IMPACT OF RED ALGAE AND DIFFERENT GAMMA IRRADIATION DOSES ON THE PHYSICOCHEMICAL PROPERTIES AND BIODEGRADATION RATE OF EPDM/EVA/TPS BLEND

Ahmed Siddiq1*, Mohamed Mohamady Ghobashy2, Sayed A. S. Mousa1, Hamdi M. D. Nasr1, Ahmed A. Atalla1

1Department of Chemistry, Faculty of Science, (Boys) Al-Azhar University, 71524, Assiut, Egypt
2Radiation Research of Polymer chemistry department, National Center for Radiation Research and Technology (NCRRT), Atomic Energy Authority, P.O.Box.29, Nasr City, Cairo, Egypt
*Corresponding author. ahmed.siddiq1993@gmail.com.

ABSTRACT

Algae-based bioplastic were prepared during this work to show the impact of red algae incorporation and gamma irradiation dose on the biodegradation and physicochemical properties of EPDM/EVA/TPS-algae blend. It was found that red algae increasing resulted in increasing of water uptake ratio and decreasing of crosslinking density percentage, also mechanical properties was enhanced by incorporation of red algae from 5 to 20wt.% but further addition of algae i.e. 30wt.% made the sample fragile and decreasing the mechanical properties. While gamma irradiation dose increasing causes decline of mechanical properties and slightly decreasing of both water uptake and crosslinking density percentage which may be attributed to the degradation effect of gamma radiation. Moreover, weight loss percentage in general was found to increase by increasing of gamma radiation dose, and anaerobic biodegradation was higher than that of aerobic one. The irradiated and un-irradiated bioplastic samples of EPDM/EVA/TPS-algae can be used as compostable materials and as soil conditioner which can supply the plant with nutrients through the biodegradation process by microorganisms and are effectively able to improve the Radish plant growth.

Keywords: Algae Bioplastic, Biodegradation, Gamma irradiation, Red algae, EVA, EPDM, Glycerin.

1. INTRODUCTION

In order to diminish environmental problems caused by plastic wastes, currently there is a major interest for biopolymers as a substitute to oil-based plastics in some applications[1,2]. Bioplastic is a plastic manufactured in whole or in part from polymers extracted from biological sources such as sugar cane, potato starch or from trees, straw and cotton cellulose. according to the European Organization for Bioplastics, a plastic material is known as a bioplastic if it is either biobased, biodegradable or has both properties [3].

Owing to its renewability, biodegradability, non-toxicity and low cost, starch is considered as a promising nominee for sustainable material development [4]. Processing of native starch granules by heating at comparatively high temperatures, in high shear conditions, and with restricted amounts of plasticizer a thermoplastic starch (TPS) matrix is formed [5]. However, TPS has two main disadvantages: namely its water sensitivity and its weak mechanical properties. Many research efforts in this field centered on the ways of overcoming these limitations. The most popular methods to enhancing TPS properties are modifying starch structure through chemical reaction and blending of TPS with other polymers [6].Blending is one of the most popular polymer manufacturing techniques for producing materials with physical properties that vary from those of the unmixed components. Blending may yield to: (i) materials with a favorable set of desired properties without needing to synthesize completely new materials. (ii) materials with improved specific properties (e.g., impact strength or resistance to moisture) [7].

Ethylene Propylene Diene Monomer (EPDM) rubber emerges mainly as an elastomer for major engineering applications. It
has a good resistance to oxidation, ozonisation, weathering effects, polar substances and steam condition too [8,9]. Ethylene-vinyl acetate copolymer (EVA) is a thermoplastic copolymer, available in the market, easy to handle and process, and low-cost, formed by various monomers: ethylene and vinyl acetate [10].

Patel et al., [11] researched the preparation of EVA/TPS blend with (70:30) as a blend optimum ratio and impact of incorporation of different clay organically modified. The TPS prepared by plasticizing and gelatinizing of maize starch through adding glycerol and water in a ratio of (70:20:10). It was found that addition of TPS lead to a decline in both tensile strength and elongation at break which was regained latter by incorporation of different clay organically modified, and thermal study showed no significant change in crystallization and melting temperature.

Chayapa et al., [12] investigated the properties of thermoplastic cassava starch (TPCS) and the effect of incorporation of sodium alginate extracted from brown algae cell walls by a ratio of 0, 10, 20 and 30 wt%. The results showed worthy phase compatibility among TPCS and sodium alginate. Moreover, the TPCS composites biodegradation was obviously hastened due to sodium alginate incorporation. Algae considered as an exceptional source of various natural materials among them biopolymers [13]. So, in recent years they gained enormous scientific interest. They are positioned at food chain bottom [14].

The aim of these work is investigation the impact of Red algae (Eucheuma spinosum) and gamma radiation doses on the physicochemical properties and Biodegradation behavior of ((EPDM/EVA/TPS)-algae) blend.

### 2. EXPERIMENTAL

#### 2.1. Materials:

Starch was obtained from local market and used without purification. Glycerin 99.5% was procured from EL Gomhouria company, Egypt. ethylene-propylene-1,4-hexadiene rubber (EPDM) and copolymer of Ethylene Vinyl Acetate (EVA) with 19 wt. % of vinyl acetate (VA) content were purchased from ExxonMobil Chemical Company. Red algae (Eucheuma spinosum) were obtained from Alexandria beaches as waste material. The solid (Eucheuma spinosum) red algae were washed numerous times to eliminate the impurities and then dried in an oven at a temperature of 45 °C for 5 hr and then stored in a plastic bag to the following procedure.

#### 2.2. Preparation of (EPDM/EVA/TPS)-algae) Bioplastic Samples:

Thermoplastic starch was firstly obtained by mixing 80gm native starch with 60ml glycerin, then heated on a plate furnace at 100°C for 15 min with good stirring, then the obtained dry (TPS) was mixed with ethylene-propylene-1,4-hexadiene rubber (EPDM) and copolymer of ethylene-vinyl-acetate (EVA) in a ratio of (30:30:30 in grams), then red algae was added with different content to the blend as shown in Table (1). finally the quaternary extruded matrix was compressed through a thermo-press at a temperature of 115°C using heated hydraulic press (CARVER model 3853) to obtain laminate plate with a thickness of 2 mm. To recognize the impact of gamma radiation doses on the properties of the prepared bioplastic, sample with the best mechanical properties was irradiated with different doses 30, 40, 50, 60 kGy.

| Sample | EPDM(gm.) | EVA (gm.) | TPS (gm.) | Algae content (wt. %) | Sample code |
|--------|-----------|-----------|-----------|----------------------|-------------|
| 1      | 30        | 30        | 30        | 5                    | ((EPDM30/EVA30/TPS30)-5algae) |
| 2      | 30        | 30        | 30        | 10                   | ((EPDM30/EVA30/TPS30)-10algae) |
| 3      | 30        | 30        | 30        | 20                   | ((EPDM30/EVA30/TPS30)-20algae) |
| 4      | 30        | 30        | 30        | 30                   | ((EPDM30/EVA30/TPS30)-30algae) |
2.1. Characterization:

2.1.1. Gamma Radiation Source:

The prepared bioplastic samples were irradiated with the $^{60}$Co Indian irradiation facility gamma rays at a dose rate of 0.866 kGy/h. The irradiation facility was established by the National Center for Radiation Research and Technology (NCRRT), Egyptian Atomic Energy Authority (EAEA).

2.1.2. Water uptake and crosslinking density (Gel fraction) percentage:

The maximum water uptake percentage for the prepared bioplastic samples ((EPDM/EVA/TPS)-algae) was estimated through immersing the prepared samples for 24 hours in distilled water at room temperature, maximum water uptake percentage was measured according to equation (1). Crosslinking density (Gel fraction) percentage was estimated by immersing the prepared bioplastic samples for 5 hours in hot water at a temperature of 80 °C. Crosslinking density percentage was measured according to equation (2).

\[
\text{Max. Water uptake} \, (\%) = \frac{W_s - W_0}{W_0} \times 100
\]

(1)

\[
\text{Crosslinking density} \, (\%) = \frac{W_f}{W_0} \times 100
\]

(2)

Where $W_s$ is the weight of the bioplastic sample in the swollen state, and $W_0$ is the initial weight of the dry sample.

2.1.3. Mechanical properties:

Mechanical properties for the prepared bioplastic samples was measured by using a Materials Testing Machine (Model 3345; Instron Industrial Products, Norwood, USA) with a load cell of 5 kN. The device was exposed to a gradually increasing vertical load (1mm/min) till the complete separation of upper and lower parts. The load recorded by Bluehill Lite computer software in Newton force was divided by area, To express strength in mega Pascal (MPa):

\[
\text{TS (MPa)} = \frac{F}{\text{Area}}
\]

(3)

The tests were applied on a triple duplications and average was taken.

2.1.4. Biodegradation test:

Biodegradability of the prepared bioplastic films were examined by burying them under agriculture soil; samples were buried in two systems i) Aerobic system at 4-6 cm depth in perforated plastic boxes which was regularly moistened with water every 5 days, ii) Anaerobic system at 4-6 cm depth in plastic boxes always covered with 3-4cm water layer. The two systems were placed out doors at natural environment conditions. Samples were taken from soil every week and gently cleaned with distilled water to remove impurities, dried with a tissue paper to remove excess water from their surfaces and weighted to estimate the variation of weight loss ratio each week according to equation (4).

\[
\text{Weight loss (\%) per week} = \frac{W_e - W_b}{W_b} \times 100
\]

(4)

Where $W_b$ is the sample weight at the beginning of the week and $W_e$ is the sample weight at the ending of the week.

2.1.2. Horticulture Experimental Procedure for Radish plant:

The debris of all the prepared bioplastic films during this work were collected and buried together within the Radish seed inside soil to assess their using as compostable materials and soil conditioner which improve the growth of Radish plant. Eight plastic pots were packed with agricultural soil, four plastic pots among them were chosen to be enriched with bioplastic debris, and the other four plastic pots contain no bioplastic debris (control plastic pots). The 8 plastic pots were divided into 4 groups; (I) plant under stress of water and without fertilizer, (II) plant under stress of both fertilizer and water, (III) plant supported with complete water and without adding fertilizer, (IV) plant with complete of both fertilizer and water. The 8 plastic pots were placed out doors at natural environmental conditions and
irrigated every 10 days for 60 days. The plants of Radish were observed regularly to recognize when plant died, by observing its leaves color change.

3. RESULTS AND DISCUSSION:

3.1. Impact of Red algae content and Gamma radiation doses on the Water uptake and Crosslinking density Percentage of (EPDM$_{30}$/EVA$_{30}$/TPS$_{30}$) Bioplastic samples:

Figure (1a) showed the measurement of the maximum water uptake and crosslinking density percentage for algae-based (EPDM$_{30}$/EVA$_{30}$/TPS$_{30}$) in various content ratios of 5, 10, 20, 30 wt.%. The results obtained showed that the increment of algae content increased water uptake but declined crosslinking density percentage. Also it illustrated that the incorporation of algae from 5 to 30wt.% lead to increase of water uptake percentage from 19.04 to 40.59% and decreasing of crosslinking density from 90.16 to 78.65%. This is due to the hydrophilic nature of algae which responsible for their high water uptake [15]. It can be concluded that the molecules of algae lead to form of voids inside the prepared bioplastic sample in addition to its hydrophilic nature resulting in the increase of water uptake and decrease of crosslinking density. These observations agreed some studies such as [16], [17], [18]. Conversely, Figure (1b) illustrate the influence of different radiation doses of 30, 40, 50, and 60 kGy on the water uptake and crosslinking density percentage for ((EPDM$_{30}$/EVA$_{30}$/TPS$_{30}$)-20algae), it was found that both water uptake and crosslinking density percentage slightly decreased with the gamma radiation dose increasing which may be attributed to the degradation of algae molecules as a result of radiation [19].

3.2. Impact of Red algae content and different Gamma radiation doses on the Mechanical Properties of (EPDM$_{30}$/EVA$_{30}$/TPS$_{30}$) Bioplastic Samples:

Figure (2 a, b, and c) showed that the mechanical properties for the prepared (EPDM$_{30}$/EVA$_{30}$/TPS$_{30}$) were strongly influenced by various weight percent of algae content. The obtained curves illustrate that the increase of algae content from 5 to 20wt.% on the prepared sample causes improvement of tensile strength, elongation at break and elastic modulus, while further addition of algae i.e. 30wt.% made the sample more fragile and its mechanical properties decreased, these foundation came in agreement with that of Bulota et al., [20] and Bharathkumar et al., [21]. Moreover, Figure (2 a, b, and c) also indicated that gamma radiation at a dose of 50kGy lead to a decline in the mechanical properties which may be attributed to the breakdown of linkage between the matrix. Based on curves of Figure (2), the sample with the content of 20 wt.% algae was recorded as the higher tensile strength than the other percentages.

Figure (2d) illustrated the decreasing in the mechanical properties for the prepared ((EPDM$_{30}$/EVA$_{30}$/TPS$_{30}$)-20algae) sample with

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**Figure 1.** The water uptake and crosslinking density percentage (a) after algae incorporation and (b) The influence of various gamma radiation doses.
increasing of the radiation doses, which may be due to the degradation effect of gamma radiation on algae molecules [19].

3.3. Impact of Red algae and different Gamma radiation doses on the Biodegradability of 

((EPDM$_{30}$/EVA$_{30}$/TPS$_{30}$)-20algae)

Implemented in Aerobic and Anaerobic environments

Composting as end-life election has gained significant attention, where the bioplastic material undergoes degradation by biological processes (primarily microorganisms’ enzymatic act), producing carbon dioxide, water and new biomass (in oxygen presence), leaving no significantly distinct materials [22]. Figure (3a and b) illustrated the anaerobic and aerobic biodegradation for the prepared bioplastic samples respectively, it's obvious that the weight of the prepared samples started to decline with burial time owing to the activity of microorganisms, in general increasing of gamma radiation dose from 30 to 60 kGy causes an increment in weight loss percentage in both anaerobic and aerobic system which may be attributed to degradation effect of gamma radiation doses. The weight loss percentage for the buried samples under anaerobic system was in average from 45.54 to 50.58%, while the same samples under aerobic system was in average from 19.36 to 21.24% at the end of 28 weeks, which manifested that anaerobic system degradation is more than that of aerobic one.

The visual observation for the prepared bioplastic samples at different times of incubation during the burial period was documented as an evidence for biodegradation process. Figure (4a and b) showed the steady biodegradation for the buried samples under anaerobic and aerobic environment conditions respectively, it was observed that after the first week of burial an increment in samples opaqueness were detected for both anaerobic and aerobic system with further pink color in aerobic system which may be attributed to microorganism growth, these notes are a sign for starting the hydrolytic degradation. This opacity is due to the refractive index changes, that can be ascribed to the absorption of water and to the producing of low molecular weight compounds by the hydrolytic degradation [23]. The results obtained confirmed that the apparent color change were related to the degradation of thermoplastic starch, the more TPS content in sample causes the deeper black color obvious during the burial period, this result was agreed with Valentina et al., [24]. Also the later stages of sample degradation was characterized by sample shrinking.
Figure 3. Impact of Red algae incorporation on the Percentage of weight loss per week for ((EPDM<sub>30</sub>/EVA<sub>30</sub>/TPS<sub>30</sub>)<sub>-20algae</sub>) irradiated with different doses 0, 30, 40, 50 and 60 kGy in (a) anaerobic and (b) aerobic environments.
4. Overview of Horticulture application:

In order to assess the advantage of the prepared bioplastic samples, agricultural application were chosen as an example. The prepared biodegradable ((EPDM/EVA/TPS)-algae) bioplastic films have highly water uptake nature which make them appropriate to be used as a soil conditioner. Moreover, they can be straight forsake on soil to be biodegraded by living microorganisms and performing as compostable materials. For this purpose a mixtures of all prepared bioplastic samples in this paper were collected and used as a compostable material and as soil conditioner. The application of horticulture will be execute to Radish plant growing in 4 statuses. In comparison to reference sample as represent in Figure (5 a). In general the shoot length increased with using of compostable bioplastic in all 4 statuses. In case of water stress {(I), (II)} conditions, the plant without bioplastic is deceased after 60 days while the plant that contain bioplastic samples persisted. In case (III) at a complete water without fertilizer conditions, the shoot length for the plant contained bioplastic sample enhanced by about 40% up in comparison to the reference plant. Likewise in case (IV) at control conditions the shoot length for the plant which contain bioplastic sample was improved about 25% up in comparison to reference sample, at control conditions minimizing the fertilizer and irrigate water consumption (about 50% fewer water) by the bioplastic sample to the root of plants is an effective technique which economize fertilizers and water. The buried bioplastic sample sucked water either from irrigation water or from moisture of the soil and providing it either to the surrounding soil or onto the root of plant directly.
Petroleum plastics became an important instrument in the horticultural industry and are used in many products, including containers of plant, sheeting and general covering films, greenhouse coverings, pesticides containers, irrigation supplies, trays, labels, packs, etc. Container-crop production is one field of horticulture which uses a huge amount of plastics [25], but demonstrate one functional problem; The non-porous properties of smooth-walled plastic containers ease root circulation that can lead to poor transplant establishment [26]. Figure (5 b) showed a promising result for such a problem as the Radish root piercing through the prepared bioplastic samples which manifested that the prepared bioplastic film have no negative effect on the transplant establishment process or the environment.

| Days | (I) 0.5 water +0 fertilizer | (II) 0.5 water +0.5 fertilizer | (III) 1 water +0 fertilizer | (IV) 1 water +1 fertilizer |
|------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| 15   | ![Image](image1.png)        | ![Image](image2.png)        | ![Image](image3.png)        | ![Image](image4.png)        |
| 30   | ![Image](image5.png)        | ![Image](image6.png)        | ![Image](image7.png)        | ![Image](image8.png)        |
| 60   | ![Image](image9.png)        | ![Image](image10.png)       | ![Image](image11.png)       | ![Image](image12.png)       |

Figure 5. The pictures of (a) the influence of the Composted Bioplastic Samples in the Growth of Radish Plant in diverse Conditions, (b) the piercing of the radish root through the composted bioplastic sample.
CONCLUSION

For the studied algae-based bioplastic samples, it was appeared that increasing of red algae content resulted in increasing of water uptake ratio from 19.04 to 40.59% and decreasing of crosslinking density from 90.16 to 78.65%. which may be attributed to the hydrophilic nature of red algae, also mechanical properties was improved by the addition of red algae from 5 to 20wt.%. but further adding of algae content made the sample fragile and decreasing the mechanical properties. Whereas, gamma radiation dose increasing lead to a decline of mechanical properties and decreasing of both water uptake and crosslinking density percentage. Moreover, weight loss percentage in general was found to increase by increasing of gamma radiation dose which may be attributed to the degradation effect of gamma radiation. Weight loss percentage for anaerobic system ranged from 45.54 to 50.58%, while the same samples under aerobic system ranged from 19.36 to 21.24% at the end of burial test indicating that anaerobic system degradation is more efficiency than that of aerobic one. For environmental application, the irradiated and un-irradiated bioplastic samples of (EPDM/EVA/TPS-algae) can be used as compostable materials and as a soil conditioner which can supply the plant with nutrients through a biodegradation process by a microorganism and is effectively able to improve the Radish plant growth. Furthermore, the root of the radish plant piercing through the prepared bioplastic samples which represent a promising solve for the root circulation caused by the plastic Container-crop production that leading to poor transplant establishment.

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