only within acid concentrations ranges from 0.15 to 1.1%. It is insoluble in phosphoric or sulphuric acid and in neutral or alkaline media. Polyvinyl Alcohol (PVA) is nontoxic, water –soluble synthetic polymer, which is widely used in polymer blends because of its good physical and chemical properties and excellent film forming characteristics and emulsifying capability³. Its use is important many applications such as controlled drug delivery systems, membrane preparations, recycling of polymer and packaging etc. The property of bio inertness makes it useful in medical applications such as artificial pancreas, hemo dialysis, nanofiltration and implantable medical devices.

Chitosan exists in form of white yellowish flakes, which can be converted to bead or powders. Degree of Deacetylation (DD) plays vital role on molecular weight of Chitosan lower DD higher the molecular weight providing higher chemical stability and mechanical strength. It has a cationic nature due to presence of amino and hydroxyl group and has strong positive charge because of presence of large amino group. It is a rigid polymer due to presence of hydrogen bonding and reactive hydroxyl groups available in the structure. It is also a biocompatible, antibacterial, biodegradable, bacteriostatic/fungi static, safe and non-toxic polymer which make it applicable in food industry and medical applications. The addition of cross linkers and plasticizers to carbohydrates films has been widely studied as a means of improving textural properties. The most studied plasticizing agent in carbohydrate films has been glycerol. Its efficacy in increasing film punctures deformation. Glycerol can be used at relatively low concentration to achieve significant plasticizing properties. Glycerine is a material of outstanding utility with many areas of application. The key to glycerine's technical versatility is a unique combination of physical and chemical properties, ready compatibility with many other substances, and easy handling. Glycerine is also virtually nontoxic to human health and to the environment physically, glycerine is a water-soluble, clear, almost colourless, odourless, viscous, hygroscopic liquid with a high boiling point. Formaldehyde is a used as a cross linking agent. Its small molecules (HCHO, of which the -CHO is the aldehyde group) dissolve rapidly in water, with which they combine chemically to form methylene hydrate, HO-CH₂-OH.

1.1 Objective of the study

- To prepare Chitosan-PVA blends.
- To study thermal stability of Chitosan-PVA blends cross linked with formaldehyde.
- To study mechanical properties of Chitosan-PVA blends plasticized with glycerol

2. Materials and methods

2.1. Chemicals used

85% degree of deacetylated Chitosan is brought from India sea foods, Thoppupady, Cochin. Glacial acetic acid is an aqueous solution clear and colourless, pH=2.4, molar mass=60.05g/mol, density1.05g/cm³ brought from Medilise chemicals, Kannur. 1% acetic acid is prepared by mixing 1ml glacial acetic acid with 99ml water. Poly vinyl alcohol (500gm) brought from (spectrum reagents and chemicals pvt. Ltd. Edayar, Cochin) Degree of polymerization =1700-1800 and pH of aqueous solution 5-7.

Formaldehyde is brought from Spectrum Chemicals Edappally Cochin(formalin) HCHO=30.03, Wt/ml at 20°C=1.085-1.095 and assay=37-41% w/v. Glycerol is brought from Spectrum Reagents and chemicals pvt. Ltd Edyar, Cochin (500ml), Wt. per ml at 20°C = 1.255-1.260g, Density=1.26g/cm³.

2.2. Methods

2.2.1. Preparation of Chitosan-PVA films

The polymer films were prepared by casting method. Chitosan solution were prepared by dissolving Chitosan about 0.05g,0.10g,0.15g,0.20g,0.25g,0.30g,0.35grams, in 50ml 1% aqueous acetic acid solution at room temperature, using sonicator. 1% aqueous acetic acid solution is prepared by mixing 1ml glacial acetic acid to 99ml water. The PVA about 5g was dissolved in 50 ml water by using mechanical stirrer. Both the polymer solutions were mixed and make homogenous solution using sonicator. Then PVA-CHITOSAN blend is prepared. After ultrasonic treatment, PVA-CHITOSAN blend was poured to a glass plate and kept on a closed oven at 70° c for 4-5 hours. The film thickness was controlled by solution volume⁶.The above experiment was conducted to get different compositions by varying the amount of Chitosan.

2.2.2. Preparation of Chitosan-PVA-glycerol films

We randomly selected 0.10g, 0.20g, 0.30g, 0.35g Chitosan and dissolved in 50ml 1%aq. acetic acid solution. To the polymer solution add 25%wt/wt of glycerol (of the polymer weight)¹ and sonicated till become a homogenous solution. Add 50 ml PVA solution and mixed well using mechanical stirrer. After becoming a homogenous solution, it poured on a glass plate and kept on the oven 70° c for 4-5 hours. The film thickness was controlled by solution volume⁹.

2.2.3. Preparation of Chitosan-PVA-formaldehyde films

We randomly selected 0.10g, 0.20g, 0.30g, 0.35g Chitosan and dissolved in 50ml 1%aq. acetic acid solution. Add 50 ml PVA solution and mixed well using mechanical stirrer. After becoming a homogenous solution add 25%wt/wt of formaldehyde (of the polymer weight)¹ and sonicated till become a homogenous solution. It poured on a glass plate and kept on the oven 70° c for 4-5 hours. The film thicknesses were controlled by solution volume

3. Result and discussion

3.1. Thermogravimetric analysis

Thermogravimetric analysis was conducted to measure the thermal weight loss of the Chitosan-PVA blends with additives at a heating rate 10°C min⁻¹ in nitrogen atmosphere. Thermogravimetric analysis⁷ was conducted to measure thermal weight loss of Chitosan-PVA blends cross linked with formaldehyde and plasticized with glycerol at a heating rate 10° C min⁻¹ in nitrogen atmosphere. The weight losses at different stages were analysed. The data collected was treated graphically x-axis temperature and weight on y-axis⁸.

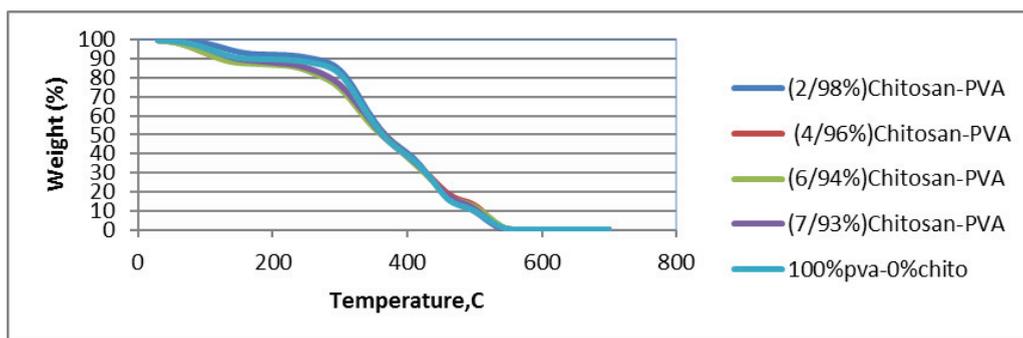


Fig.3.1 TGA curve for Chitosan/PVA blends

After 10% reduction, 2% Chitosan have better thermal stability, when compared with other 0, 4, 6, 7% Chitosan. Similarly, after 20% reduction 2% Chitosan have better thermal stability than others. From these values, we can understand that lower amount of Chitosan has higher thermal stability without adding a cross linker like formaldehyde.

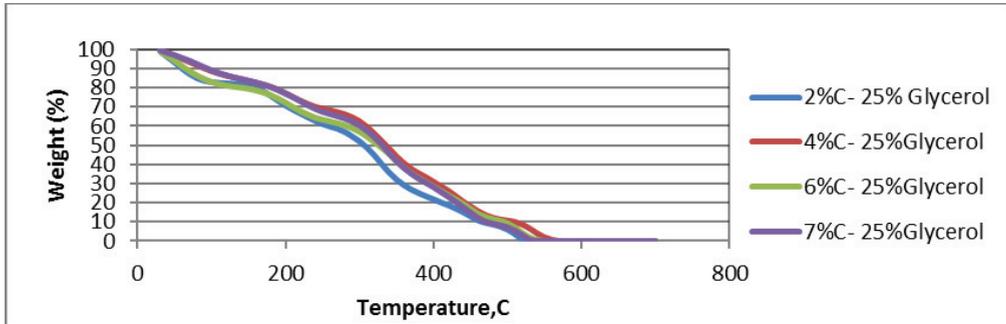


Fig.3.2 TGA curve for Chitosan/PVA blends with glycerol

After 10% reduction, 4% Chitosan have better thermal stability, when compared with other 2, 6, 7% Chitosan. Similarly, after 20% reduction 4% Chitosan have better thermal stability.

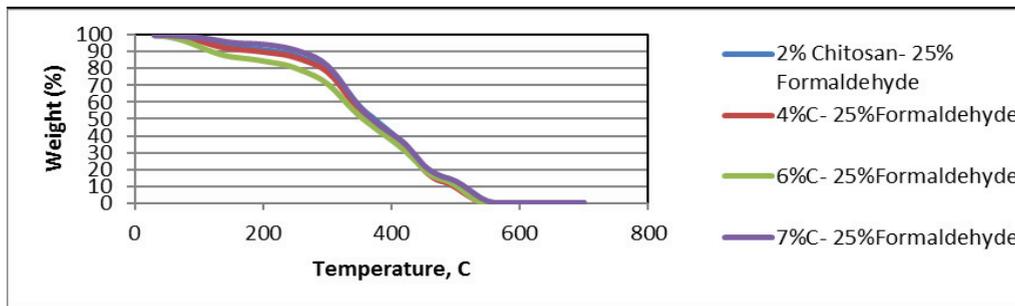


Fig.3.3 TGA curve for Chitosan/PVA blends with formaldehyde

After 10% reduction 7% Chitosan with 25% formaldehyde have better thermal stability, when compared with other 2, 4, 6% Chitosan -PVA formaldehyde. Similarly, after 20% reduction 7% Chitosan -PVA formaldehyde have better thermal stability than others. From this we can understand that higher the amount of formaldehyde has higher thermal stability.

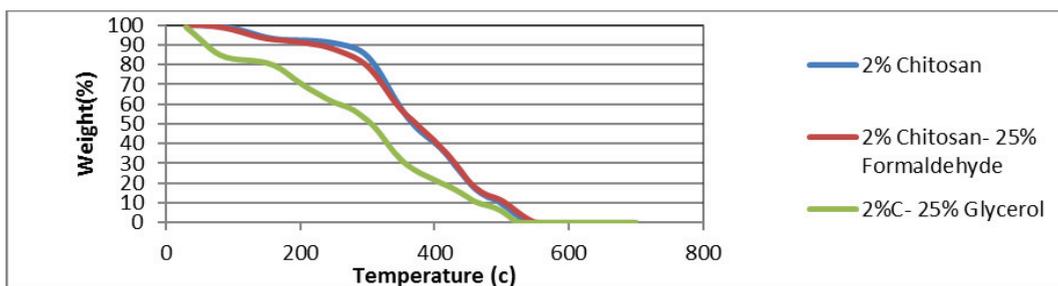


Fig.3.4 TGA curve for 2% Chitosan/98%pva blends

After 10% reduction 2% Chitosan have better thermal stability when compared with other 2% Chitosan 25% formaldehyde and glycerol. Similarly, after 20% reduction 2% Chitosan have better thermal stability there is only a small difference. From this we can understand that lower amount Chitosan has higher thermal stability. Chitosan-PVA blend is a stable material without adding a cross linker it shows higher thermal stability.

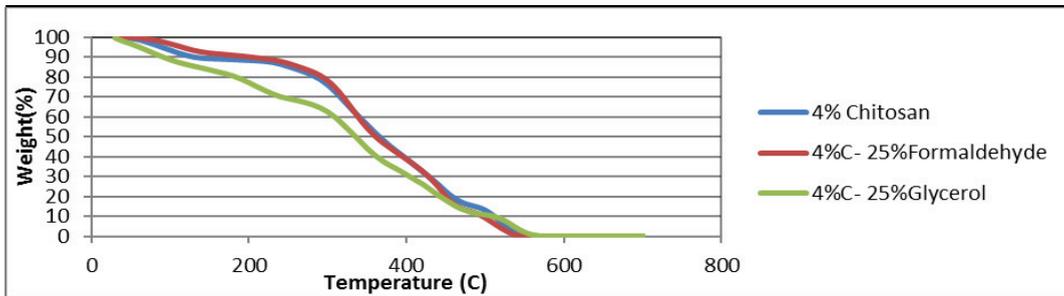


Fig.3.5 TGA curve for 4% Chitosan/96%pva blends

After 10% reduction 4% Chitosan with 25 % formaldehyde have better thermal stability, when compared with other two 4% Chitosan with glycerol and 4%Chitosan –PVA blend. Similarly, after 20% reduction 4% Chitosan with 25% formaldehyde have better thermal stability compared with other two. From this we can understand that the addition of formaldehyde to the polymer blend enhances the thermal stability.

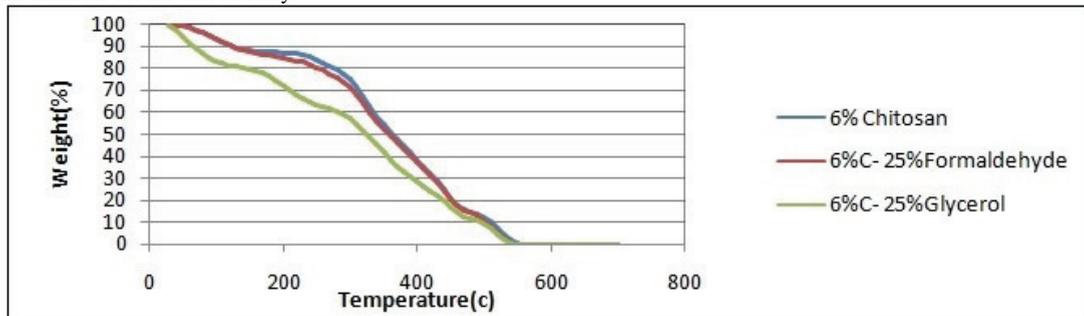


Fig.3.6 TGA curve for 6% Chitosan/94% PVA blends

After 10% reduction, 6%Chitosan with 25% formaldehyde have better thermal stability, when compared with Chitosan with 25% glycerol and 6% Chitosan-PVA blends. Similarly, after 20% reduction 6% Chitosan have better thermal stability. From this we can understand that formaldehyde helps to increase the thermal stability than glycerol. Because of the presence of formaldehyde, the thermal stability increases due to the Schiff's base mechanism takes place.

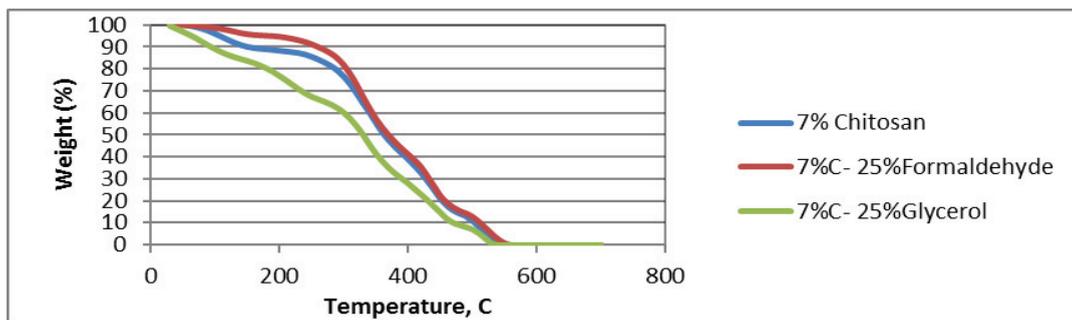


Fig.3.7 TGA curve for 7% Chitosan 93%pva blends

After 10% reduction, 7% Chitosan with 25% formaldehyde have better thermal stability than pure Chitosan-PVA and plasticized Chitosan. Similarly, after 20% reduction 7% Chitosan with 25% Formaldehyde have better thermal stability. From this we can understand that substance contain glycerol should have low thermal stability.

The better thermal stability is due to the presence of aldehyde group present in the cross linker. The thermal stability of Chitosan-PVA blend membrane was enhanced by adding formaldehyde as cross linker. The biodegradable polymer, Chitosan a linear polysaccharide has been found to be a good chemical entity for synthesizing blends because of its greater cross linking ability due to the presence of (-NH₂) amino group. This amino group and aldehyde group forms a Schiff's base reaction causing high thermal stability to blends.

3.2. Universal testing machine (UTM) analysis

Mechanical properties⁹ of Chitosan-PVA blends without glycerol and Chitosan-PVA blends with glycerol were determined using Tensile Testing Machine. The thickness of prepared films was measured using a thickness dial gauge at three different places and mean values were calculated. Tensile test shows the film strength and elasticity which are determined according to strength at break.

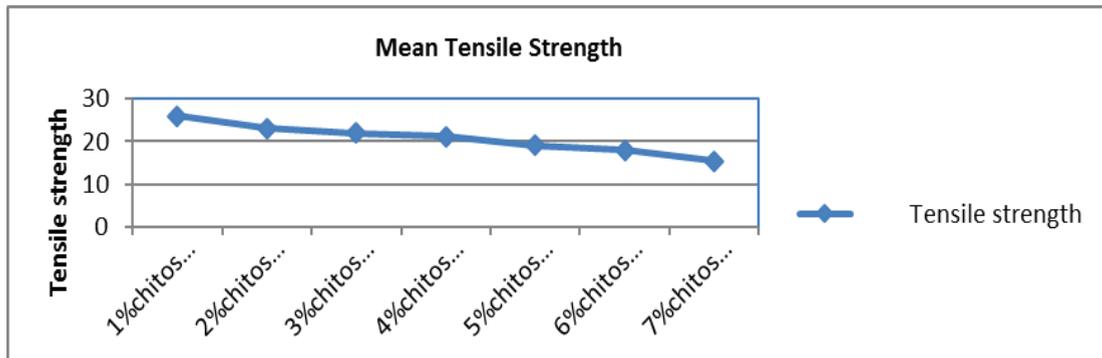


Fig.3.8. Mean tensile strength of Chitosan-PVA films (without glycerol)

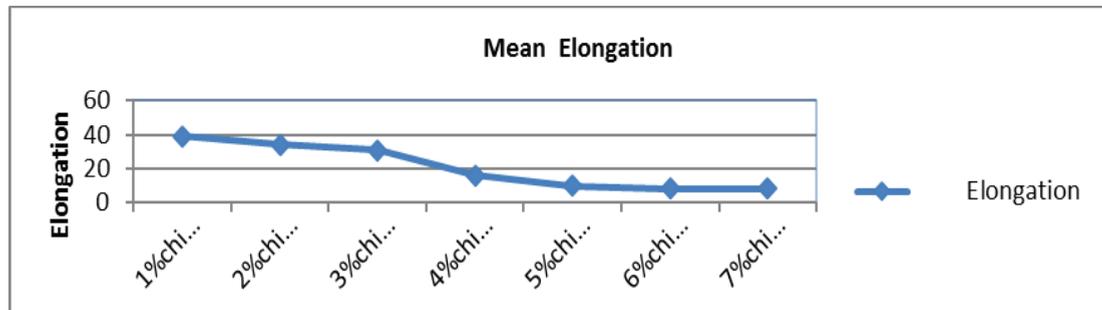


Fig.3.9. Mean elongation of Chitosan-PVA films (without glycerol)

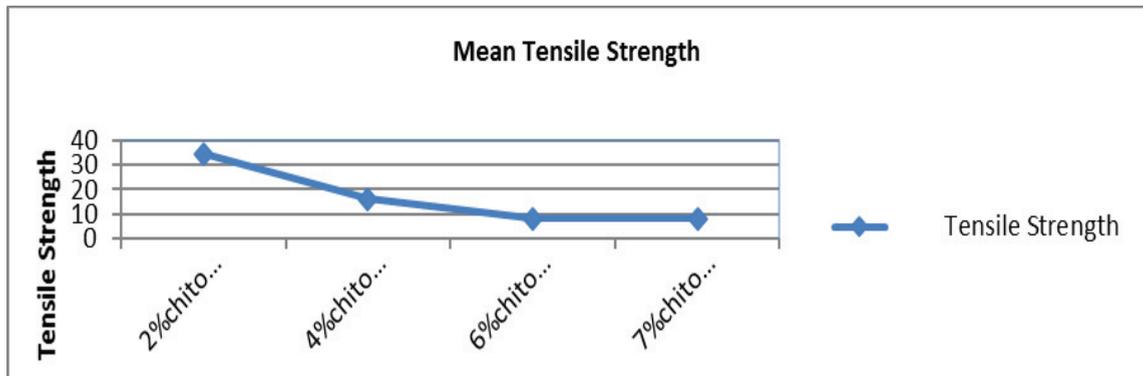


Fig.3.10. Mean tensile strength of Chitosan-PVA (with glycerol)

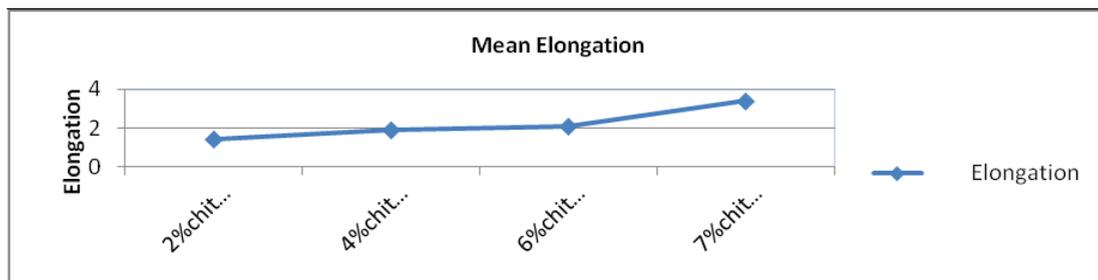


Fig.3.11. Mean elongation of Chitosan-PVA (with glycerol)

It was noted that increasing the amount of Chitosan and decreasing amount PVA decreases the mean tensile strength and percentage elongation of the plastic films in strength. Addition of glycerol as plasticizer affected the mechanical properties of the plastic film there is an increase of percentage elongation and a decrease in tensile strength. In some studies, increase in the amount of PVA also increases the mean tensile strength and percentage elongation. This is because of the positively charged polysaccharide Chitosan moved towards the negatively charge of the hydroxyl group of the Polyvinyl Alcohol which improved the tensile strength and elongation of the plastic film due to the occurrence of intermolecular interactions between Chitosan and Polyvinyl Alcohol through hydrogen bond formation⁴. Decreasing the amount of PVA results in the lower degree of intra- and intermolecular hydrogen bonding which is due to anionic property of the hydroxyl group. In the Fig.3.11 Shows that the amount of plasticizer was increased the percentage elongation also increases. In this work also, Chitosan-PVA film also shows decrease in tensile strength and an increase in elongation as the level of plasticizer increased. Glycerol reduces the intermolecular Vander Waals forces between polymers, which makes the plastics flexible and reduces its stiffness. When plastics compounded with plasticizers usually becomes more flexible, the tensile strength was reduced and provides better elongation⁵.

4. Conclusions

Thermogravimetric analysis was conducted to measure the weight loss of the Chitosan-PVA blends and also cross linked with formaldehyde and plasticized with glycerol at the heating rate $10^{\circ}\text{C min}^{-1}$ in nitrogen atmosphere. The weight loss at different stages was analysed. Cross linked Chitosan-PVA blends with 25% formaldehyde should have much better thermal stability compared with glycerol. Due to the presence of aldehyde (-CHO-) group in the formaldehyde, forming cross links with amine (-NH₂-) group present in the Chitosan. This reaction is based on the Schiff's base mechanism. In this study 7% Chitosan- PVA blend with 25% formaldehyde shows better thermal stability than pure Chitosan-PVA blends and 25% glycerol. From this we can come to a conclusion that the amount of Formaldehyde increases the thermal stability of blends. When compared with glycerol, Formaldehyde shows much higher thermal stability.

Decrease in PVA percentage and increase in Chitosan percentage shows that mean tensile strength decreases for both Chitosan-PVA blends without glycerol and Chitosan-PVA blends with glycerol. Decrease in PVA percentage also shows that the mean percentage elongation decreases in the case of Chitosan-PVA blends and increases with Chitosan-PVA-glycerol system. It is thought that glycerol reduces the intermolecular Vander Waals forces between polymers, which makes the plastics flexible and reduces its stiffness. Glycerol reduces the rigidity network of the intermolecular bonding of Chitosan polyvinyl alcohol films, producing a less ordered film structure and increasing the ability of movement of polymer chains. Three hydroxyl groups of glycerol, makes a moisturizing and lubricant effect that diminishes the brittle nature of the film and provides improved results in elongation. These results show that the addition of plasticizer significantly improved the percentage elongation while the tensile strength decreased with increasing plasticizer content because increasing the amount of plasticizer will make the plastic very flexible making the plastic very soft and pliable.

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