Reinforcement of Biodegradable PLA-PVA Composite Films with Carbon Nanotubes: Mechanical and Thermal Property Analysis

Abstract

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 poly lactic 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 as well as without treat showed 3.37 N/mm^2 and 3.03 N. In TGA analysis, 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. This manuscript presents a new step in the field of sustainable materials to develop high-performance, biodegradable packaging solutions. By incorporating processed carbon nanotubes (CNTs) with polyvinyl alcohol (PVA) and poly-lactic acid (PLA), they achieve significant improvements in mechanical strength, thermal stability, and barrier

Keywords: Carbon nanotubes, MWCNT film, Packaging Material, Poly-lactic acid, Poly-vinyl 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 fibers 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, poly-hydroxy butylate, and poly-lactic 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 that renewable material is how durable when using it long time [7]. For example, the brittle nature of polylactic acid limits its importance, but the drawback has improved by adding reinforcement [8]. Poly-lactic 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 [9]. PLA is not soluble when dissolved in solvents including toluene, acetone, acetonitrile, methanol, and ethyl acetate [10]. PLA films made with toluene, xylene, acetone, and ethyl acetate displayed surface segregation and enhanced hydrophobicity [11-12]. Methylene chloride and acetonitrile when combined with PLA thin films changed the crystalline structure, improving heat stability but making the material brittle [13]. The currently available PLA pellets are made from lactic acid, which is created by the fermentation of biomass like corn, potato, and rice [14]. Although PLA may be produced commercially using procedures that are comparable to those used with conventional polymers, its use is currently limited by brittleness [15], 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 [16].

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 [16], fuel cells, paper covering, textile sizing agents, etc. [17]. Water-soluble synthetic polymers are artificial polymers of natural, semi-synthetic, or synthetic origin that dissolve, split and swell in water [15-18]. 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 [19]. In semi-crystalline polymer, the majority of the phases are amorphous, and there is only a small percentage of crystallinity in PVA [20]. 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 [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]. The crystalline nanoparticle have an outstanding properties like mechanical, stability, strain and etc [41-50]. This study focuses on making a polymer composite film of Polylactic acid and Poly-vinyl 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. This manuscript is significant for the scientific community as it offers an innovative approach to developing biodegradable and sustainable packaging materials. By utilizing PLA-PVA film stacking technology reinforced with MWCNT, this research has the potential to replace traditional plastics with environmentally friendly alternatives. The mechanical and thermal analyses contribute significantly to understanding material property enhancements through nano-based reinforcement.

2.0 Material and Method

2.1 Material

Poly lactic acid (PLA), poly vinyl alcohol (PVA), Xylene and hydrochloric acid (HCL) was purchased from Sigma-Aldrich, Germany and Distilled water (DI water) collected from Hatkhloa market, Bangladesh. Multi wall carbon nano tube (MWCNT) was collected from DUET Laboratory, Gazipur, Bangladesh.

2.2 Methods

2.2.1 Preparation of PLA (poly lactic acid) Film

For preparation PLA solution 0.5 gm PLA with 30.0 ml xylene (solvent) was taken in an air-tight 100.0 ml bicker. The solution was heated up to 80 to 105.0 ^{0}C for 60.0 minutes [DLab, UK] and made shake hands several times during the process until dissolved into solvent with uniformly distributed. A neat PLA (1.67 %) film was prepared as a reference using the Hand Layup Method on a cake-baking dish (6.0 cm diameter) and stored in a drying oven at 120.0 to 130.0 ^{0}C temperature for 1.0 hour.

2.2.2 Preparation of PVA (Poly Vinyl Alcohol) Film

2.0 gm PVA with 50.0 ml DI water (solvent) was taken in an airtight 100.0 ml bicker. The solution was heated up to 70.0 to 80.00 ºC for 40.0 minutes with a magnetic stirrer [DLab, UK]. A neat PVA (4.0 %) film was prepared as a reference using the hand layup method on a cake mold dish (6.0 cm diameter) and stored in a drying oven at about 120.0 ºC for 1.0 hour.

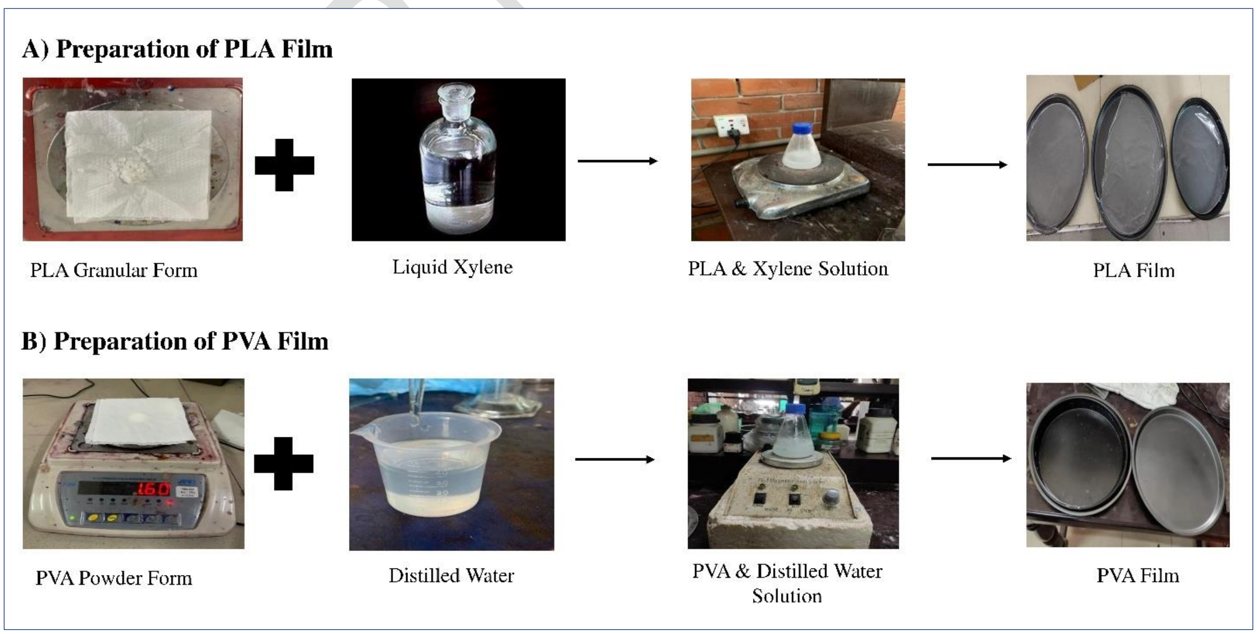

Fig. 1. (a) PLA film preparation, (b) PVA film preparation.

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 [DLab, UK]. 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 DI water [Herolab, Germany] until a neutral pH [Lutorn 221E, Taiwan] was achieved. For instance, the centrifuge tube contained 12.0 ml of solution and after once completing the centrifuge distilled water was added until the optimal pH (7.0) was reached. In a hot air oven, the remaining neutral CNT was filtered by using filter paper and dried overnight at 100.0^{0} C. The CNT was obtained in powder form and then restored.

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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 about 120.0 ^{0}C temperature for 1.0 hour. The constant weight of the film was obtained by weighing the dried film and the constant weight of the film was achieved when at least 3.0 times the weight matched.

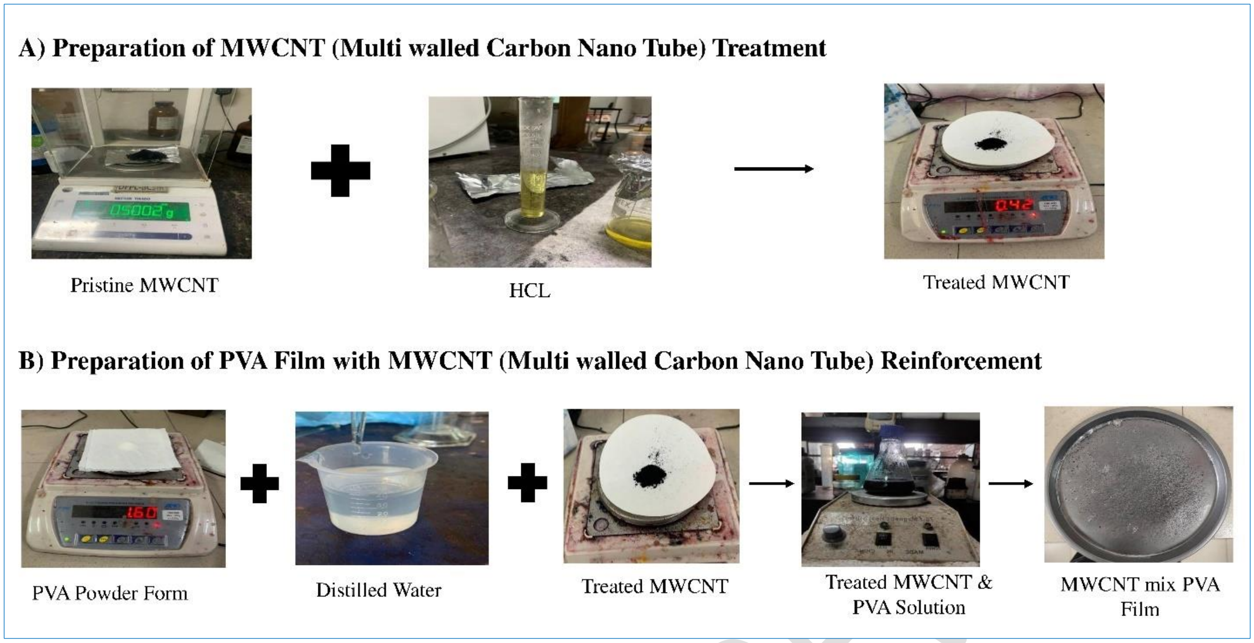

Fig. 2. (a) Treatment of MWCNT, (b) MWCNT reinforcement PVA film.

2.2.5 Preparation of Stacked PLA-PVA Film with MWCNT 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.

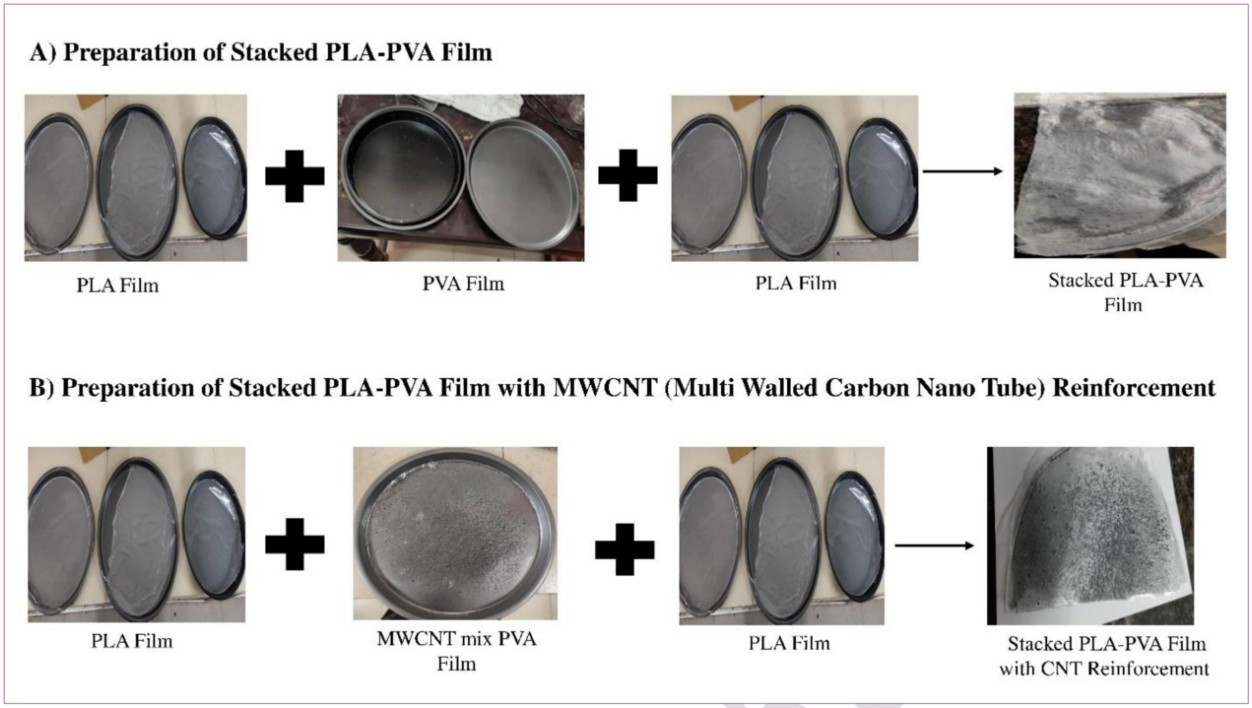

Fig. 3. (a) Stacked PLA-PVA film, (b) Stacked PLA-PVA with MWCNT reinforcement PLA-PVA with MWCNT-PLA film were stacked at the sandwich structure in a compressing molding machine at 120.0 ^{0}C temperature and 65.0 Kilo Newton pressure for 15.0 minutes.

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 thermos-gravimetric analyzer that measures a sample's weight loss as a function of temperature was used to analyze the thermal stability [25] by thermos-gravimetric analysis [TGA], differential thermal analysis [DTA] and differential thermos-gravimetric [DTG]) of composite samples [36-

38]. Under a nitrogen atmosphere, TGA was operated at a rate of 10.0 ^{0}C per minute from ambient temperature to 600.0 ^{0}C. 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 [7]. Three samples of 100.0 × 20.0 mm, were taken from each film formulation. The average thickness of the specimens varied according to the composite film compositions. Each composition was computed 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 40.0 × 40.0 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 [7]. The tests were conducted using a Universal Testing Machine (UTM).

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 area. 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 40.0 × 40.0 mm.

3.2 Thermo-gravimetry 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 [36-38]. Thermo-gravimetric analysis or thermal gravimetric analysis (TGA) is a method of thermal analysis in which the mass of a sample is measured over time as the temperature changes [51-58]. The activation energy, crystallization enthalpy, mass change, reaction kinetics and degree of crystallinity also explored by TGA [59-65]. On the other hand the reacting nanospecies that were activated the reaction also observed in TGA [66-70].

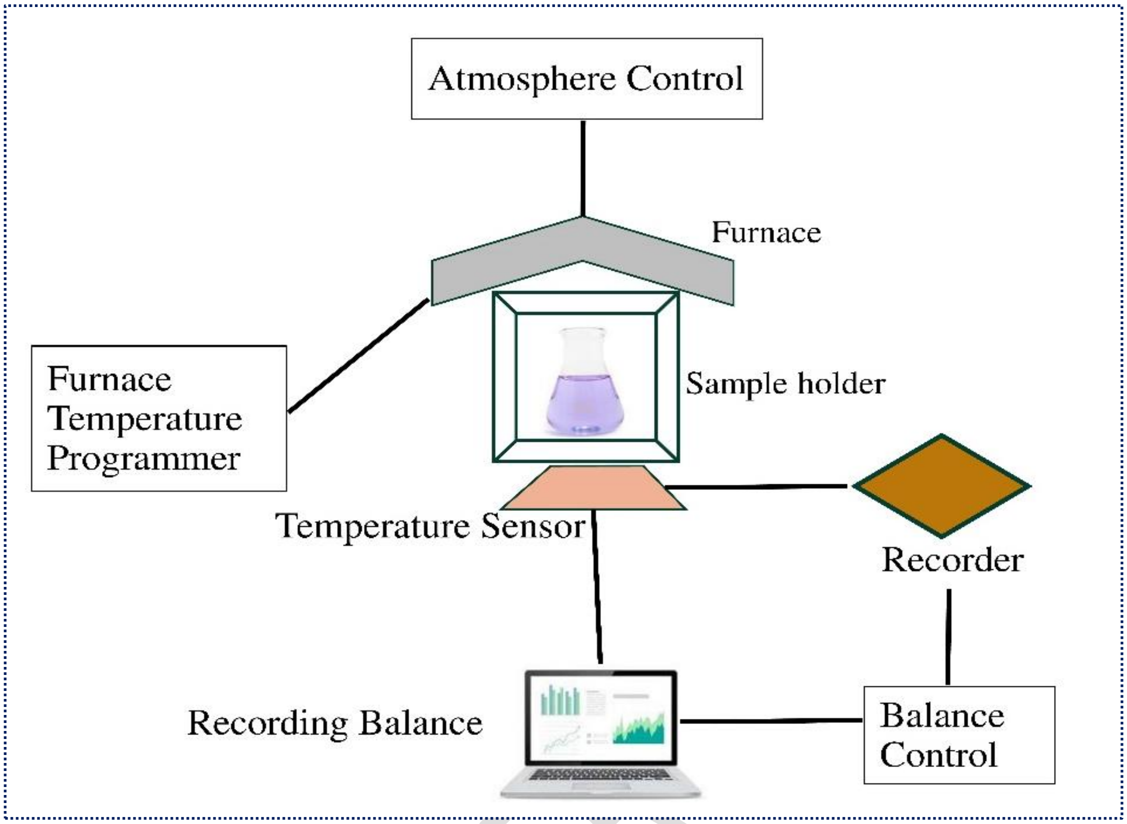

Fig. 4. Block diagram of TGA instrumentation [35].

Endothermic, exothermic, weight loss during heating and cooling, and other properties are determined by TGA analysis [25, 36-38]. Each film cut off into very small pieces then put into a small container in the TGA instrument. The block diagram of TGA shown in Fig.4.

4.0 Result and Discussion

4.1 Analysis of Mechanical Properties

4.1.1 Tensile Test Analysis

Extension versus force Fig. 5, illustrate tensile strength and 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. 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. 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 and with MWCNT film 7.13 mm^2 and 6.04 mm^2 respectively.

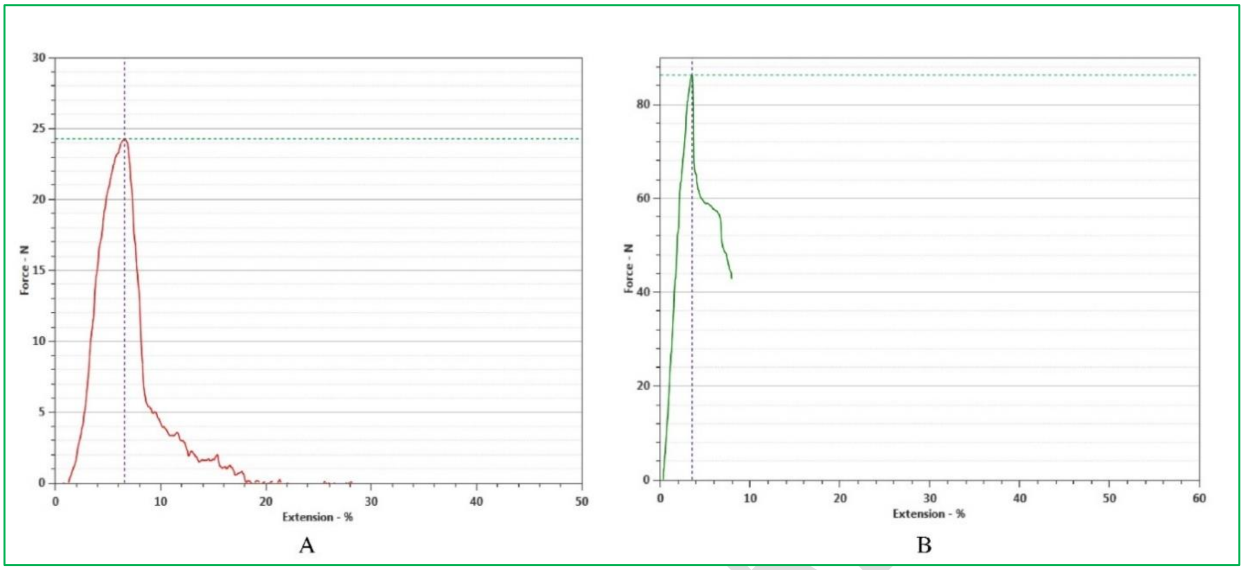

Fig. 5. (a) PLA-PVA stacked film without MWCNT mixed, (b) with MWCNT reinforcement.

Tensile strength is the maximum amount of stress a material can withstand before breaking when stretched or pulled. It's a key property of materials like metals, polymers, and composites. 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.

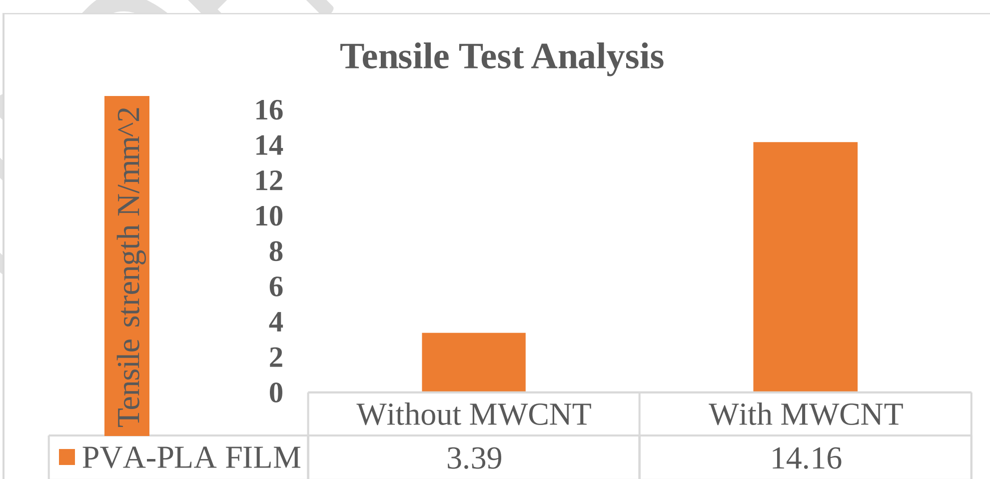

Fig. 6. Tensile strength comparison analysis.

The more tensile strength of any property, the more has the ability of taking load [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.

4.1.2 TEAR Test

From Fig. 7, 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 comparison for with and 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.

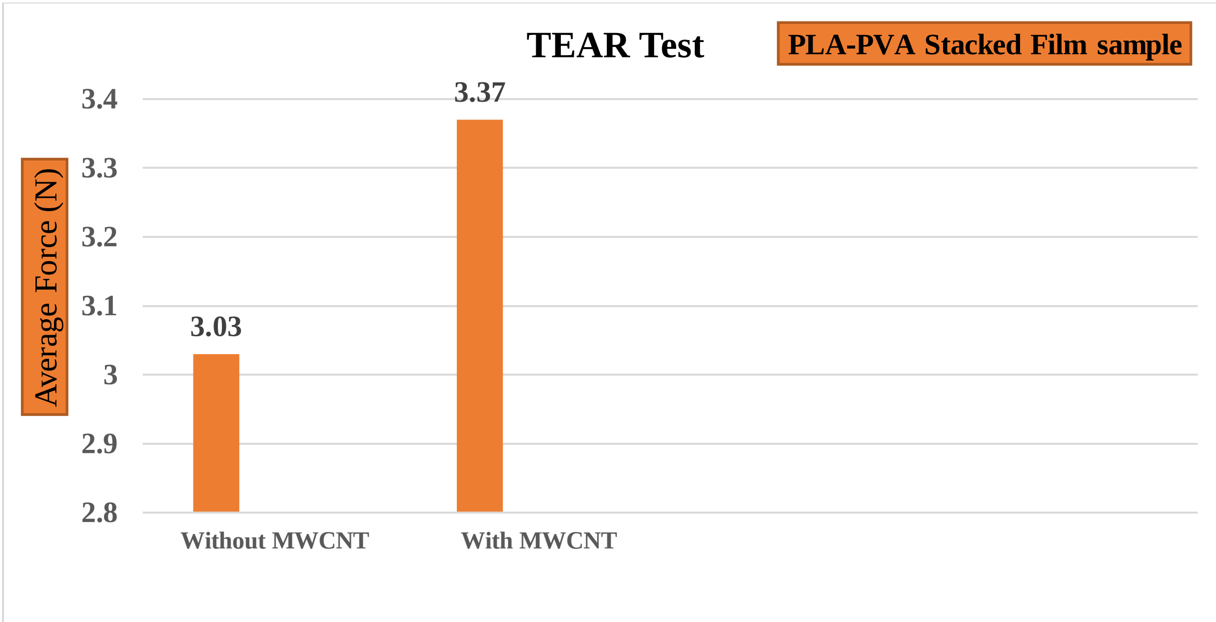

Fig. 7. Average force plot.

4.2 Thermo-gravimetric Analysis

TGA is an analytical techinque

TGA curves Fig. 8, 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 45.10 ^{0}C for pure PLA-PVA stacked film and 25.6 ^{0}C for MWCNT reinforced PLA-PVA film and till 150.0 ^{0}C 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 213.70 ^{0}C lasts up to 370.1 ^{0}C with maximum temperature 348.7 ^{0}C and weight loss was 59.9 % which has higher maximum temperature 298.3 ^{0}C and weight loss 56.5 % [27-31].

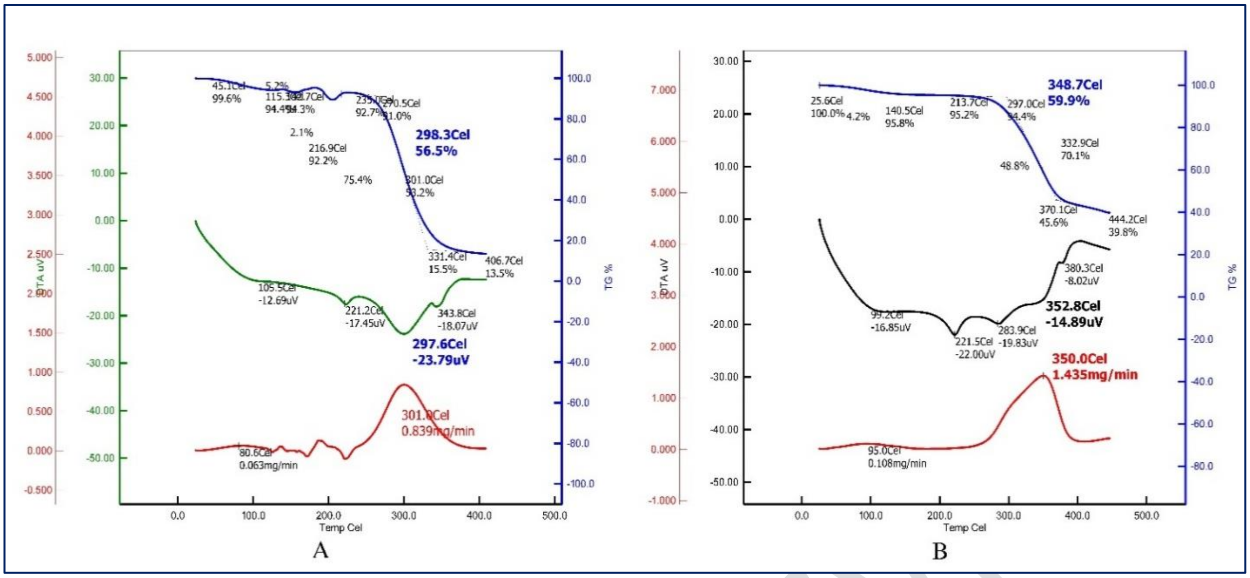

Fig. 8. (a) TGA/DTG carve for without MWCNT and (b) with MWCNT reinforced film.

The primary degradation of standard PLA-PVA film began at 300.0 ^{0}C and it ended at 400.0 ^{0}C [31]. As referred, the developed PLA-PVA film Maximum thermal decomposition at 297.6 ^{0}C 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 ^{0}C temperature respectively. So, we found that treated MWCNT mixed stacked PLA-PVA Film shows higher thermal stability than pure PLA-PVA stacked film. So the data obtained in TGA is useful in determining purity and composition of composite PVA materials, drying and ignition temperatures of materials and knowing the stability temperatures of composite compounds [71-76]. The data obtained in DTA is used to determine temperatures of transitions, reactions and melting points of substances [77-78] or prepared composite were explored.

5.0 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 ^0C and weight loss was recorded 59.9 %. CNT mixed film has the maximum DTG 1.435 mg/min at 350.0 ^0C. 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.

Highlight of Manuscript

1. Tensile strength of CNT reinforced film is 14.16 N/mm^2.
2. MWCNT mixed PLA-PVA film shows higher TEAR force at 3.37 N.
3. CNT mixed film has the maximum DTG 1.435 mg/min at 350.0 ^0C.
4. In TGA, max. degradation temperature 348.70 ^0C and weight loss was 59.9 %.
5. MWCNT film maximum force 85.5 N with 1.8 % extension.

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Data Availability

The data is available on request.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during the writing or editing of this manuscript.

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