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Effect of gamma radiation on the characterization of polystyrene/rosin polymer blends

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ABSTRACT

By using the solution casting technique, blends of polystyrene and rosin (PS/rosin) plasticized by dibutyl phthalate (DBP) were created with various rosin content (5, 10, 20, and 30%). These blends were then exposed to various gamma radiation dosages (50, 100, 150, and 200 kGy). Scanning electron microscopy (SEM), and mechanical characteristics were used to analyze the mixes (PS/rosin). FTIR and SEM were used to demonstrate the two polymers' physical miscibility. TGA is used to study thermal properties. The TGA thermograms demonstrated that as the PS component ratio in the blend is increased, the thermal stability of the unirradiated polymer blends (PS/rosin) also increases. Additionally, it was shown that the PS polymer provides protection against radiation degradation and enhances their thermal stability additionally, it was determined that adding PS to rosin improved its tensile strength and other mechanical qualities. On the other hand, by increasing the proportion of rosin in the blend, elongation was reduced.

1. INTRODUCTION:

When the qualities of two or more polymers are blended synergistically, polymer blends have always been thought of as intriguing possibilities for creating novel, high-performance polymeric materials without manufacturing entirely new polymers. One might be able to combine the many materials in useful ways to create a single product by blending them. Additionally, a continuous variety of qualities can be anticipated by merely varying the composition of the mix. In addition, industrial polymer science is drawn to polymers with high glass-transition temperatures due to the possibility for significant financial rewards.

In order to optimise processing, lower manufacturing costs, or increase characteristics, polymer blending is becoming more and more crucial in a variety of applications [1]. It is also possible to blend polymers by combining two or more distinct polymers in a liquid phase [2]. Phase separation phenomenon can cause mixes of miscible and immiscible polymers when various types of polymers are combined [3].

Due to their distinctive qualities, such as biocompatibility, biodegradability, low cost, and the ability to undergo chemical modifications because of their unique structure, rosin derivatives have attracted significant interest in the field of pharmaceutical applications [4]. Rosin is a natural polymer that is solid and brittle and is derived from pine trees. Additionally, they have been utilised in the creation of dental varnishes, chewing gum, medications, and adhesives [5]. It can be broken down in ethanol, ether, benzene, and chloroform but not in water. Rosin is very compatible with almost all polymers. They are widely known for their influence on the adhesive's peel and tack, but they often reduce cohesive strength. Rosin is a valuable component in many products because of its natural origin, low cost, abundance, and capacity for chemical modification. [6-19].

In addition to the above benefits, rosin is biosafe [20]. It has long been influential in a variety of applications, from treating violin bows, to soldering fluxes, viscosity modifiers in printer inks, and paper covers [21, 22].

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Various approaches have been investigated, such as [23], but so far there are no large-scale applications such as in mechanical engineering or building materials. The simple problem is that rosin is a particularly brittle material. Arushgari et al. [24] attempted to improve the mechanical properties by mixing nanoclays with polymers.

PS is one of the most important materials in the modern plastics industry and is used worldwide due to its excellent physical properties and low cost [25]. Polystyrene is an amorphous, colorless and transparent thermoplastic resin**.** It is stiff, brittle, relatively hard, has good gamma radiation resistance, good electrical properties, but poor chemical and UV resistance. The effect of gamma rays on PS indicates that PS is crosslinked [26]. Many studies have been conducted on post-irradiation PS (C8H8) [27-32]. Using a PS concentration as the second polymer in the PVC doping solution improved the chemical and physical properties of the polymer [33].

Mixing rosin with polyvinylpyrrolidone and dibutyl phthalate (30% w/w) produces smooth films with excellent elongation and tensile strength [34]. A rosin-PEG 1500 derivative was successfully synthesized from natural rosin and his PEG using ZnO 2% as catalyst and 2 mol of rosin at 250 °C for 9 h. These derivatives were completely water soluble and can be called water soluble rosins (WSRs). The resulting rosin PEG1500 derivative was completely water soluble, and the rosin PEG1500 derivative exhibited a melting point of 40.6 °C, which was lower than that of natural rosin [35].

Preparation of polyvinylpyrrolidone (PVP)/abitic acid (AA) hydrogels was performed by gamma irradiation at 50 kGy. Hydrogel characterization shows that bioadsorbed composite hydrogel networks have advantages over conventional fabrication techniques. PVP/AA hydrogels were used in a batch process to study the effects of different parameters, such as radiation dose**,** on the sorption of the metal ions under study. PH, contact time, metal ions, V/m, and temperature [36]. PS/rosin blends have another advantage. That is, PS imparts film-forming properties to rosin. On the other hand, rosin imparts stickiness to PS. For this study, a masterbatch material that can be used as a masterstock for applying the adhesive can be used.

This work was conducted to investigate the effect of gamma irradiation on the structural properties and thermal stability of PS/rosin polymer blends. The produced plasticized PS/rosin blends were characterized by various techniques such as FT-IR, scanning electron microscopy (SEM), TGA, and mechanical properties.

2. EXPERIMENTAL

2.1. Materials

The PS was in pellets form, had an average molecular weight (Mw) of 280,000, a density of 1.047 g/cm3 and a melting point of approximately 237°C. Rosin obtained from HAB. Co, India.

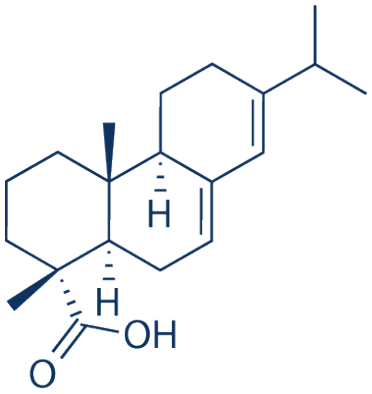

Fig. (1): The structure of Rosin

2.1.1. Solvent

A PS/rosin blend was created using pure benzene purchased from Advent in Egypt. Laboratory grade dibutyl phthalate (DBP) plasticizer was obtained from Merk-Germany

2.1.2. Plasticizer

A laboratory grade dibutyl phthalate (DBP) was obtained from Merk-Germany. It was used as a film former to make the polymer flexible and soft and to improve the flexibility and plasticity of the film.

2.2. Preparation of plasticized PS/Rosin Blends

Films of plasticized PS/rosin blends were made by the cast solution technique. Benzene solutions of PS and rosin have been prepared with different compositions. 100%, 95/5, 90/10 and 80/20, 70/30 (PS/rosin) (wt/wt %). They are then exposed to varying doses (50, 100, 150, and 200 kGy) of gamma radiation. The polymer solution was stirred with 3% DBP until completely mixed. The DBP plasticizer was added to the blend solution used as **a** film former to make the polymer flexible and pliable, thereby improving the flexibility and plasticity of the film. The solution was then poured into a Petri dish to form a clear film, dried under ambient conditions for 24 hours and placed under vacuum.

2.3. Gamma irradiation

Gamma irradiation of the samples was performed using a Gamma Chamber-4000A, Cobalt-60 source manufactured by Atomic Research Center India located at the National Radiation Research and Technology Center, Cairo, Egypt. The composites were exposed to gamma irradiation at a dose rate of approximately 1.11 kGy/h in air at room temperature.

2.4. Characterization

2.4.1. Tensile Strength and Elongation at Break

Mechanical tests (tensile strength and elongation at break) were performed on the triplets at room temperature using a Mecmesin, model 10-I, UK, with a crosshead speed of 500 mm/min.

2.4.2. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was performed using his Shimadzu-50 model TGA instrument equipped with a platinum cell. Thermal experiments were performed on all samples at a heating rate of 10 °C/min using nitrogen as carrier gas at a flow rate of 30 mL/min.

2.4.3. IR spectroscopic analysis

A Vertex 70 Fourier Transform Infrared (FTIR) spectrophotometer from Bruner Optics Germany was used for his FTIR measurements.

2.4.4. Scanning electron microscope (SEM)

Scanning electron microscopy (SEM) was used to examine the surface morphology of various samples. SEM images were taken with an EVO15 instrument from Zeiss-Germany.

3. RESULTS AND DISCUSSION

3.1. Mechanical properties

Gamma radiation affects the properties of polymeric materials. Adequate cross-linking of polymeric materials is beneficial to improve their properties, but excessive cross-linking makes them brittle and less valuable for industrial applications. Figures 2 and 3 show the mechanical properties of various concentrations of unirradiated and irradiated PS/rosin blends at various irradiation doses of 100 kGy and 200 kGy. The mechanical properties of rosin are very poor as it is very brittle at room temperature and these properties need to be improved to make it a useful natural material. Although the term fragility is used, there is no generally accepted quantitative definition [37].

It can be observed that the tensile strength increases with increasing PS content in the blend and increasing irradiation dose. This was due to the cross-linking behavior of PS with respect to the irradiation process, as shown in figure 2. On the other hand, incorporating rosin into PS significantly reduced the mechanical properties of the blend. Also, the tensile strength of the blends decreases with increasing rosin concentration. This may indicate the effect of progressive chain crosslinking on radiation-induced PS content on the Ts value of the whole mixture [38]. Figure 3 shows the change in elongation at break (Eb) upon irradiation with different rosin ratios. In general, increasing radiation dose decreases the elongation at break of PS and its blends. Increasing radiation dose produces stronger crosslinks within the sample matrix, preventing structural reorganization during stretching [39]. This ever-increasing three-dimensional gel-like structure leads to reduced internal chain mobility and elongation. Radiation cross-linking occurring at the PS content is thus confirmed by the Eb dependence on the blend composition.

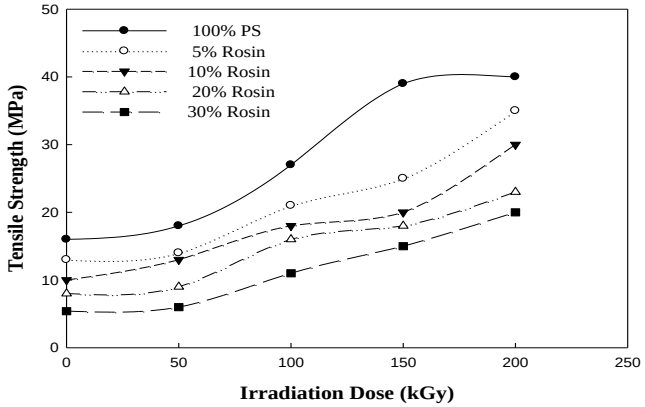

Fig. (2): Effect of irradiation dose on the Ts of PS and its blends (PS/ rosin) at various compositions

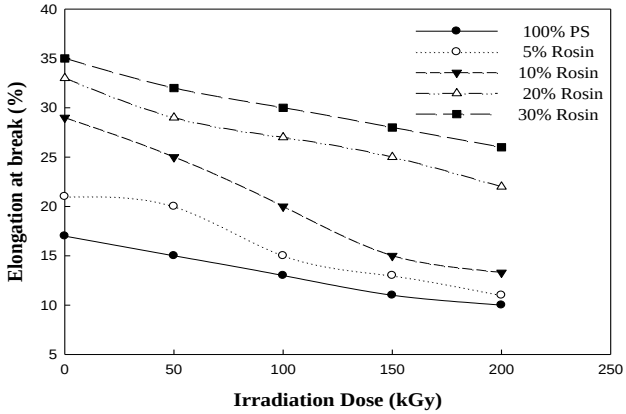

Fig. (3): Effect of irradiation dose on the Eb% of PS and its blends (PS/ rosin) at various compositions

3.2. Thermal Decomposition Behavior

Figures (4-6) show unirradiated pure PS and rosin and their PS/rosin at different ratios of 5% and 20% rosin before and after exposure to gamma irradiation at doses of 100 and 200kGy. TGA thermograms were performed over a temperature range from room temperature to 600 °C with a heating rate of 10 °C/min. For rosin, as seen in Figure 4 two consecutive weight loss stages were observed for rosin. The initial weight loss that occurred at temperatures below 200°C corresponded to the evaporation of physically absorbed water. A second weight loss occurred at temperatures up to 600°C. According to the TGA thermogram of pure, unirradiated rosin, decomposition temperatures above 200 °C correspond to decomposition of the rosin backbone. A total weight loss of rosin chains was observed at about 500°C and reached 96.05%. Here a final decomposition step takes place where the organic residue decomposes into ash.

On the other hand, it is found that the unirradiated pure PS polymer loses about 8.79% and 62.12% weight at 300°C, respectively. It was found that the weight loss of PS was smaller than that of rosin by increasing the heating temperature from 300°C to 350°C. From this**,** it can be concluded that unirradiated PS polymer is more stable against thermal aging than unirradiated rosin. On the other hand, the thermal stability of the unirradiated PS/rosin blend is lower than that of PS and higher than that of rosin for each composition.

For the polymer blends irradiated at 100 kGy and 200 kGy, it can be observed that the thermal stability increases with increasing PS content, as shown in Figures 5 and 6. Therefore, it can be concluded that PS provides some form of protection against radiolytic degradation of rosin polymer in blends.

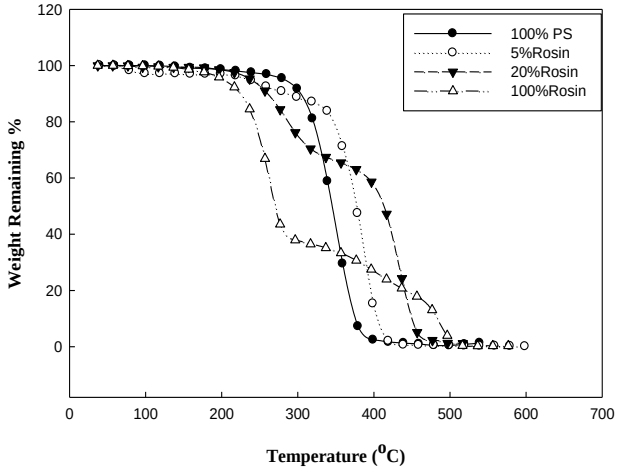

Fig. (4): TGA thermogram of unirradiated PS and its blends (PS/ rosin) at various compositions

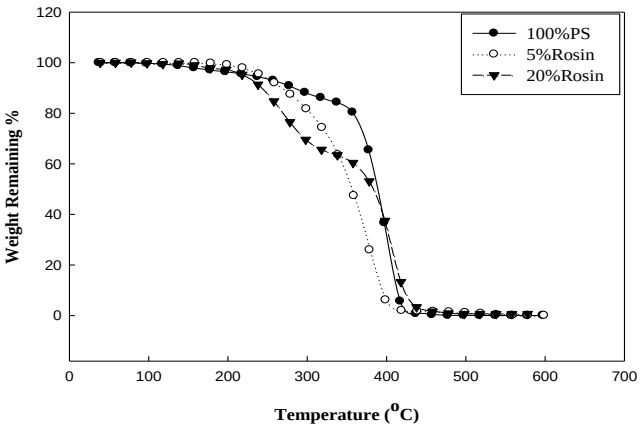

Fig. (5): TGA thermogram of PS and its blends (PS/ rosin) at various compositions irradiated at 100 kGy

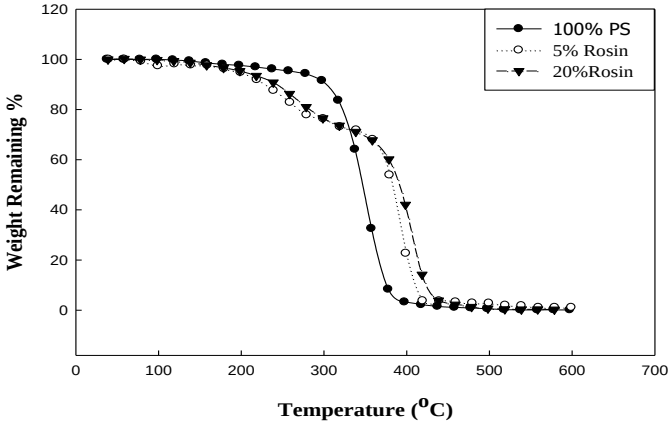

Fig. (6): TGA thermogram of PS and its blends (PS/ rosin) at various compositions irradiated at 200 kGy

The reaction rate (dw/dt) was determined as a function of heating temperature for neat PS and its blends with 5% and 20% rosin before and after gamma irradiation at doses of 100 and 200 kGy, as shown in Figures (7-9). It can be seen that these types of curves show similar trends for unirradiated and irradiated mixtures, exhibiting multiple maxima with increasing temperature. This behavior indicates that the thermal decomposition of these mixtures undergoes two steps. The maximum rate of reaction (T_{max}) temperature is mixture dependent. The (T_{max}) values of unirradiated and irradiated PS have higher thermal stability than PS/rosin blend as shown in table 1.

This indicates that the thermal stability of PS/rosin increases with increasing proportion of PS in unirradiated and irradiated blends. Also, the thermal stability of the irradiated PS/rosin polymer blend at 100 kGy is more thermally stable than that at 200 kGy due to PS cross-linking. This may indicate the effect of stepwise chain

cross-linking of PS content by radiation. Thermal analysis data therefore, indicate strong interactions between the mixture components.

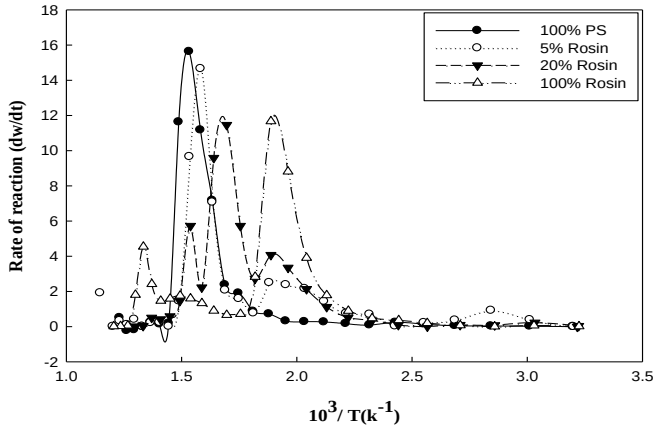

Fig. (7): Rate of reaction (dw/dt) of unirradiated PS and its blends (PS/ rosin) at various compositions

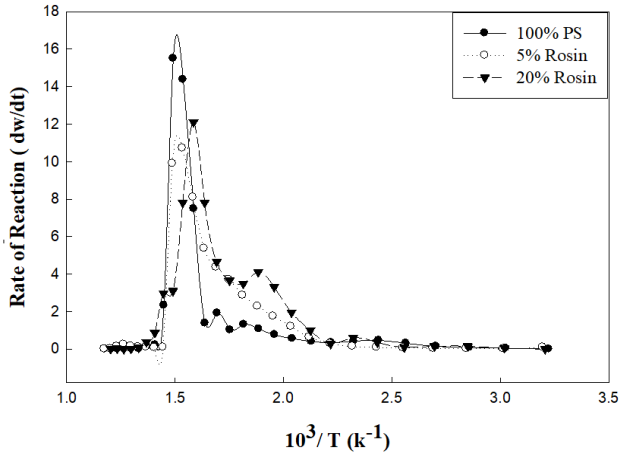

Fig. (8): Rate of reaction (dw/dt) of PS and its blends (PS/ rosin) at various compositions irradiated at 100 kGy

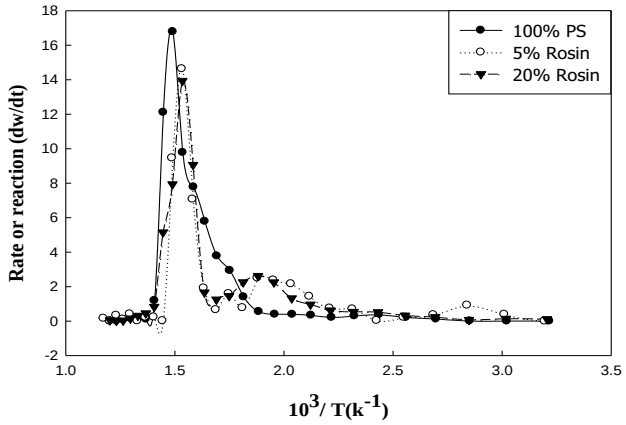

Fig. (9): Rate of reaction (dw/dt) of PS and its blends (PS/ rosin) at various compositions irradiated at 200 kGy

Table (1): Temperature of maximum values of the Rate of reaction of unirradiated and irradiated of Polymer Blends having different ratios of PS and Rosin

Polymer Blend Composition	Temperature of Maximum Rate of Reaction (C)		
	unirradiated	100 kGy	200 kGy
100% PS	379	397	397
95%PS/5%R	358	378	379
80%PS/20%R	336	357	398

3.3. FTIR spectroscopy

FTIR spectra provide information about structural aspects of polymers such as chemical composition, conformation, and structural arrangement. The positions and relative intensities of absorption bands can provide information about interactions between mixture components. Figures (10-12) show the IR spectra of unexposed films with 100% PS, 100% rosin, and PS/ (5 and 20%) rosin mix ratios and the same polymer after exposure to 100 and 200 kGy. The IR spectrum of unirradiated rosin shows that absorption bands at 2872 and 2952 cm $^{-1}$ are assigned to methyl and methyl asymmetric and symmetric stretches**.** The band at 3344 cm^{-1} is due to the OH group of the rosin carboxyl groups.

The rosin absorption bands at 1695 cm $^{-1}$ and 1701 cm $^{-1}$ are associated with C=O groups, and the bands in the region from 1460 to 945 cm $^{-1}$ are due to aromatic rings. For pure PS polymer, the IR spectrum shows an absorption band around 3000 cm $^{-1}$ due to C–H stretching of organic compounds. The presence of a benzene ring in PS can be confirmed from two regions. A broad absorption band due to -CH stretching is around 3023 cm^{-1}, and a conjugation-characteristic absorption band gives rise to a series of four peaks around 1670 cm^{-1}. The IR spectra of PS/rosin polymer blends containing different ratios of PS and rosin show characteristic absorption bands for both PS and rosin. A careful examination of the IR spectra of the PS/ (5&20%) rosin mixtures reveals that the characteristic bands of PS and rosin are combined and superimposed, the wavenumbers are shifted, the strong interaction between PS and rosin increases and the intensity of some bands decreased.

The IR spectra of the same polymer blends after exposure to 100 and 200 kGy and the intensities of different specific absorption bands are shown in Figures (11 and 12). It can be observed that the intensity of the absorption band of pure PS polymer decreases slightly with increasing irradiation dose. This indicates the stability of this polymer against degradation by gamma rays. For PS/5% rosin polymer blends, specific characteristic bands of PS in the blends exposed to 100 kGy were not significantly affected. Furthermore, we find that the intensity of the characteristic absorption band of the rosin component decreases with increasing irradiation dose up to 200 kGy and decreasing PS ratio of the polymer mixture. From this, we can conclude that the presence of PS in the polymer blend protects the rosin polymer from radiation degradation.

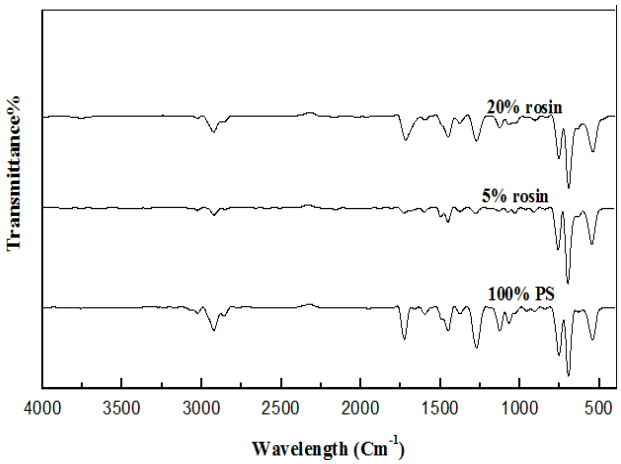

Fig. (10): IR spectra of unirradiated PS and its blends (PS/ rosin) at various compositions

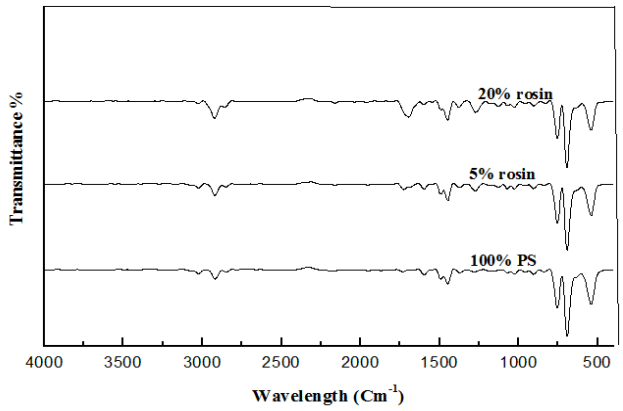

Fig. (11): IR spectra of PS and its blends (PS/ rosin) at various compositions irradiated to 100kGy

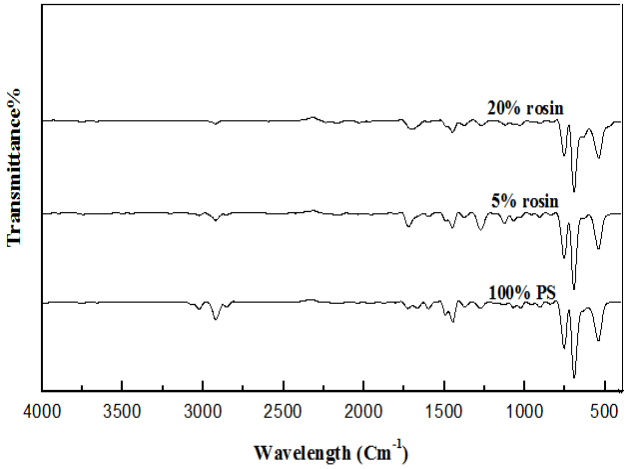

Fig. (12): IR spectra of PS and its blends (PS/ rosin) at various compositions irradiated to 200kGy

3.4. Morphological studies

Figure 13 (a–c) show SEM images of unirradiated 100% PS blended with 5% and 20% rosin. The SEM pattern of PS is shown in Figure 12a**.** The surface of PS is dense, plate-like and smooth, showing no sign of porous structure in the sample, showing regular layered structure perpendicular to the direction of tension. In Figure 13b**,** the SEM of PS/5% rosin was observed to have a rough, stone-like surface with sharp edges. An unirradiated polymer blend containing PS/20% rosin exhibits rough surfaces**,** holes, and some elongated features**.** PS dispersion indicates that a small interfacial tension exists between rosin particles. This mixture reveals a network of pinholes and channels**,** as shown in Figure 12c. Improved compatibility of PS/rosin mixtures at 100 kGy was observed in Figure 13 (e and f). A photograph of the PS/rosin mixture at 100 kGy shows a more homogeneous structure compared to the unirradiated mixture. The percentage of PS in the blend creates an interpenetrating polymer network, making the sample more flexible. Irradiation alters the polymer network. Therefore, the morphological state of the polymer changes. Radiation dose at 200 kGy gamma irradiation leads to an increase in the degree of cross-linking and an increase in the molecular weight of the amorphous regions**,** as shown in figures 13 (h and i) [40].

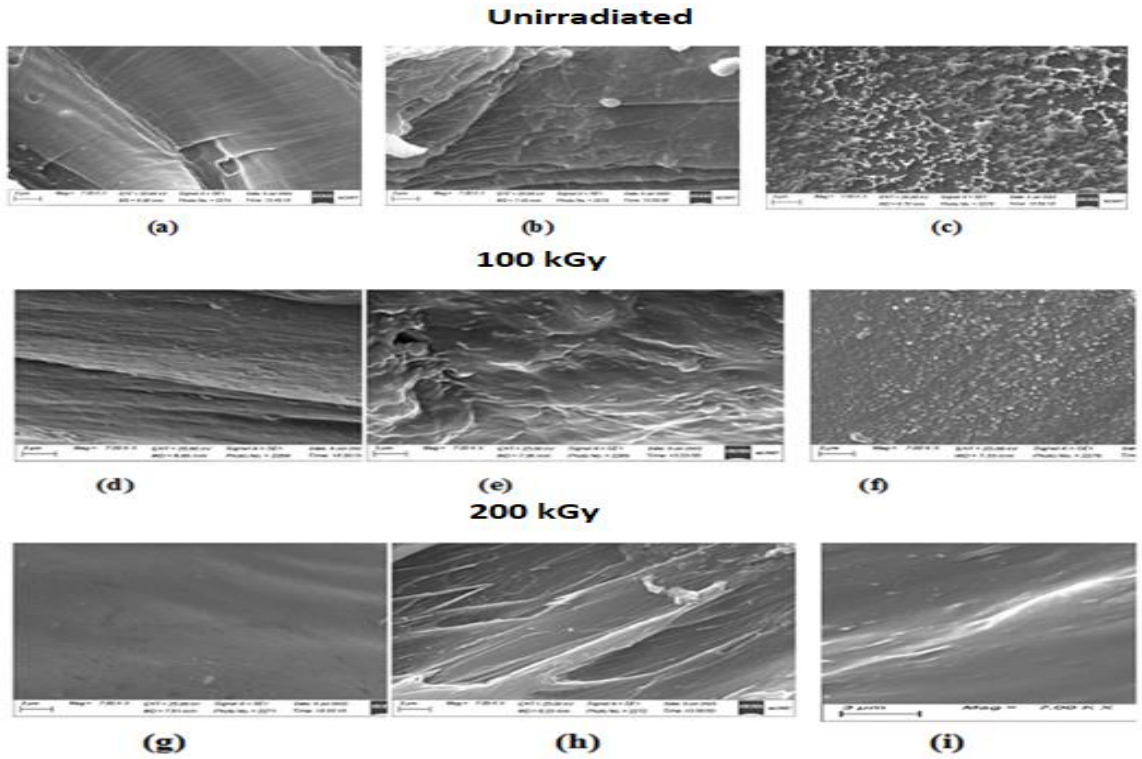

Fig. (13): SEM of unirradiated100% PS (a), PS/5% rosin (b) PS/ 20% rosin (c), PS irradiated at 100 kGy (d), PS/ 5% rosin irradiated at 100 kGy (e), PS/ 20% irradiated at 100 kGy (f), PS irradiated at 200 kGy (g), PS/ 5% rosin PS irradiated at 200 kGy (h) and PS/ 20% rosin PS irradiated at 200 kGy (i).

4. CONCLUSIONS

Plasticized blend (PS/rosin) films with DBP were prepared with different compositions and irradiated with different doses of gamma radiation. TGA thermograms show that unirradiated PS polymer is more stable to thermal decomposition than unirradiated rosin. On the other hand, the thermal stability of the unirradiated PS/rosin blend is lower than that of PS and higher than that of rosin for each composition. It can be observed that the thermal stability increases with increasing PS content in polymer mixtures irradiated at 100 kGy and 200 kGy. Therefore, it can be concluded that PS provides some protection against radiolysis of rosin polymers in blends. It can be concluded that the presence of PS in the polymer blend protects the rosin polymer from radiolysis at low doses. IR also shows that the presence of PS in the polymer blend protects the rosin polymer from low dose radiolysis**.** Increasing the rosin content in the blend has been found to decrease the TS and increase the elongation percentage. On the other hand, the presence of PS, which protects rosin from radiolysis, reduces the TS of all prepared (PS/rosin) blend compositions upon exposure to radiation up to 200 kGy. Therefore, SEM shows significant interactions between the mixture components. Blends with high PS concentration improve the interfacial adhesion between PS and rosin.

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