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# Preparation and Characterization of Reinforced Poly(Lactic Acid) Composite for Food Packaging Applications

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## ABSTRACT

This study investigated the preparation and characterization of poly(lactic acid) (PLA) composites reinforced with Vitamin $K_3$ (MD) for potential use in dry food packaging. The aim is to create a more sustainable alternative to traditional petro-based plastics, MD, a food-safe additive with antioxidant and antimicrobial properties, was incorporated into PLA at 1%, 3%, 5%, and 10% (w/w) using solvent casting. The resulting composite films demonstrated several improved functional characteristics. Field emission scanning electron microscopy (FESEM) showed uniform dispersion of MD within the PLA matrix. Ultraviolet-visible (UV-vis) spectroscopy revealed a significant enhancement in UV-blocking capability, with composites containing 5% and 10% MD effectively blocking almost 100% of UV-C and UV-B radiation. X-ray diffraction (XRD) analysis indicated that the MD acted as a nucleating agent, increasing PLA crystallinity. Thermogravimetric analysis (TGA) confirmed improved thermal stability of the composites. Mechanical testing showed that adding MD significantly enhanced mechanical properties, including a six-fold increase in elongation at break and higher tensile strength compared to pure PLA. Additionally, the composites exhibited strong antioxidant activity, which increased with MD concentration. These results highlight the potential of PLA-Vitamin K composites as a multifunctional and sustainable packaging material for food applications.

**Keywords**: Vitamin K, Bioactivity, Composite, Food Packaging, Poly(lactic acid), Sustainability

## INTRODUCTION

Since the second half of the 20th century, petro plastics have increasingly dominated the possessions of our daily lives. The main advantages have been their unrivalled physical properties, being light weight, having low manufacturing temperatures, ease of handling, and certainly their extensive mechanical, wetting, optical and UV blocking characteristics [1]. They are also inexpensive and offer long period of storage with protection against spoilage or contamination. These unique properties have allowed plastics to be the choice material in a wide ranging applications from automobiles, packaging and agriculture to higher-end tech industry materials, clothing, children toys, home construction and furniture [1-3].

The largest application of plastics is in the packaging industry, with a significant 59% usage in India [4] and about 39% in the European Union [5], with about half of these percentages utilized in the food packaging industry. At the moment food packaging in plastics is viewed as crucial to safeguarding food products, offering numerous advantages like shelf life extension which reduces food wastage and see-through packaging which aids marketing, increase patronage and profitability. For food packaging applications, plastics like polyesters, polyethylene, polyolefin, polystyrene, polyethylene terephthalate etc. are used, all of which originate from petroleum sources. Nonetheless, these positive pictures of plastics to the food industry, packing represents the number one risk to environmental pollution and contamination. To address this problem, new packing materials which are biodegradable and green but also suitable for especially food packaging applications are desired as possible replacement to the existing plastics in the food packaging sector. Biopolymer are touted in these regards due to their exceptional biodegradability, eco-friendliness and endless natural resource base. As of today, biodegradable polymers represent just 1% of the plastics market [6].

PLA has emerged as the biopolymer of choice for the food packaging industry because it possesses similar properties with some conventional polymers like polystyrene (PS) and polyethylene terephthalate (PET). PLA is a thermoplastic which is linear, aliphatic and polyester in nature, and is primarily a product of either ring opening polymerisation of lactide or condensation polymerisation of lactic acid monomers [7, 8]. PLA monomers are sourced from renewable resources like sugar beets, sugarcane and corn, it is biodegradable and can be recycled. Additionally, it is also non-toxic and safe. Nevertheless, PLA has some draw backs which hinders its whole acceptance in the food packaging industry, and these include brittleness, poor elongation and barrier properties. The main solution to these limitations of PLA is by mixing it with other polymers or reinforcing it with fillers. Importantly, the proper dispersion of these fillers in the matrix of the PLA is necessary for the whole improvement of its mechanical, physical and barrier properties. PLA blends with other polymers or reinforced with fillers have been used to enhance its mechanical and physical properties. For example, Cellulose, poly caprolactone, starch, ZnO etc. have been used to modify the properties of PLA [9-11].

Additionally, organic, inorganic and synthetic fillers have been used as reinforcement agents for improving the mechanical and barrier properties of PLA biopolymer. Food additives have emerged as a major source of the reinforcing fillers because they are compatible, safe and non-toxic and induce active properties such antimicrobial and antioxidant activities in the packaging material [12-14]. Antioxidant and antimicrobial properties are important in food packaging material because they prevent the food from spoilage thereby extending it shelf life. These food additive not only give enhanced barrier and elongation properties but also improve wetting and induce faster crystallisation rates of the PLA biopolymer. Furthermore, various functional fillers have been used to enhance the physical and mechanical properties of PLA and this include nanocellulose, montmorillonite, nanoparticles of metal origin (ZnO, Ag, $TiO_2$, etc.), talc, nanoclay etc [15]. Also, essential oils, plants, animals, microbial extracts and other substances of bioactive origins have been used to improve PLA standing for food packaging applications [16].

Vitamin K belongs to the lipophilic vitamin group which is found to naturally occur in two forms, Vitamin $K_1$ (phylloquinon) present in green plants and $K_2$ (menaquinon groups) found in the intestine and synthesized by bacteria. Vitamin $K_3$ (MD) is a synthetic vitamin K without side chains needed for it to undergo prenylation. Vitamin $K_3$ like its counterparts is metabolically active. MD are found to be safe for use as feed additives at practical level of use, and are safe for all animal species. The use of Vitamin $K_3$ in animal feeds and supplements does not raise any concern for customer safety [17-19]. The use of MD in the animal feed does not pose any environmental risk and is considered an important and effective vitamin K source in animal feeds and supplements. Vitamin K plays essential roles in bone health and blood clothing. In patients with medical conditions like diabetes, heart or kidney diseases, vitamin K stops the dangerous accumulation of calcium in their blood vessels, organs and tissues. Vitamin $K_3$ has interestingly demonstrated anti-inflammation and anti-cancer properties in *in-vitro* studies. In a particular instance using distinct class of proteins it killed kidney, breast and colorectal cancer cells from human samples. Vitamin $K_3$ is also found to increase the presence of reactive oxygen species and these molecules are known to kill or damage cancer cells. Additional studies have also revealed the antimicrobial activities of vitamin $K_3$ [20-23].

In this study, PLA-MD composite is proposed as a biodegradable and bioactive packaging material for dry food. The novel composite was fabricated using solution casting method. Mechanical studies, thermal stability and chemical characterisation of the resulting composites were carried out as a function of MD content. In addition to their suitability for use as food packaging materials, further investigations to test the effectiveness of the various MD loadings in PLA matrix regarding oxygen permeability (OP), MD release and antioxidant properties were carried out.

## MATERIALS AND METHODS

Poly (lactic acid) (PLA 4043D) was acquired from Nature works (USA) and used as polymer matrix. Vitamin $K_3$ and 2, 2-diphenyl-1-picrylhydrazyl (DPPH) used as reinforcement filler and antioxidant analyser, respectively were supplied by Sigma-Aldrich, USA. Chloroform was used as solvent and was procured from Sisco research laboratories Pvt. Ltd, India. Tenax dry food simulant was procured from Sigma-Aldrich, USA and was used for dry food migration analysis.

### Preparation of PLA/ Vitamin $K_3$ composite films

PLA-MD composite films were fabricated via the simple solvent casting method [6]. Initially, different amounts of Vitamin K3 (MD) (1%, 3%, 5% and 10% based on pure PLA) were added in to 30 mL pure chloroform and dissolved on a magnetic stirrer for an hour and ~1 g of PLA was dissolved in 70 mL of chloroform for an hour and half on a magnetic stirrer were mixed and stirred for another two hours. The resulting homogeneous solutions of the composite were gently poured into flat bottom petri dishes and allowed for 24 hours under atmospheric temperature to dry. The resulting thin films were carefully pilled off the petri dish and oven dried for 48 hours at 40 $^{o}$C to remove any traces of chloroform solvent remaining. The final films were free standing and of uniform thickness and designated as PLA-MD-1, PLA-MD-3, PLA-5, PLA-MD-10 respectively. Pure PLA film sample was prepared using the same procedure. The PLA/MD composite and neat PLA were prepared under ambient conditions.

### Sample Characterisation

*Morphology*

The smooth dispersion of the MD bio filler in the PLA matrix was observed using a Field Emission Scanning Electron Microscope FESEM, (Carl Zeiss, Germany, model: SUPRA 55VP, Gemini Column, with air lock system and a resolution of 1.2 nm gold particle separation on a carbon substrate).

*UV Spectrophotometry Analysis*

Ultra Violate-Visible spectrophotometer of the ( SHIMADZU UV-3600 plus UV-VIS-NIR Spectrophotometer) was used for transmittance and transparency measurements of samples across the various segments of the Ultra-violet and visible regions of the electromagnetic spectrum for the ordinary PLA and PLA-MD composites. The measurement was recorded between 800-200 nm.

### *X-ray Diffraction (XRD) Analysis*

X-ray diffraction patterns for neat PLA and PLA-MD composites were taken from an XRD analyser ( Bruker, model: D8 Advance, with angular range of 5° to 140°, Cu Target X-ray source, LynxEye & Scintillation Counter detector and 40 KV; 30 mA power). The analysis was carried out under normal atmospheric conditions. The instrument's operation voltage is 30 kV and 30 mA. The XRD data of the analysed samples were obtained at $2\theta$ range of $5\text{-}50^{o}$ and scanning rate of $3^{o}$.

### *Thermal Analysis*

Thermogravimetric analysis (TGA) of the ordinary PLA and PLA-MD composite was carried out with the aid of a thermo gravimetric analyser (SDT Q600 V8.3 Build 101, Canada. Module DSC-TGA Standard) with empty alumina pan as reference under nitrogen gas atmosphere supplied at 100 ml/min flow rate to ascertain their various thermal stability and degradation temperatures. For this purpose about 5 mg of the samples each was taken for the analysis. All sample were heated between 25 to $600^{o}$C at $10^{o}$C heating.

### *Antioxidant Properties*

The free radical scavenging activity (RSA) of the PLA-MD composite films was monitored in 2, 2-diphenyl-1-picrylhydrazyl radical (DPPH) and ethanol solution decolourisation using UV-Vis spectrophotometer with absorbance measured at 517 nm (SHIMADZU UV-3600 plus UV-VIS-NIR Spectrophotometer). The antioxidant activity of composite films was carried out by placing 100 mg sample of each sample into 10 mL of DPPH-ethanol solution for 24 h incubation at room temperature. For the control sample, pure DPPH solution was used. After 24 h of incubation and absorbance measurement at 517 nm, the antioxidant activity of the polymer and composites were calculated using the formula in Equation 1: [7].

$$RSA\% = \left[1 - \frac{A1}{A2}\right] x\,100 \qquad (1)$$

Where $A_1$ and $A_2$ are the absorbance of DPPH of the control and Sample, respectively.

## RESULTS AND DISCUSSION

### *Morphology*

The results of morphological characterisation conducted using FESEM are shown in Figure 1. The FESEM result revealed the surface and cross sectional features of the films at different resolutions. The PLA only and PLA-MD composites were found flexible, intact and freestanding. The PLA film was highly transparent. The FESEM micrograph captured the surface and cross section of the films. The PLA films showed smooth and defect- free surfaces. The FESEM analysis further showed that no cavities were present in the films and the polymer matrix and the filler had an even distribution throughout the films. This portrayed a high compatibility between PLA and the MD filler, and also an enhanced intermolecular force. The addition of MD to the PLA matrix showed less agglomeration at lower concentrations. In contrast composites films fabricated at higher MD weight loads showed increased agglomeration. This was more obvious with PLA-MD-10 composite. The FESEM results showed that the food additive, MD, was properly mixed and compatible with the PLA polymer. Several other food additives have shown good compatibility with PLA such as soya bean oil and natural rubber [24, 25], curcumin [7], cellulose [26], and Toddy Palm [27].

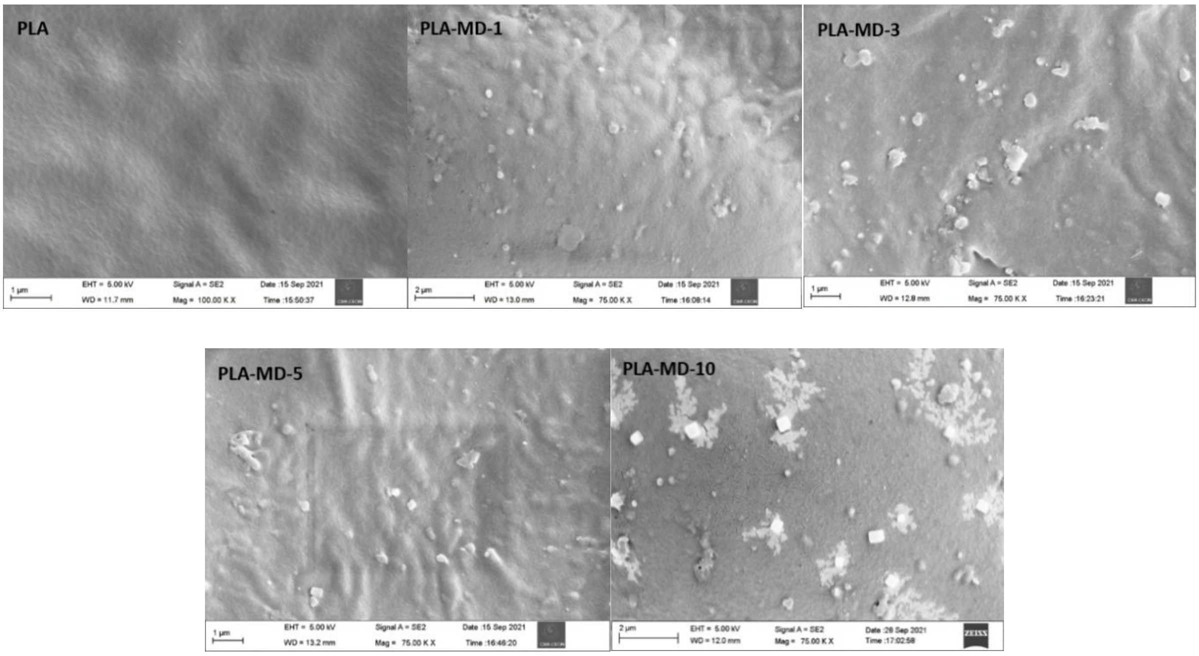

Figure 1: The FESEM micrographs of the PLA only and PLA-MD composites.

*UV-Visible spectroscopy*

In Figure 2 is the UV-Vis spectra of PLA and PLA-MD composite films. UV-Visible light energy can cause oxidation of certain food products upon exposure leading to the degradation of the food item reducing food quality and lowing it shelf life. This circumstances makes UV light blocking characteristics a necessity for any polymeric material intended for use as a food packaging material [32, 33]. The UV region is categorised into three, UV-A has the lowest energy and longest wavelength (400-315 nm), UV-B has the most energy of the UV region capable of causing polymer degradation (315-280 nm) and UV-C at 280-100 nm which is from artificial light sources [29]. PLA exhibited high transmittance at both UV region (250-400 nm) and visible region (400-700 nm) of the spectrum. This results in the research to improve UV blocking capacity [32]. Figure 2 shows the UV-Visible spectra of PLA and PLA composites of Vitamin K3. In the UV region all the composites films showed reduced transmission of light compared the neat PLA. This shows that bio fillers are effective in UV light blocking when added into PLA polymer matrix [34, 35].

From the UV-Visible graph (Figure 2) the PLA film absorbed very little across the UV spectrum, permeating almost 40% of the UV-C, 53% of the higher energy UV-B light and up to 65% of the UV-A but in the visible region a very high transparency of up to 83% was recorded PLA learning credence to the solvent casting method effectiveness. However for the Vitamin K3 composites of PLA a general improvement was recorded in the important UV region and especially the UV-B segment whose absorption by food products can lead irreversible deterioration and spoilage. In the UV-C segment almost a 100% blockage of the light rays was observed with negligible exception of PLA-MD-1 and PLA-MD-3 but the blockage was complete in the PLA-MD-5 and PLA-MD-10. In the UV-B segment of the UV region a slight permeation of 2% and 4% was recorded in the films of the PLA-MD-1 and PLA-MD-3 respectively and this is due the higher energy of the UV-B, 426 – 380 KJ mol$^{-1}$. However, in the cases of PLA-MD-5 and PLA-MD-10 absolute blocking was recorded. Additionally, In the UV-A range of the UV region variable permeation was recorded according to filler weight loading in the PLA matrix, from complete blocking of the permeation of up to 45% in the case of PLA-MD-3, 40% in PLA-MD-1 film, 21% in PLA-MD-5 and the least was recorded in PLA-MD-10 at 17%. In the visible region of the electromagnetic spectrum also variable transparency was recorded as a function of filler weight load, for PLA-MD-1 transparency reached 60% before reducing to 53% in the film of PLA-MD-3 and further down to 39% for PLA-MD-5 and finally to 26% for PLA-MD-10. This is consistent with other PLA composite of similar food additive fillers [35].

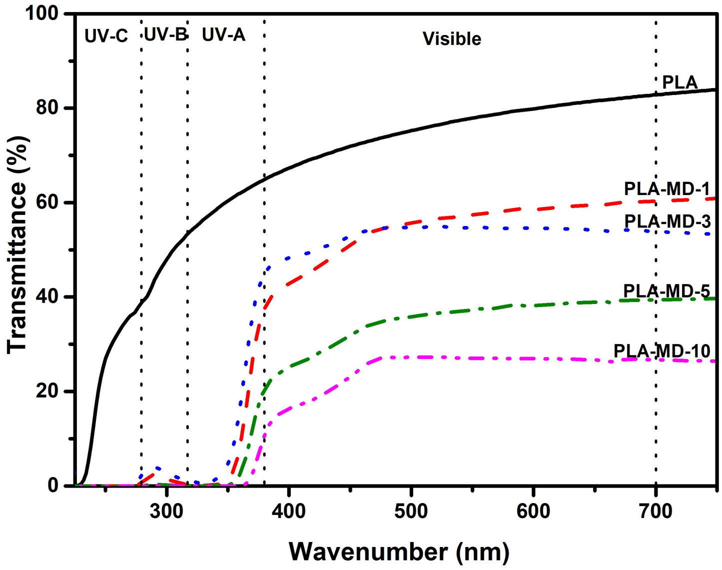

Figure 2: UV-Vis Transparency of PLA and PLA-MD composites.

*XRD Analysis*

XRD analysis was carried out to understand the impact of the filler weight load on the crystallinity of PLA as shown in Figure 3. The crystalline structure is consistent with the conditions under which it is prepared. The defractograms of the neat PLA and its meandione composites obtained in XRD transition mode, an important parameter in understanding the crystallinity of samples. The pristine PLA shows two intense peaks at 16.8° and 19.2° which are assigned to the 200 and 203 planes respectively which is related to the orthorhombic α-crystalline phase of the polymer. Thetwo other small peaks at 14.9° and 22.6° respectively assigned to 104 and 211 planes are associated with α-phase planes. , The most intense of the peaks was recorded at 16.8°. These difractograms are characteristic of the α- polymorph form of PLA which is the commonest and most stable form of PLA with cell units which are orthorhombic in nature [36, 37]. The broad peak exhibited by the PLA in the graph is as a result of its amorphous nature. Moreover, slight improvement of the degree of crystallinity is observed with the addition of the Vitamin K3 in the PLA matrix. This indicates that the manadione is acting as nucleating agent, thereby improving the crystallinity of the composite system. The PLA composites exhibited a broad halo signifying amorphous state. The enhanced peaks recorded in the PLA composites are due to an increased diffraction of the x-rays due to increasing weight load of the Vitamin K3 filler in the composite film. It is characteristic of pure PLA biopolymer to exhibit the peak at unaltered at 16.8°. It is also obvious that the PLA lattice parameters was not changed by the addition of the Vitamin K3.

The dominance of PLA crystal structure in all the composites shows the limited impact the filler has in disrupting the crystal structure of the PLA matrix.

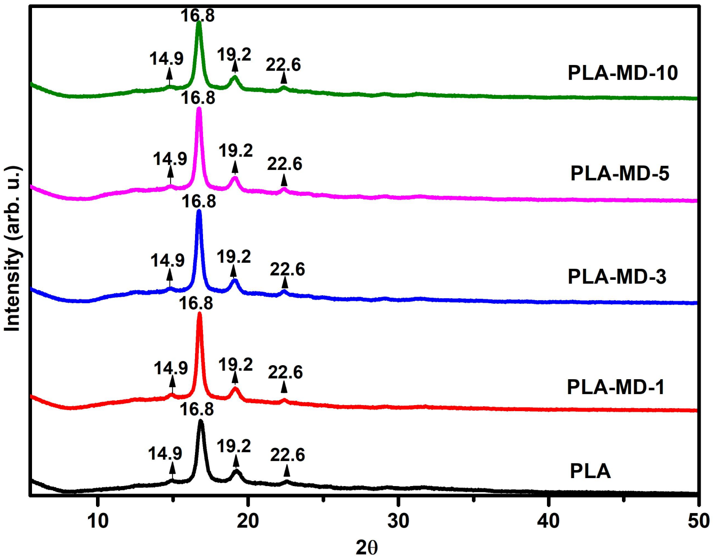

Figure 3: XRD of the PLA only and PLA-MD composites.

*Thermal Analysis*

The thermograph of the PLA films showed a two stage weight loss profile as shown in Figure 4. The initial stage occurred at 100 ºC as a result of evaporation of moisture in the polymer sample and secondly, the thermal degradation of the polymer recorded between 300-370 ºC (Table 1), which is as a result of intra molecular backbiting reaction. Additionally, the onset degradation (Tonset) which relates to 10 % weight loss is deduced at the peak of the degradation of the samples. The same observation is made in regards to the PLA-MD composite sample films. At the Tonset point, for the PLA film, it was recorded at 309 ºC and increased to 313 ºC for PLA-MD-1, but reduced to 309 ºC again for PLA-MD-3. An increase was recorded for PLA-MD-5 and 10 at 311 and 313 ºC, respectively (Table 1). It generally observed that the impact of the bio-filler is that of enhanced thermal stability of the composite system at the level of Tonset indicating good compatibility and proper dispersion of the filler within the polymer matrix. Additionally, at 50% weight loss the following weight loss was recorded for PLA and its MD composites 349, 349, 340, 351 and 352 ºC respectively. It can be deduced that there was increase in the decomposition temperatures of PLA and PLA-MD-1 as the 1% weight load did impact the thermal stability of the PLA matrix at this point. Conversely, a reduction was recorded in the PLA-MD-3 which can be attributed the filler acting to bring instability to the system at this point rending it slightly unstable. For PLA-MD-5 and 10 an increased system stability was recorded resulting in increased temperatures of 351 and 352 °C respectively (Table 1). Another thermal property of importance is the temperature at which the maximum weight loss occurs. This usually corresponds to the peak value of the first TGA derivative curve (Figure 4).

Table 1: The thermal behaviour of PLA and PLA-MD films at different temperatures.

| SAMPLES | $T_{10\%}$ (°C) | $T_{50\%}$ (°C) | $T_{max}$ (°C) | Residue (%) |
|---|---|---|---|---|
| PLA | 309 | 349 | 363 | 0 |
| PLA-MD-1 | 313 | 349 | 420 | 0.9 |
| PLA-MD-3 | 309 | 340 | 416 | 5 |
| PLA-MD-5 | 311 | 351 | 377 | 12 |
| PLA-MD-10 | 313 | 352 | 376 | 24 |

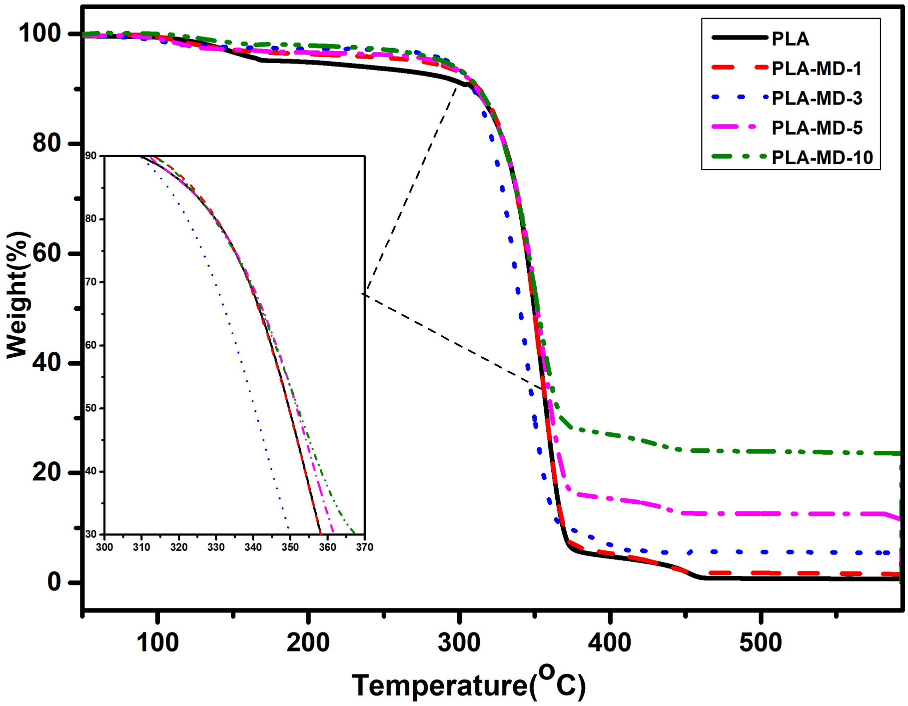

Figure 4: Thermal behaviour of PLA and PLA-MD composites.

*Mechanical Properties*

The mechanical characteristics of PLA and PLA-MD composite films are showed in Figure 5. From the stress-strain curve of these films valuable and important mechanical properties parameters such as the tensile strength, elongation at break and young's modulus were obtained. The addition of MD fillers was found to have significantly enhanced these mechanical properties of the composites compared to that of pure PLA bioploymer. The increasing weight load of MD resulted in general increase in yield stress, stress at break, young's modulus and elongation at break. The tensile strength of the composites increased dramatically with PLA-MD-3 giving the best performance at ~75 MPa which is closely followed by PLA-MD-1 which recorded 70 MPa while PLA-MD-10 recorded the least improvement at 60 MPa. Additionally, percentage elongation of the composited was found to have significantly increased with PLA-MD-5 showing almost six fold increase compared to PLA at ~7%. At 5% weight load ~45% increase was observed against PLA with 7% elongation at break. The elongation at break of PLA-MD-5 came at ~34% and the least composite performance was recorded by PLA-MD-1 which only expanded to ~14% twice the performance for pure PLA. Young's modulus for composites improved except for PLA-MD-10, which can be attributed to the impact its 10% weight load of the filler which reduced its inability to withstand stretching thereby deforming easily. PLA-MD-5 gave the best performance for young's modulus, and this is closely followed by PLA-MD-3 and PLA-MD-1. This results shows composites can withstand stretching pressure without deforming. Notably, all the composites gained increased rigidity and yield resistance while maintaining their ductile characteristics. Additionally, the composites generally showed appreciable plastic deformation i.e. they did not show brittleness despite the induced stiffening.

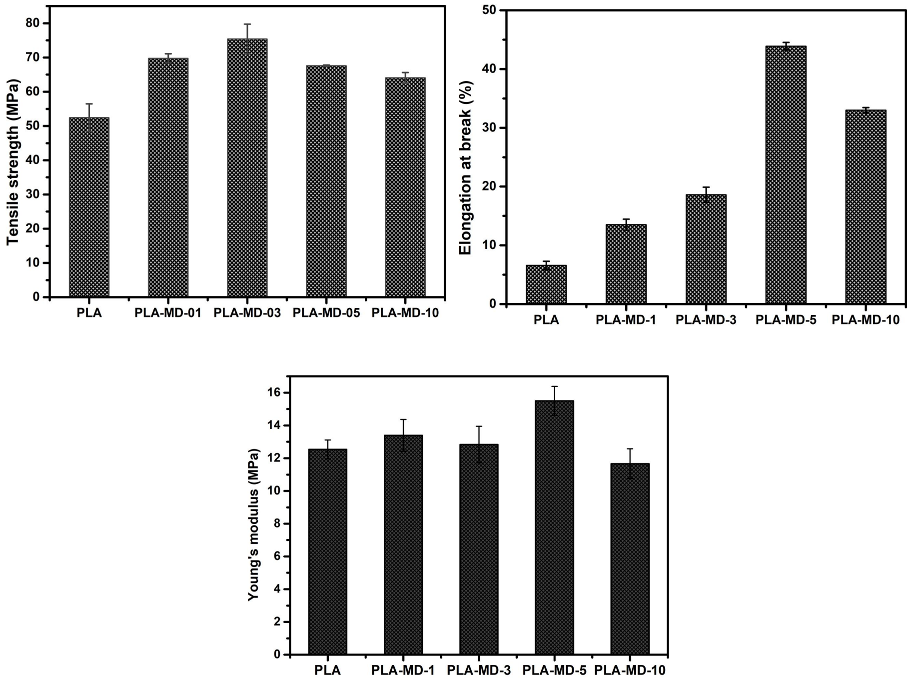

Figure 5: Tensil strength (a), Elongation at break (b) and Young's modulus (c)

### *Antioxidant Activity*

The antioxidant activity of PLA and PLA/MD composites are shown in Figure 6. The antioxidant performance was determined by evaluating the radical scavenging activity of the films in DPPH solution. This also noticeable in the discoloration of the DPPH solution occasioned by the presence of the films after the period of incubation. The PLA film recorded a low antioxidant activity at ~10.7 % while the PLA/MD composites showed strong performance which was depended on the wt. load of MD. At 1% wt. load of MD the activity was found to have increased to ~30 % a tenfold increase, the highest antioxidant activity was recorded at ~97 % for PLA/MD-10 which was closely followed at ~96 by PLA/MD-5. The addition of MD into the PLA matrix was found to have increased antioxidant activity from 10.7 % to 96 % thereby recording ~8 fold increase. MD has been reported to have potent antioxidant activities [2]. The PLA/MD films have demonstrated high antioxidant activity and can be used for packaging foods that are sensitive to oxidative stress to thwart degradation or spoilage and for shelf life extension of foods.

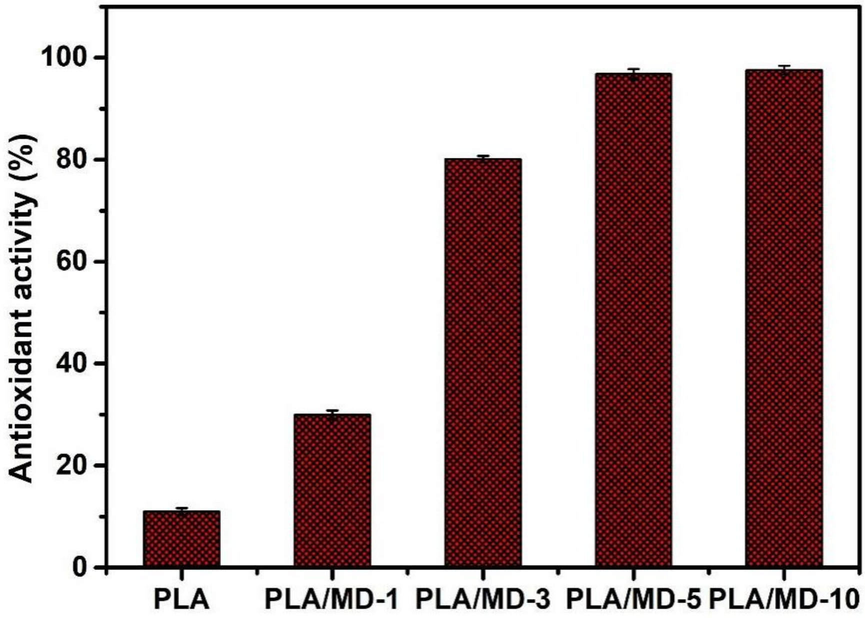

Figure 6: Antioxidant activity of the PLA and PLA/MD films.

## CONCLUSIONS

In this study, Vitamin $K_3$ (MD), a food additive, was successfully incorporated into a PLA polymer matrix. The solution casting method produced PLA-MD composite films that are flexible, uniform in thickness and visibly transparent. FESEM showed that the Vitamin $K_3$ filler was well dispersed and compatible with the PLA polymer. The addition of MD enhanced the UV light blocking properties of the PLA biopolymer. The incorporation of the filler generally improved the thermal stability of the PLA matrix. Remarkably, the mechanical properties of the composites were enhanced with significant increases in tensile strength, percentage elongation, and Young's modulus. The composite films also exhibited high antioxidant activity, with activity increasing with filler loading. The results indicate that Vitamin $K_3$ is a promising bioactive filler for enhancing PLA's properties for dry food packaging applications.

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