Regular Article

Durable Polylactic Acid (PLA)-Based Sustainable Blends and Naringin: Recent Developments, Challenges, and their Properies and Applications

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Photostabilizing polymeric materials are vital in safeguarding against aging and ultraviolet (UV) irradiation. Consequently, the modification of polymers to enhance their resilience to photodegradation and photooxidation during prolonged exposure to UV light in challenging settings is necessary. Specifically, recent advancements have led to the design and synthesis of various polymeric additives, which their potential utility as photostabilizers have been extensively investigated. In this work, thin films of Polylactic acid (PLA) were developed by incorporating diverse concentrations of naringin alongside the commercial stabilizer TINUVIN 622. The study focuses on assessing the role of naringin and TINUVIN 622 as effective UV blockers against PLA photodegradation. Detailed examination encompassing weight loss analysis, surface morphology observations, determination of the photodecomposition rate constant Kd, and analysis of changes in infrared spectra of irradiated polymeric blends, revealed the efficacy of 0.075% naringin concentration in significantly mitigating UV-induced degradation, thereby providing PLA with robust protection. Overall, the study demonstrated that 0.075% naringin emerged as the most efficient additive in stabilizing PLA against UV-induced degradation.

INTRODUCTION

Within the food packaging industry, a noticeable inclination has emerged towards the adoption of renewable plastics as substitutes for petroleum-based counterparts, thereby minimizing the environmental footprint. Notably, poly (lactic acid) (PLA) has garnered significant attention as a highly promising material due to its compelling blend of favorable physical and functional attributes, coupled with its cost-effectiveness and widespread commercial availability. Despite its commendable melt processability, PLA encounters certain limitations in food-related applications, primarily concerning its proneness to brittleness, sluggish crystallization rate, and relatively modest thermal and mechanical properties, especially in comparison to traditional polymers of similar nature. To bolster its viability in creating appealing materials suitable for diverse industrial applications, extensive research endeavors have been dedicated to surmounting these inherent drawbacks [1,2].

Lactic acid exhibits significant potential as a key chemical commodity for the fabrication of eco-friendly polymers. A breakthrough occurred within a span of six years, leading to the development of cost-effective methods for the large-scale production of polylactic acids [3]. The

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inherent characteristics of these polymers, both in terms of their physical and chemical structures, play a fundamental role in governing the processes of degradation and biodegradation. Notably, PLA can assume highly crystalline configurations, which are recognized for their relatively greater resistance to hydrolysis when compared to the amorphous segments of the polymer [4].

Extensive research has been conducted to comprehend the degradation mechanisms of PLA and its copolymers, involving the utilization of microbial organisms or enzymes [5]. A crucial aspect pertains to the chemical recycling of PLA back into its monomeric form, serving as a vital strategy for the regeneration and synthesis of this renewable resource. This approach effectively curtails the environmental impacts associated with both the production and disposal of PLA. Furthermore, the production of PLA using recycled constituents offers considerable energy savings in contrast to the use of pristine raw materials. Depolymerization through hydrolysis yields high-quality lactic acid, which can subsequently be utilized to regenerate high-quality PLA, bypassing the intricate and costly process of glucose fermentation commonly employed for obtaining virgin lactic acid [6,7].

Due to its inherent capacity for environmentally friendly degradation into lactic acid, PLA finds diverse applications in various biomedical fields, including the development of resorbable sutures and orthopedic implants. The incorporation of plasticizers stands out as a significant modification approach to enhance the mechanical characteristics of PLA. Elsawy *et al.* [8] explored the utilization of jojoba oil, a natural substance, as a potential plasticizer for PLA. The choice of jojoba oil as a suitable plasticizer for PLA was based on the favorable solubility compatibility between the two materials. Through comprehensive mechanical testing, the study unveiled the positive plasticizing impact of jojoba oil on the properties of PLA, with notable enhancements observed in terms of elongation and impact strength compared to pure PLA [8].

Lignin, a key constituent of lignocellulosic biomass and the second most abundant biopolymer globally, is recognized for its innate capacity as a natural broad-spectrum UV blocker/absorber, owing to its phenolic structure [9]. Consequently, lignin has emerged as an effective UV absorber, enabling the formulation of UV-resistant materials.

Even a minimal incorporation of lignin into the matrix has shown the potential to significantly enhance the UV absorption capabilities of the composite while maintaining high transparency [10].

The renewable and biodegradable nature of polylactic acid (PLA) has positioned it as a sustainable and eco-friendly alternative to conventional petroleum-based materials. In recent developments, modified lignin or its derivatives, characterized by commendable biocompatibility, have been integrated into the PLA polymer matrix. This integration aims to produce films or composites with exceptional UV light-absorbing or resistant properties [11].

In the current study, the potential of naringin as a photo-stabilizer for PLA was investigated. Various concentrations of naringin, in conjunction with TINUVIN 622, were employed, crucially contributing to the photochemical process owing to their distinctive polar characteristics. This interplay fosters interactions within the polymer series, thereby enhancing the efficiency of the composite in mitigating the detrimental effects of UV light. This combined approach exhibits promising potential in curtailing the photodegradation of PLA.

EXPERIMENTAL

General

PLA with a polymerization degree of approximately 800 units was provided by Petkim Petrokimya, located in Istanbul, Turkey. The FTIR spectra were acquired at room temperature using an FTIR 8400 instrument from Shimadzu in Tokyo, Japan. The PLA films were subjected to radiation at 25 °C using an accelerated weather-meter QUV tester from Q-Panel Company based in FL, USA. Surface imaging of the materials was conducted utilizing a Meiji Techno microscope from Tokyo, Japan. Additionally, atomic force microscopy (AFM) images were captured at room temperature using a Veeco device located in New York, United States.

Extraction Process

A total of 100 g of ground peels were combined with 250 ml of 96% ethanol in a Soxhlet apparatus (0.5 m × 6 cm) and subjected to extraction for 30 min as previously reported (Fig. 1) [12].
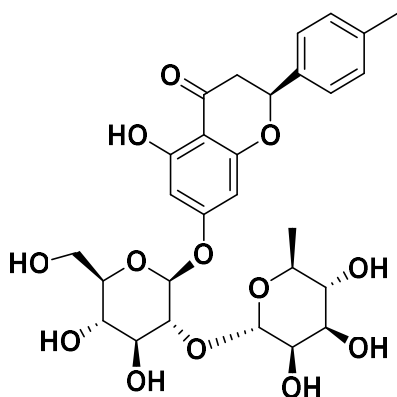
Fig. 1. Structure of naringin.

Fabrication of PLA Films

A blend of 4 gm PLA and 100 mL of chloroform (CHCl₃) was agitated at 25 °C for 90 min. The PLA solution was then mixed with different concentrations of natural extract naringin (0.025, 0.05, and 0.075 wt%). Similarly, the blend was mixed with 0.075% of TINUVIN 622 (a commercial stabilizer) in order to compare the extract effect with a known stabilizer. The whole mixture was stirred at 25 °C for 0.5 h until it became uniform. This homogeneous blend was then poured onto clear glass slides until it reached a thickness of roughly 40 μm, then left to dry for 24 h at 25 °C.

Irradiation of PLA *via* Ultraviolet (UV) Rays

The PLA thin films underwent UV light irradiation for durations ranging from 50 to 300 hours, with an interval time of 50 hours. The UV light intensity was set at 6.0×10^{-9} ein dm^{-3} s^{-1} at $\lambda_{max} = 365$ nm. To ensure uniform exposure of the films to UV light from all directions, the films were periodically flipped into various orientations.

RESULTS AND DISCUSSION

Exposure to ultraviolet (UV) light poses a significant threat to materials utilized in outdoor applications. Plastics, when subjected to severe conditions, such as prolonged sunlight, elevated temperatures, and humidity, in the presence of oxygen, undergo photooxidation. The consequences of this process include discoloration, formation of cracks, and deterioration of mechanical and physical properties. It is important to note that photooxidation, triggered by UV light absorption, bears resemblance to autooxidation resulting from prolonged heat exposure, with the critical distinction being the primary influence of UV light rather than heat. Consequently, in the realm of plastic manufacturing, it becomes imperative to implement preventive measures that can effectively prolong the lifespan of materials and inhibit the detrimental processes of photooxidation and photodegradation [13]. Several thin films, approximately 40 μm in thickness, were prepared, including blank PLA films, along with those incorporating varying concentrations of the natural extract naringin (0.025%, 0.05%, and 0.075% by weight). Similarly, the blend with 0.075% of TINUVIN 622 (a commercial stabilizer) was also present. Figure 2a illustrates a representative pure PLA FTIR spectrum, cast onto an IR transparent disk with KBr, prior to UV light exposure. The spectrum exhibits distinct and intense peaks within the 2850-2998 cm^{-1} range, corresponding to C-H stretching bonds. Additionally, a highly pronounced peak at 1773 cm^{-1} signifies the presence of the carbonyl C=O in the ester group. Furthermore, the C-H deformation manifests as a peak at 1452 cm^{-1}, while the C-O stretch is evident through bands at 1298 and 1260 cm^{-1}. In Fig. 2b, the changes in various FTIR peaks, selected for monitoring PLA photodegradation after 300 h of irradiation, are portrayed. Interestingly, minimal modifications were observed in the bands within the 2850-2998 cm^{-1} range, indicative of the C-H stretch, across all the pure and doped PLA film samples, both before and after UV exposure. Consequently, the C-H peak was utilized as a reference point for calculating the functional group indices, as elaborated in the forthcoming sections. The FTIR analysis further unveiled the emergence of a prominent and wide band, ranging between 3200-3600 cm^{-1}, subsequent to irradiation. Evidently, this signal corresponds to the presence of hydroxyl from a carboxylic group [14]. This group is generated as a consequence of the photo-degradation of PLA films following prolonged exposure to UV light for 300 hours. The intensity of the signal corresponding to the carbonyl group in the IR spectrum of PLA was able to give an indication of the rate of photodegradation.
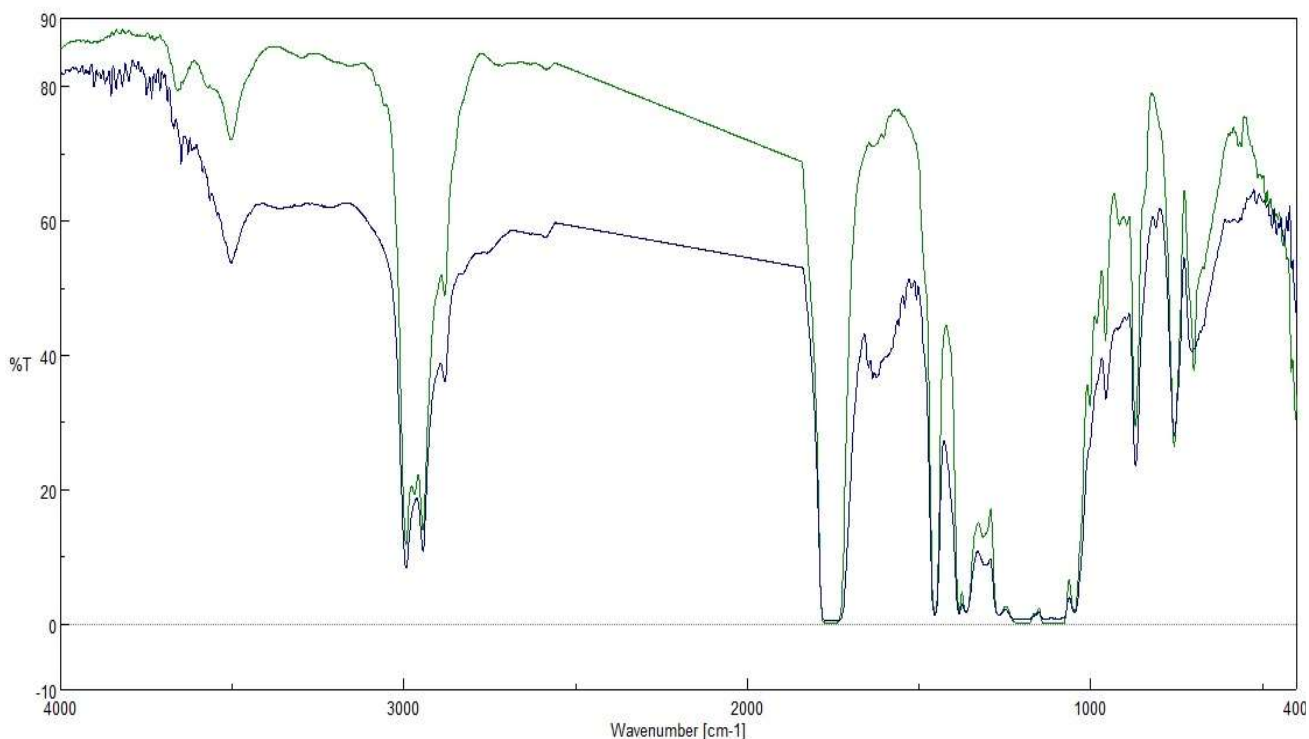
Fig. 2. FTIR spectra of PLA film before and after irradiation.

Different concentrations of natural extract naringin (0.025, 0.05, and 0.075 wt%) were considered. Similarly, the blend was mixed with 0.075% of TINUVIN 622 (a commercial stabilizer) to compare the extract effect with a known stabilizer introduced into the doped polymer to explore its additional stabilization effects on PLA. The degradation of PLA during irradiation was monitored using the FTIR technique, with a 50-hour interval. Equation (1) was employed to derive the functional group indices (Is) for the carboxylic group's OH and C=O bands, which manifest due to the photo-dissociation of PLA under UV light irradiation. Consequently, the absorbance of the functional groups' OH and C=O (As), along with that of the C-H band, was utilized to determine the reference peak (Ar) unaffected by degradation. The IOH and IC=O were calculated between 50 and 300 hours of irradiation. Figures 3 and 4 illustrate the alterations in both IOH and IC=O indices induced by the irradiation of PLA sheets [12].

$$I_s = A_s/A_r \qquad (1)$$

The observed increase in both I_{OH} and $I_{C=O}$ indices in the blank PLA sheets was notably higher compared to the doped PLA films. Notably, the incorporation of all the additives led to a considerable reduction in both I_{OH} and $I_{C=O}$ indices, clearly demonstrating the impact of additives in mitigating PLA photodegradation. Specifically, the PLA films containing 0.075% naringin exhibited the lowest IOH and $I_{C=O}$ indices, followed by the other PLA films.

The weight loss of PLA exhibited a direct correlation with the duration of irradiation. By an increase in the irradiation time, a corresponding acceleration in PLA weight loss was expected. Consequently, the PLA samples were subjected to prolonged radiation exposure lasting 300 hours. Employing Eq. (2), the percentage of weight loss resulting from photo-irradiation was calculated based on the initial weight of the films before UV light exposure (W0) and the weight after UV light exposure (W1) [12,13]. Figure 5 illustrates the fluctuations in weight loss (%) at different irradiation intervals, each spanning 50 h.
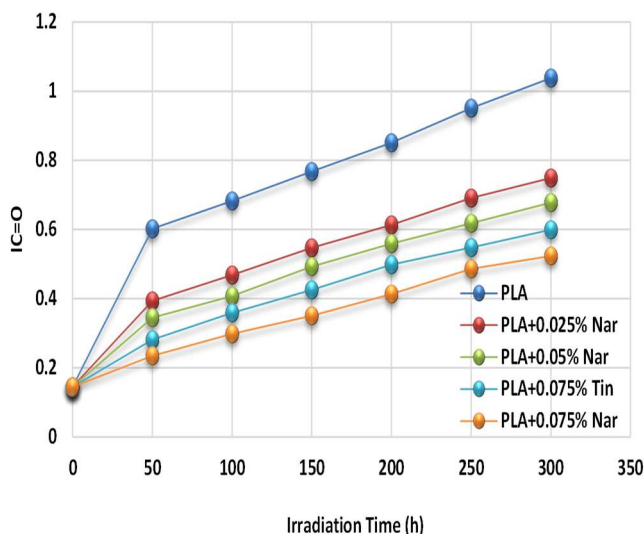
$$Weight\ loss\ (\%) = \frac{W_0 - W_1}{W_0} \times 100$$

Fig. 3. Relationship of $I_{C=O}$ index with irradiation time for PLA films.
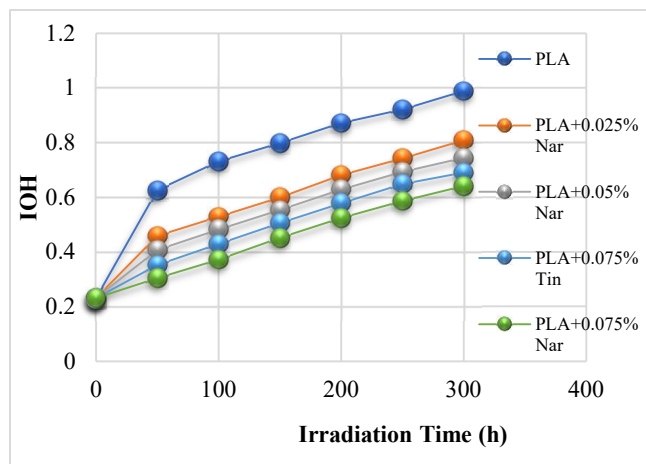

Fig. 4. Relationship of I_{OH} index with irradiation time for PLA films.

Over time, the rate of weight loss exhibited a steady and pronounced increase. Comparatively, the incorporation of additives resulted in reduced weight loss in contrast to the blank film. Evidently, all additions, particularly those featuring a higher concentration of naringin and TINUVIN 622, effectively mitigated the rate of PLA photodegradation. Notably, the pure PLA demonstrated the highest weight loss, while the blend containing 0.075% naringin experienced the least weight loss.

PLA films resulted in a clear improvement in the decomposition rate of PLA films. Figures 6 and 7 shows the relationship of (At-$A\infty$) *versus* irradiation time (t); the plot was a straight line. The graph showed 1st order kinetics behavior, where the slope was equal to the rate of decomposition rate constant (k_d) for PLA blank film. It has been noted that during the photolysis process, all films used were decomposed. Table 1 shows that all the PLA + 0.075% naringin film had a lower K_d compared with the blank PLA material. The rate of decomposition was highest for the unmodified film (4.2×10^{-3}) and lowest for PLA + 0.075% naringin film (3.4×10^{-3}).
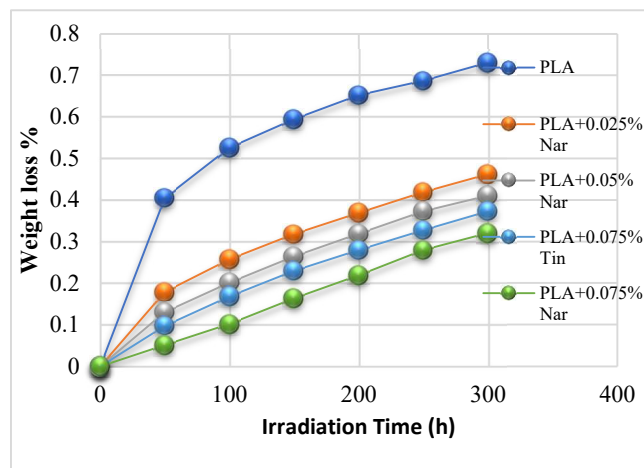

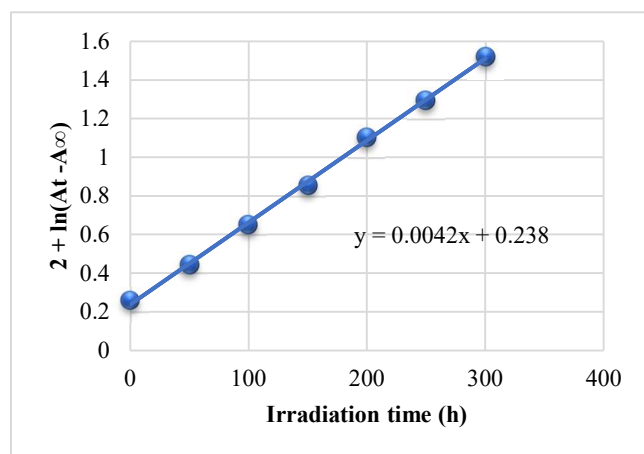**Fig. 5.** Effect of irradiation of PLA films on weight loss.

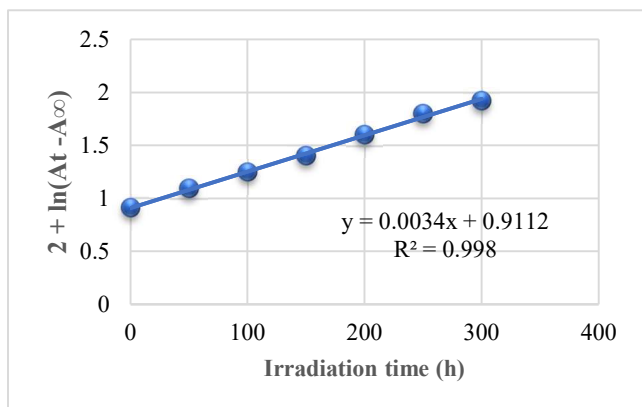**Fig. 6.** Changing in (A_t-A_∞) *versus* UV irradiation time for irradiated PLA blank film.

Fig. 7. Changing in (A_t-A_∞) *versus* UV irradiation time for irradiated PLA blank film.

Table 1. Photodecomposition Rate Constants (k_d) of PLA Films

Film	K_d (s^{-1})
PLA	4.2×10^{-3}
PLA + 0.025% Nar	3.9×10^{-3}
PLA + 0.05% Nar	3.8×10^{-3}
PLA + 0.075% Tin	3.5×10^{-3}
PLA + 0.075% Nar	3.4×10^{-3}

Table 1 and Figs. (6, 7) demonstrate the effectiveness of PLA and its type on the k_d values for PLA prepared films. As shown in Table 1, the highest k_d value (4.2×10^{-3} s^{-1}) was for PLA blank film. The rate constant decreased considerably

(3.9-3.4×10^{-3} s^{-1}) when PLA + 0.075% naringin film used. Hence, PLA + 0.075% naringin film was the most effective photostabilizer for PLA.

Optical Microscope Technique

An analysis conducted through an optical microscope on the surface of the irradiated PLA blends provides critical insights into surface irregularities, fractures, dark patches, and chain scission induced by the irradiation process [12]. In contrast, the surface of non-irradiated blank PLA typically appears uniform, smooth, and free of blemishes or disruptions. However, upon 300 hours of exposure to UV light, the irradiated PLA displays noticeable cracks, spots, and imperfections, as depicted in Fig 8.

Nevertheless, the presence of additives reduced the number of white spots compared to the PLA film (blank), demonstrating the efficiency of naringin and TINUVIN 622 as photostabilizers for PLA films, as shown in Fig. 9.

Atomic Force Microscopy Technique

AFM has proven to be an effective technique for studying polymer surfaces. Figure 10 presents the two and three-dimensional atomic force microscopy images of the exposed PLA thin films. Notably, the choice of additive exerted an influence on both the surface roughness and the occurrence of black spots on the PLA film's surface. The pure PLA film exposed to UV light exhibited a notable increase in roughness, along with the presence of imperfections and dark patches, in contrast to the films containing additives [14].
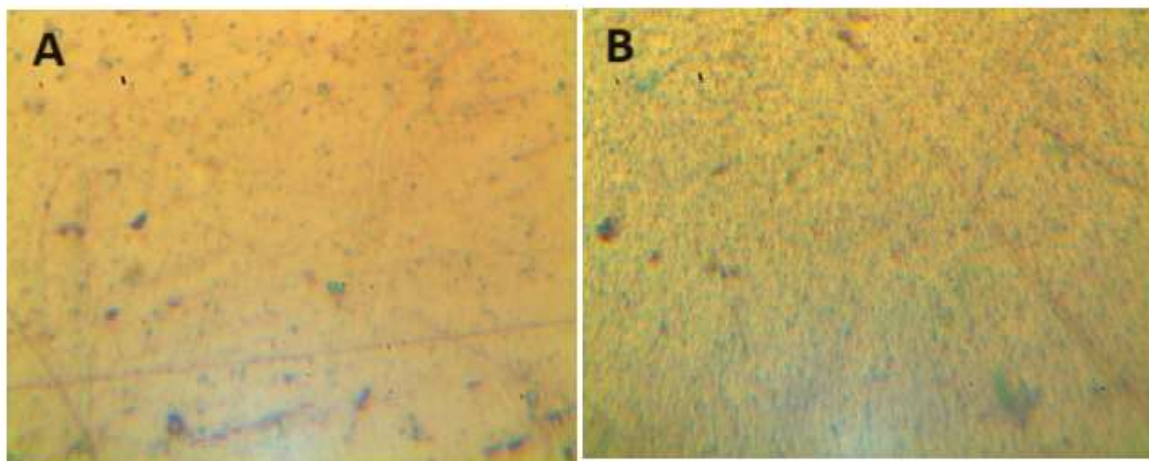

Fig. 8. Microscopic images of PLA (A) before and (B) after irradiation.
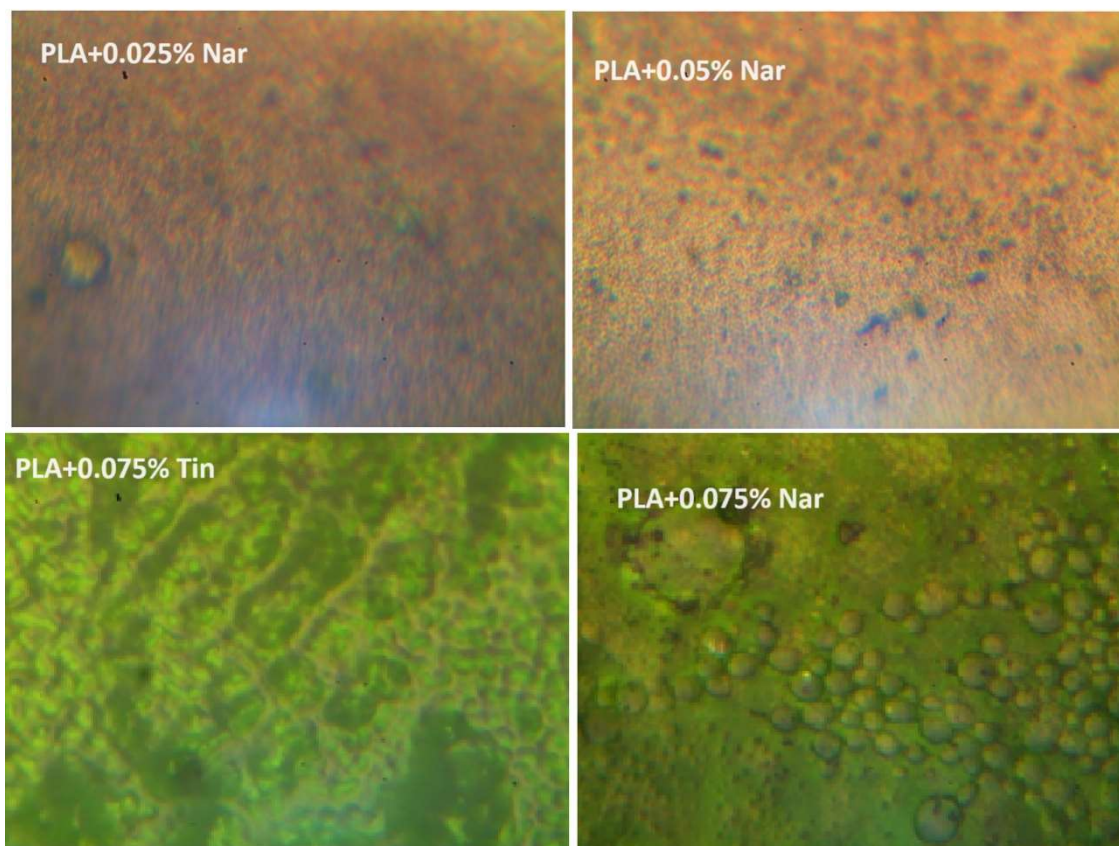
Fig. 9. Microscopic images of PLA with different concentrations of naringin and TINUVIN 622 blends after irradiation.
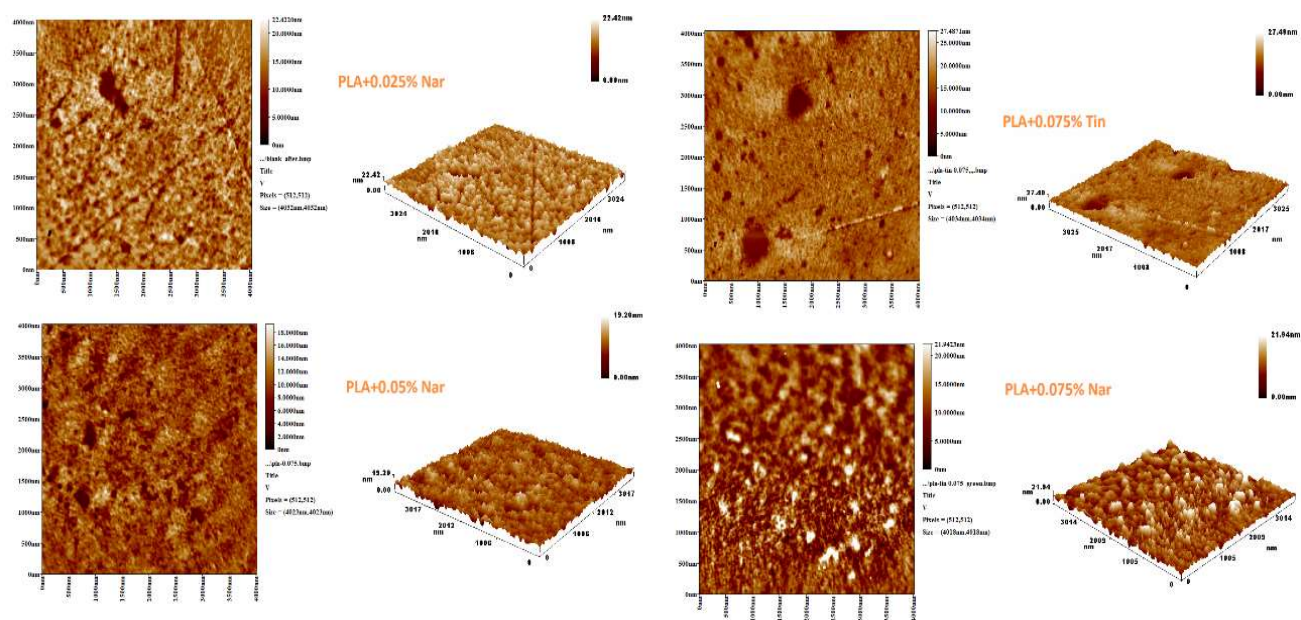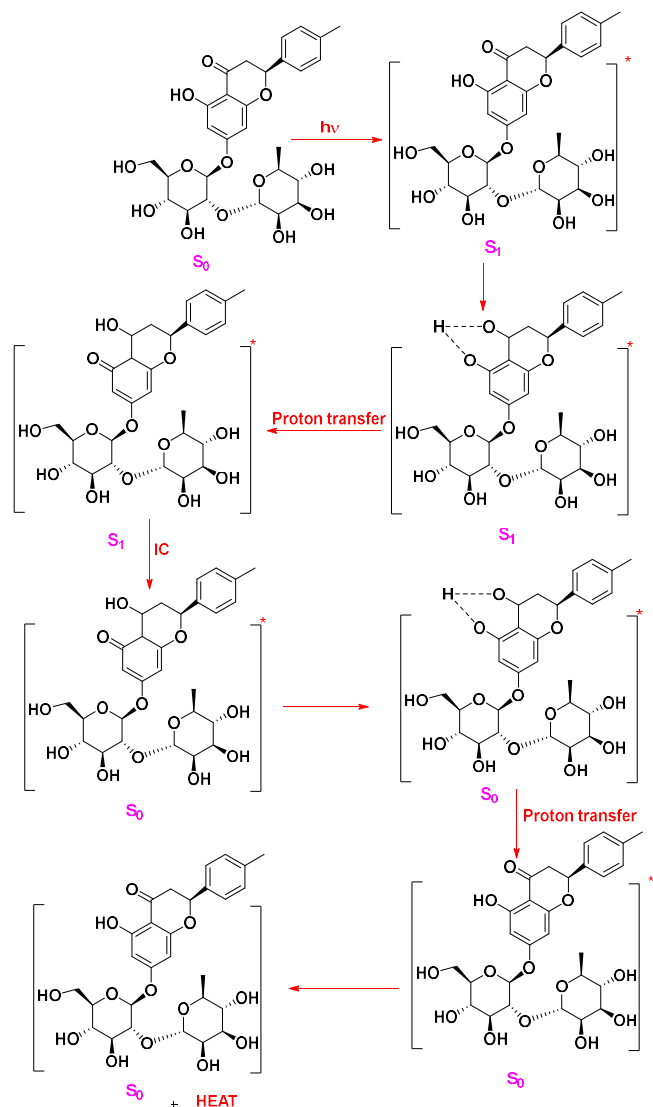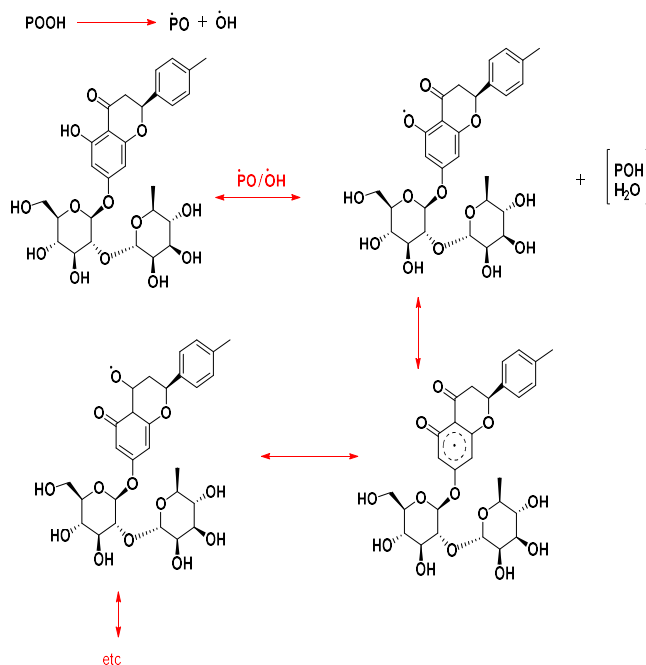

Fig. 10. AFM images for PLA films.

UV-Vis and IR spectroscopy results were used to suggest a mechanism for additives affecting PLA films after radiation. The additive used was a blend of flavonoids that included naringin, which was studied as a single material. The commonly accepted mechanisms for additives in photostabilization include UV absorption (screening), free radical scavenging (chain-breaking donors), and excited state quenching (physical quenching). Based on these mechanisms, we propose Scheme 1 for the absorption of UV

Scheme 1. The suggested mechanism of photostabilization through absorption of UV light and dissipation light energy as heat

Scheme 2. The suggested mechanism of photostabilization as a radical scavenger

light by naringin and its conversion into heat energy, which protects the PLA films from direct photo-excitation [15].

It is also known that β-substituted hydroxybenzo-phenones or benzotriazoles can act as radical scavengers (chain-breaking donors) in the photostabilization process. Hence, besides its role as a UV absorber, naringin exhibits the potential to function as an additive with radical scavenging properties, acting as a chain-breaking donor, as depicted in Scheme 2 [15].

CONCLUSIONS

Exposure to ultraviolet radiation triggers a photooxidative deterioration mechanism in plastics, resulting in bond breakage, release of volatile substances, overall weight reduction, generation of free radicals, and loose crosslinking. Different concentration (0.025, 0.05 and 0.075%) of naringin were extracted with excellent yields using a simple procedure and TINUVIN 622 as a commercial stabilizer. To investigate their impact on the photostability of the polymeric blends, naringin and TINUVIN 622 were combined with PLA. As expected, when PLA was exposed

to ultraviolet light, naringin and TINUVIN 622 notably decreased the photodegradation of the material. To investigate how naringin and TINUVIN 622 stabilize the polystyrene, a number of approaches, including infrared spectroscopy, weight loss analysis, molecular weight reduction, photodecomposition rate constant and surface alterations in PLA were employed. PLA+0.075% naringin had the most stabilizing effect, compared to compounds with other concentrations.

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