Composite Film of Poly Lactic Acid and Polyvinyl Alcohol with Carbon Nanotube Reinforcement: Insight Mechanical Property Analysis

Abstract

PLA-PVA film stacking is a promising approach for developing sustainable and biodegradable packaging materials. The technology involves stacking films made from polylactic acid (PLA) and polyvinyl alcohol (PVA) in a layered arrangement. PLA-PVA films have desirable properties such as good oxygen and moisture barrier, excellent mechanical strength, and low toxicity. The stacking technique offers versatility in film composition and layer thickness, enabling customization to meet specific packaging needs. Additionally, the biodegradability of PLA and PVA offers a sustainable alternative to traditional plastic packaging. This abstract provides an overview of the PLA-PVA film stacking technology and its potential benefits for sustainable packaging. Recent years, there has been an increasing interest in developing sustainable and high-performance packaging materials. This research aims to investigate the properties of a novel packaging material composed of polyvinyl alcohol (PVA) films with treated carbon nanotube (CNT) mix, stacked with polylactic acid (PLA) films. The PVA-CNT mix was prepared by treating the CNTs with a silane coupling agent, which improved the dispersion and compatibility of the CNTs in the PVA matrix. The PVA-CNT films were then stacked with PLA films to form a multilayered structure. The mechanical, thermal, and barrier properties of the PVA-CNT/PLA film were characterized using various analytical techniques. The results showed that the PVA-CNT mix improved the mechanical strength and thermal stability of the PVA film. The tensile strength of CNT reinforced film obtained 14.16 N/mm^2 and shows higher TEAR Force 3.37 N. In TGA analysis, maximum degradation temperature 348.7^0C and weight loss was recorded 59.9 %. CNT mixed film has the maximum DTG 1.435 mg/min at 350.0^0C. Moreover, the addition of the PVA-CNT layer to the PLA film stack resulted in a significant enhancement of the oxygen barrier property, which is a critical factor for food packaging applications. Overall, this research demonstrates the potential of PVA-CNT/PLA film stacking as a promising approach for developing sustainable and high-performance packaging materials. The use of CNTs as a reinforcing agent for PVA films could lead to the development of packaging materials with improved mechanical and barrier properties, while the use of PLA offers a biodegradable and environmentally friendly alternative to traditional plastic packaging.

Keywords: Carbon nanotubes, MWCNT film, Packaging Material, Polylactic acid, Polyvinyl alcohol, Reinforcement

1.0 Introduction

Due to concerns and growing awareness regarding the protection of the environment, new regulations and laws are obligated for industries to source better environment-friendly materials [1]. Present investigations focus on alternative sources that are non-toxic, non-abrasive, environmentally sustainable, biodegradable, and petrochemical-free [2,3]. Sustainable composites made of natural fibres and biodegradable polymers can potentially substitute traditional petrochemical-based products [4]. Several polymers are made from renewable resources, including plastics based on starch, lignin, cellulose esters, polyhydroxy butylate, and polylactic acid [5,6]. Researcher trying to solve the drawbacks of polymers which are their low toughness, high cost, poor moisture stability, challenging production, and lack of commercial availability

[6,7]. The important thing is that renewable material is how durable when using it long time[6]. For example, the brittle nature of polylactic acid limits its importance, but the drawback has improved by adding reinforcement [2,8].

Polylactic acid (PLA) is well-known and very soluble. The film's nature depends on the characteristics of different solvents and is affected by each solvent. Such as, mobility of the polymer's chain is increased by chloroform and when the evaporation rate is slow then the dioxane results in a rough surface on the film [31]. PLA is not soluble when dissolved in solvents including toluene, acetone, acetonitrile, methanol, and ethyl acetate. PLA films made with toluene, xylene, acetone, and ethyl acetate displayed surface segregation and enhanced hydrophobicity [9,31,32]. Methylene chloride and acetonitrile when combined with PLA thin films changed the crystalline structure, improving heat stability but making the material brittle [8]. The currently available PLA pellets are made from lactic acid, which is created by the fermentation of biomass like corn, potato, and rice [10]. Although PLA may be produced commercially using procedures that are comparable to those used with conventional polymers, its use is currently limited by brittleness [2,8], poor thermal stability, poor gas barrier qualities, and expensive manufacturing costs. By examining how processing factors affect the final characteristics of PLA, our work helps to solve these problems [11].

Polyvinyl alcohol (PVA) is a water-soluble, biocompatible, biodegradable, odourless, and non-toxic polymer that has applications in Agricultural mulch films, biodegradable packaging, food coating [27], fuel cells, paper covering, textile sizing agents, etc. [12,13,14,26]. Water-soluble synthetic polymers are artificial polymers of natural, semi-synthetic, or synthetic origin that dissolve, split and swell in water [15]. Due to the hydrophilic nature of PVA the lignocellulose fibers are compatible with it. In natural fibers -OH groups can create hydrogen bonds with the -OH groups of PVA [16,29,30,32]. In semicrystalline polymer, the majority of the phases are amorphous, and there is only a small percentage of crystallinity in PVA [17,18,25,26,28]. The degree of hydrolysis is generally in the range of 80.0 to 99.0 % which depends on the factors in together use to determine the substance qualities. The molecular weight of PVA is between 20,000 and 400,000 depending on the length of vinyl acetate used to create PVA [19,20,21].

Carbon nanotubes (CNTs) are excellent alternatives for use in a wide range of applications because of their potential for use as an enhanced filler with better physical and chemical properties integrated with composites [22]. The lightweight polymer-based composite is carbon nanotube (CNT) due to its exceptional mechanical, electrical, and thermal properties [22,23]. Composites of polymers reinforced with nanotubes are becoming interesting building materials. Because of its high specific stiffness and strength, it is used not only in the weight-sensitive aircraft industry but also in the maritime, civil engineering, automotive, railroad, and sports goods industries [23]. In the area of scientific and technological purposes, nanoparticle consolidated polymer composites have been recognized as one of the most effective materials. Investigations on nanocomposites have revealed that the unique properties of nanoparticles can result in remarkable properties when paired with conventional reinforcement [24]. This study focuses on making a polymer composite film of Polylactic acid and Polyvinyl alcohol. To reinforce the polymer composite with treated Carbon nanotube. To analyze the mechanical properties of polymer matrix composite. Polymer composite film consisting of PLA and PVA is made here to improve the strength of the polymer and keep it biodegradable and environmentally friendly. Furthermore, carbon nanotube is used as a reinforcing agent to enhance the quality and tensile strength of the polymer matrix. These findings will be useful in forecasting the mechanical properties like impact and tensile strength of polymer matrix composite. The final composite will be biodegradable, strong and environment friendly.

2.0 Material & Method

2.1 Material

PLA- Poly(lactic) acid, PVA – Poly(vinyl) alcohol, Xylene, Distilled water ,HCL- Hydrochloric acid was purchased from a local market in Hathkhola , Dhaka, Bangladesh. MWCNT- Multi Wall Carbon Nano Tube was collected from Dhaka University of Engineering Technology (DUET), Gazipur, Bangladesh.

2.2 Methods

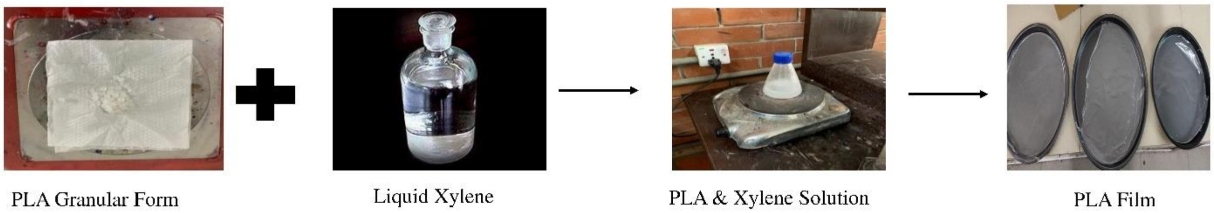
2.2.1 Preparation of PLA (Poly Lactic Acid) Film

For making PLA solution 0.5 gm PLA with 30.0 ml xylene (solvent) was taken in an air-tight bicker. The solution was heated up to 80-105.0^0 C by the heater machine for 60.0 minutes and made shake hands several times during the process. A neat PLA (1.67%) film was prepared as a reference using the Hand Layup Method on a cake-baking dish and stored in a drying oven in WET PROCESSING LABORATORY at 120.0-130.0^0C temperature for more than 1.0 hour until fully dried.

2.2.2 Preparation of PVA (Poly Vinyl Alcohol) Film

2.0 gm PVA with 50.0 ml distilled water (solvent) was taken in an airtight bicker. The solution was heated up to 70.0 to 80.00 C for 40.0 minutes in a magnetic stirrer machine. A neat PVA (4.0 %) film was prepared as a reference using the hand layup method on a cake mould dish and stored in a drying oven in WET PROCESSING LABORATORY at about 120.00C for more than 1.0 hour until fully dried.

A) Preparation of PLA Film



B) Preparation of PVA Film

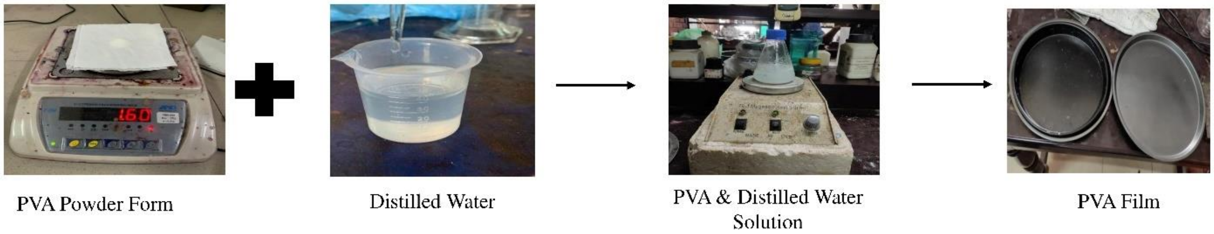


Fig.1. A) PLA film Preparation, B) PVA Film Preparation

2.2.3 MWCNT (Multi-walled Carbon Nano Tube) Treatment

0.5 gm pristine CNT was added to 30.0 ml HCL acid solution. The solution was stirred at room temperature at 500.0 rpm for 2.0 hours. After that, centrifuge machine was used to separate the CNT from the acid solution. The CNT mixture was centrifuged multiple times (5.0 to 6.0 times) to separate the CNT and washed with distilled water until a neutral pH was achieved. For that, after centrifuging for one time water is added to the centrifuging tube. The tube contains 12.0 ml solution. When the optimal pH (7.0) was achieved the remaining CNT was filtered by the filter paper and dried at 100.0^0C in a hot air oven overnight. And the CNT was again formed like powder.

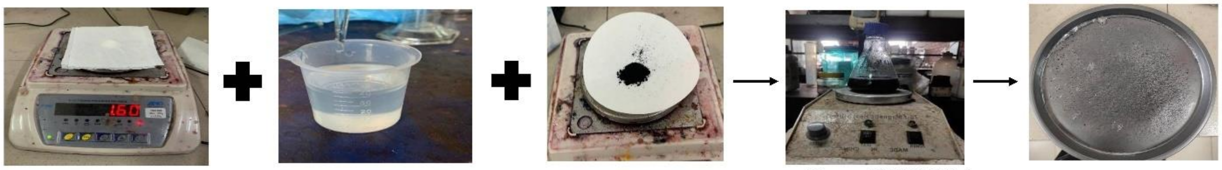
2.2.4 Preparation of CNT-treated PVA Film

An MWCNT Treated (4.0 %) PVA film was prepared as a reference using the hand layup method on a cake mould dish and stored in a drying oven at WET PROCESSING LABORATORY about 120.0^{0}C temperature for more than 1.0 hour until fully dried.

A) Preparation of MWCNT (Multi walled Carbon Nano Tube) Treatment

Pristine MWCNT HCL Treated MWCNT

B) Preparation of PVA Film with MWCNT (Multi walled Carbon Nano Tube) Reinforcement



PVA Powder Form Distilled Water Treated MWCNT Treated MWCNT & PVA Solution MWCNT mix PVA Film

Fig. 2. A) Treatment of MWCNT, B) MWCNT Reinforcement PVA Film

2.2.5 Preparation of Stacked PLA-PVA Film with MWCNT (Multi Walled Carbon Nano Tube) Reinforcement

Three films (PLA-PVA with MWCNT-PLA) were taken and three thermoplastic composite laminates were produced by film-stacking, and the processing parameters such as heating rate, processing temperature, and pressure were established by rigorous material inspection and a trial-and-error process. PLA-PVA with MWCNT-PLA film were stacked at the sandwich structure in a Compressing Molding Machine at 120.0^0C temperature and 65.0 Kilo Newton pressure for 15.0 minutes at BCSIR.

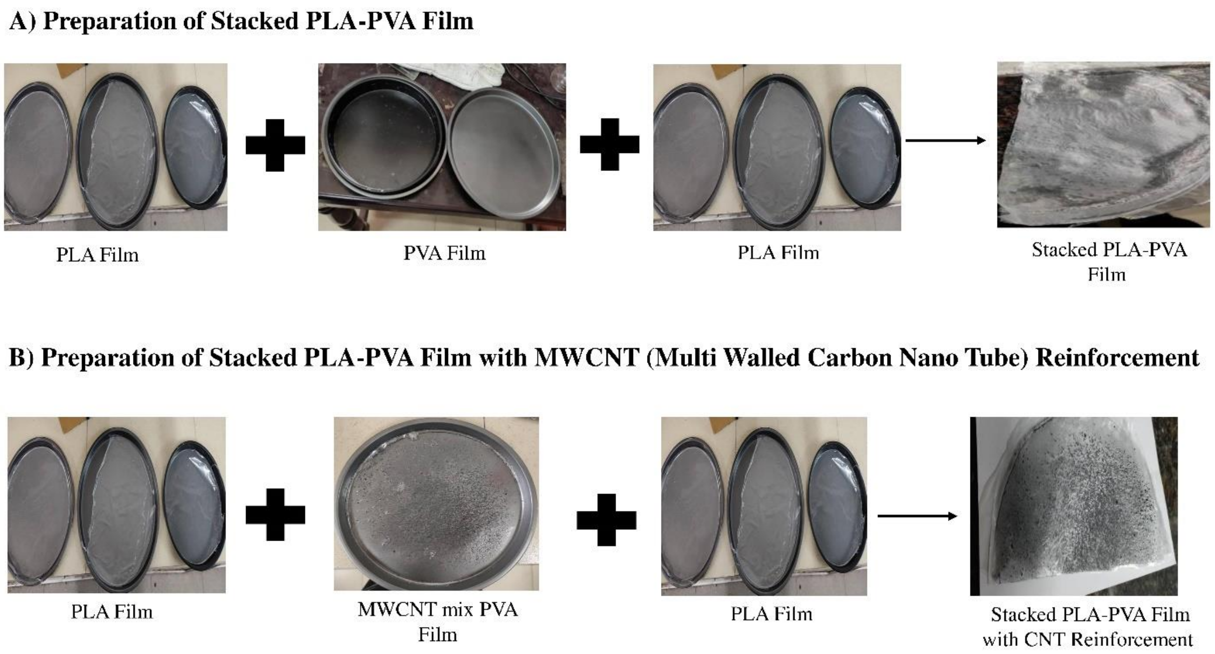


Fig.3. A) Stacked PLA-PVA Film, B) Stacked PLA-PVA with MWCNT reinforcement

2.2.6 Mechanical Properties

The materials' tensile, flexural, compression shear and other mechanical and physical characteristics were tested using the Hounsfield UTM 10KN (H10KS). The ASTM Method was followed in the preparation of the tensile specimen [7].

$$Tensile\ strength = \frac{\text{Applied load}}{\text{Cross sectional area of the load bearing area}}$$

2.2.7 Thermal Properties

A thermogravimetric analyzer that measures a sample's weight loss as a function of temperature was used to analyze the thermal stability [25] (thermogravimetric analysis [TGA], differential thermal analysis [DTA] and differential thermogravimetry [DTG]) of composite samples [7,36,37,38]. Under a nitrogen atmosphere, TGA was operated at a rate of 10.0^0C per minute from ambient temperature to 600.0^0C. Every analysis was performed twice for every sample to achieve excellent accuracy [7].

3.0 Characterization

3.1 Tensile Properties

Tensile properties such as tensile strength and strain at break were determined according to ASTM D882 utilizing a Hounsfield H10ks machine [7]. Three samples of 100 × 20 mm, were taken from each film formulation. The average thickness of the specimens varied according to the composite film compositions. Each composition was tested an average of three times at room temperature. TEAR testing measures the force needed to continue tearing a sample of cloth, presuming that a rip has already been made. Three samples of 40 × 40 mm, were taken from each film.

3.1.1 Tensile test

Tensile testing is a destructive method used to find out a material's tensile strength and how effortlessly it can be elongated. It measures how much force it requires to break a composite or plastic sample and how much the sample has to stretch or lengthen to break. Three specimens from each sample for their tensile strength have been tested. The composite specimens were cut following the ASTM D638 standard for this test [7]. The tests were conducted using a Universal Testing Machine.

3.1.2 Tear Test

TEAR test of film is a special case of a high-speed stress/strain measurement performed on two type polymer sample with similar cross-section. The tear resistance of film is a function of all the parameters that characterize the stress/strain curve of the composites: stresses and strains at the yield, the necking, and the breaking points. Three samples of each film were taken with an area of 40×40 mm.

3.2 Thermogravimetry Analysis (TGA)

To investigate thermal stability, composition, decomposition kinetics, and different thermal transitions, thermal analysis methods such as Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) are utilized [36,37,38]. Electrical conductivity and associated parameters, as well as dielectric, capacitive characteristics and conductive are measured by impedance and conductivity analyzers [25,26,33,34]. Endothermic, exothermic, weight loss during heating and cooling, and other properties are determined by TGA analysis [25,36,37,38]. Each film cut off into very small pieces then put into a small container in the TGA machine. The block diagram of TGA shown in **fig.4.**

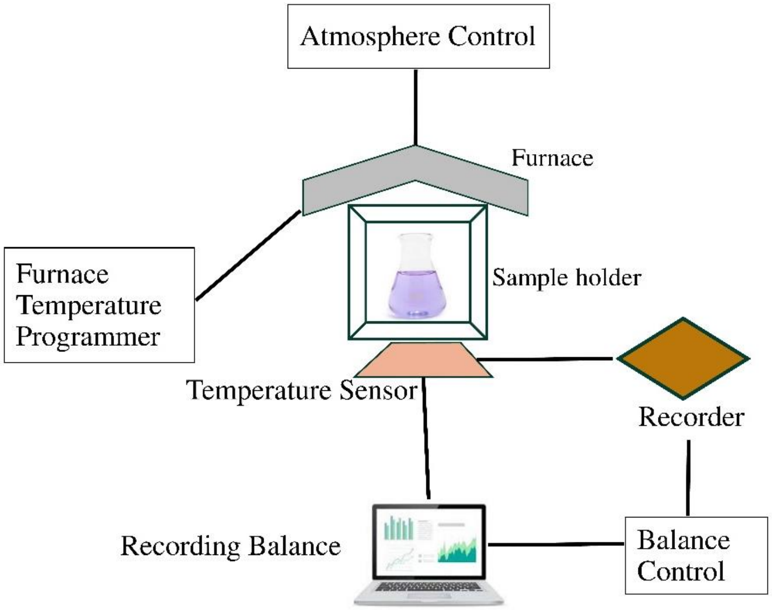


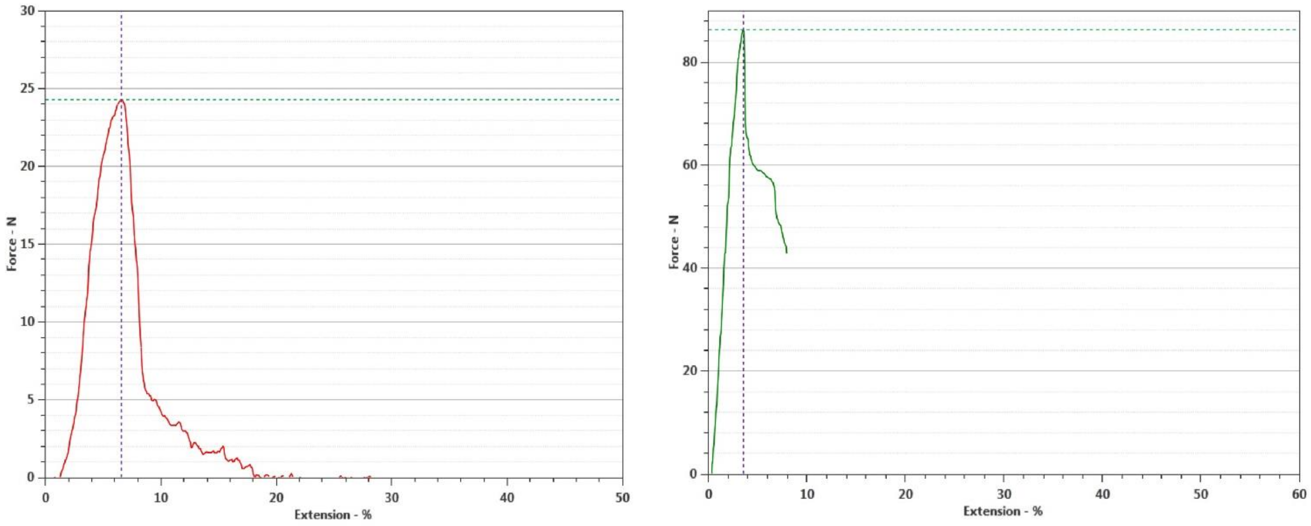
Fig.4. Block diagram of TGA machine [35]

4.0 Result and Discussion

4.1 Analysis of Mechanical Properties

4.1.1 Tensile test

Extension versus force graph illustrate tensile strength & elasticity constant of any properties. Maximum load a material can bear without breaking when it is stretched, divided by the material's initial cross-sectional area [39,40]. From Fig. 5(A) maximum force 24.2 N with 6.4 % extension. Pure PLA-PVA stacked film has a very lower capacity of tensile load [7,30,32]. On the other hand, from the Fig. 5(B) maximum force 85.5 N with 1.8 % extension. Sample average cross sectional area of without & with MWCNT film 7.13mm^2 and 6.04mm^2 respectively. Tensile strength value showed in fig.6 for pure PLA-PVA stacked film is 3.39 N/mm^2 and treated MWCNT mix PLA-PVA stacked film is 14.16 N/mm^2 [39,40]. The more tensile strength of any property, the more has the ability of taking load [7,30,32]. From the following test, we found that treated MWCNT mixed stacked PLA-PVA Film shows higher tensile strength than pure PLA-PVA stacked film.



A B

Fig. 5. (A) PLA-PVA Stacked film without MWCNT mixed, (B) PLA-PVA Stacked film with MWCNT reinforcement

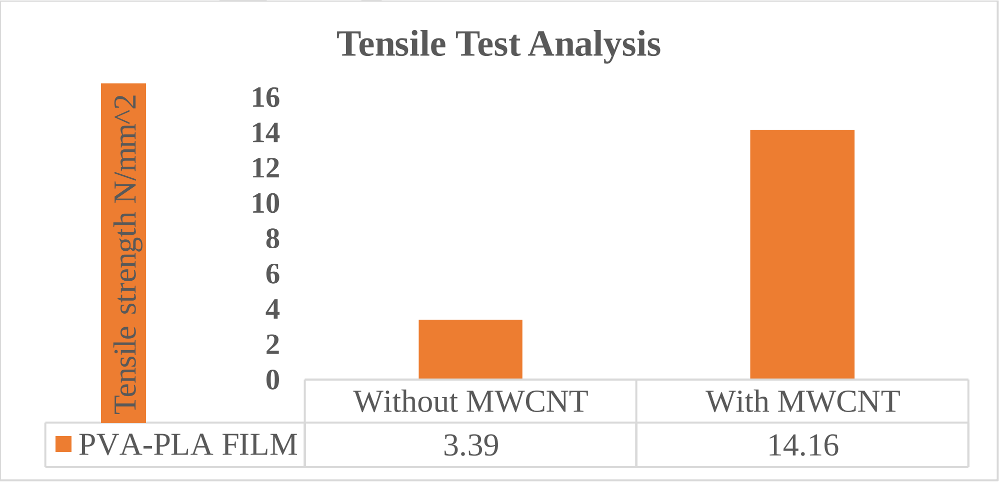


Fig. 6. Tensile strength comparison.

4.1.2 TEAR Test

From the following Fig. 7. we determined that, Treated CNT stacked PVA–PLA Film has required more force (3.37N) than without MWCNT mixing film. For all the three samples required force for both types has showed in table 1. Where the CNT reinforced samples showed higher tear strength.

Table 1. Tear test results for with & without MWCNT film

No of sample	Stacked film without MWCNT (N)	Stacked Film with MWCNT(N)
1	3.5	3.7
2	3.1	3.3
3	2.5	3.1
Average	3.03	3.37

Higher TEAR Force significance the better Stress vs strain curve, necking, and breaking point of the properties[39,40]. So, treated MWCNT mixed stacked PLA-PVA Film shows higher TEAR Force than pure PLA-PVA stacked film.

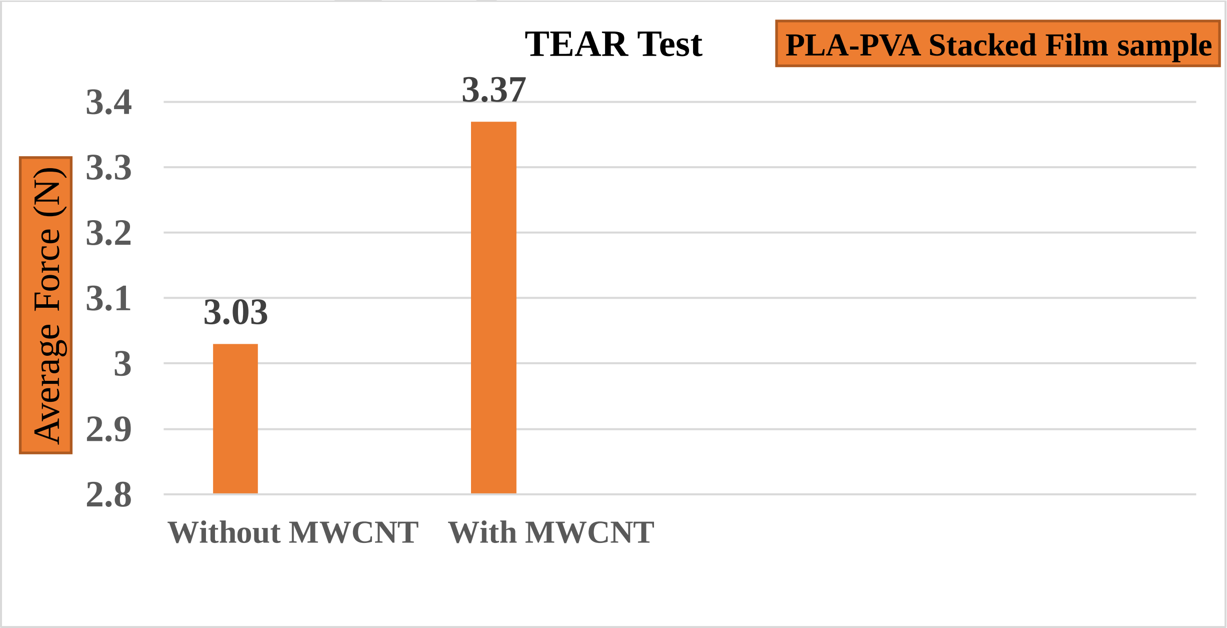
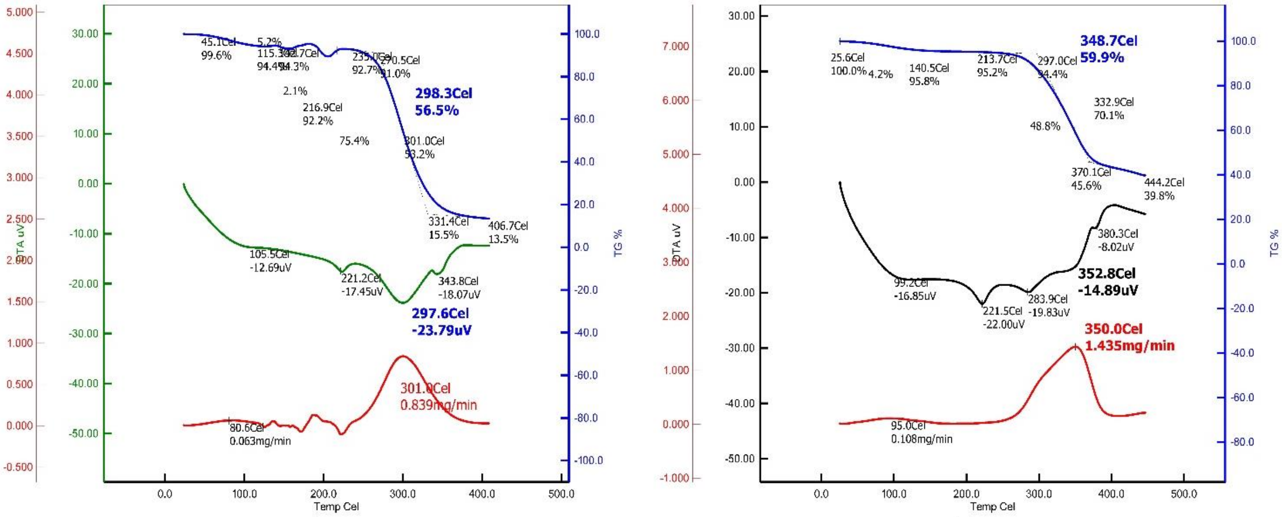


Fig. 7. Average force plot.

4.2 Thermogravimetric analysis

TGA curves illustrate the weight loss of films as they degrade thermally, whereas the DTGA curves illustrate the thermal decomposition temperature. From fig: 8 TGA curves for the entire film demonstrated two distinct weight-decreasing steps throughout thermal degradation. The first weight loss occurred at 45.1^0C for pure PLA-PVA stacked film and 25.6^0C for MWCNT reinforced PLA-PVA film and till 150.0^0C due to primarily the moisture evaporation and desorption for elimination of low molecular weight components from the film. For treated CNT mix PLA-PVA film, the second weight loss was started at 213.7^0 C lasts up to 370.1^0C with maximum temperature 348.7^0C and weight loss was 59.9 % which has higher maximum temperature (298.3^0C) and weight loss (56.5 %) [31]. The primary degradation of standard PLA-PVA film began at 300.0^0C and it ended at 400.0^0C[31]. As referred, the developed PLA-PVA film Maximum thermal decomposition at 297.6^0C temperature and decomposition was -23.69 which is almost similar to treated MWCNT mix film decomposition rate -22.00 (UV) [31]. Treated CNT mix film has the maximum DTG 1.435 mg/min at 350.0^0C temperature respectively. So, we found that treated MWCNT mixed stacked PLA-PVA Film shows higher thermal stability than pure PLA-PVA stacked film.



A

B

Fig.8. A) TGA/DTG carve for without MWCNT reinforced film, B) TGA/DTG carve for with MWCNT reinforced film.

Conclusion

PLA in xylene solution and PVA in distilled water dissolved to prepare a solution for making two different biodegradable polymer film and stacked as sandwich structure that exhibited improved thermal & mechanical stability. The resulting MWCNT reinforced film was demonstrated excellent thermal and mechanical stability. The tensile strength of CNT reinforced film obtained 14.16 N/mm^2 and shows higher TEAR Force 3.37 N. In TGA, maximum degradation temperature 348.7^{0}C and weight loss was recorded 59.9 %. CNT mixed film has the maximum DTG 1.435 mg/min at 350.0^{0}C. Further research can be conducted to determine the PLA-PVA blend that will be developed this biodegradable film with outstanding thermal and mechanical characteristics. Additionally, few analytical characterizations and Biodegradability may be carried out in future for developing a sustainable film for packaging purpose instead of plastics.

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