International Journal of Scientific & Engineering Research, Volume 11, Issue 12, Desamber-2020
ISSN 2229-5518

Measurements of Some Physical Properties of PMMA/PS Blend and Studying the Dielectric properties of Gamma- Irradiated Composites

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Abstract— Polymer blends of polymethylmethacrylate/polystyrene (PMMA/PS) were prepared with different concentrations. The electrical properties such as the DC & AC conductivity, dielectric constant, and dielectric loss were investigated. The 2/8 (PMMA/PS) blend was then selected for studying the effect of gamma-ray irradiation on its physical properties. The 2/8 (PMMA/PS) composite was exposed to 10 kGy, 25 kGy, and 50 kGy by ^{60}Co source of gamma facility. Gamma radiation significantly improved the dielectric properties of the 2/8 (PMMA/PS) composite. The highest values of dielectric constant and AC conductivity were found at 50 kGy. The mechanical properties of the 2/8 (PMMA/PS) blend at only low doses were also improved, and the optimum dose was found to be at 25 kGy. The variation of mechanical behavior of 2/8 (PMMA/PS) composite after exposure to gamma-ray radiation was also discussed.

Index Terms— Dielectric properties, electrical conductivity, gamma radiation, mechanical properties, Polymer composite, PMMA/ PS.

1 Introduction

In recent years, polymer science's robust progress and widespread use of polymeric materials in all technology fields that led to increased interest in the different problems of polymer physics and chemistry [1]. It is understood that the clarification of the relationship between the chemical and physical structure and the physical properties of the polymers is one of the critical objectives of polymer physics.

Poly(methyl methacrylate) (PMMA) is one of the transparent polymers that are most available because it has many advantages, such as substantial light transmission, precious weather resistance, low birefringence, and low refractive index. Owing to its possible use in many applications, it has attracted growing interest. Besides, as a homopolymer, PMMA has excellent transparency with high rigidity and toughness. Although PMMA has all these outstanding properties, it still has poor characteristics such as low impact strength, poor thermal stability, and resistance to solvents that in some areas prevent its application.

Hence, polymer blend has a significant interest as it provides a powerful route to establish new materials superior to each component. The polymer blend systems' main advantages are the simplicity of preparation and the ease of control of physical properties by compositional changes. However, the miscibility between a polymer mixture's constituents on the molecular scale is responsible for material with superior properties [2]. Therefore, the polymer blend has been of great interest as it offers a powerful way to develop new properties in materials that are superior to that of each polymer component.

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polystyrene (PS) and PMMA are commonly used as binary model systems to study the development of thin-film polymer structure, polymer-polymer, and polymer-substrate interactions.

Polymethylmethacrylate (PMMA) and polystyrene (PS), due to their unusual combination of superior mechanical, electrical, optical, chemical, and thermal properties [2–4], are widely used in situations requiring high-performance plastic materials. Due to their excellent durability, and ability to cope with different environmental conditions, these polymeric materials have a wide range of applications, especially in industries and consumer end-products.

The effect of radiation on polymeric materials, on the other hand, is of great importance because it enables the physical properties of polymers to be modified and improved for the development of new polymeric materials that can be engineered with unique physical properties [5].

Irradiation of polymeric materials with gamma rays, X-rays, accelerated electrons, and ion beams contributes to the formation of reactive intermediates and free radicals, resulting in major reactions such as degradation or cross-linkage. These interactions were regulated by the calculated amount of radiation dose [6].

Different polymers are influenced by different radiation doses that are intrinsically related to the polymers' chemical structures. The properties of polymers, such as optical, electrical, mechanical and chemical properties, are then modified. It is also well known that irradiation of solid materials causes structural defects known as colour centers. The presence of such colour centers in a thick film matrix results in improvements in the material's optical as well as electrical properties.

The purpose of the present work is to investigate the modifications induced by gamma irradiation on the structural,

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ISSN2229-5518

dielectric and mechanical properties of PMMA/ PS and analyze these effects as a function of gamma dose.

2 Experimental

2.1 Materials

Polystyrene has been supplied from El-Nasr Company for chemicals and drugs. Egypt. (MMA) was purchased as a solution from Aldrich and has been polymerized by gamma-irradiation with a dose rate of 6.5 kGy/hr, and approximately 150 kGy in ^{60} Co source of gamma facility. The solvent used in the blend preparation was Chloroform HPLC with 99.8% purity purchased from Aldrich to be used in this study.

2.2 Preparation of the Samples

PMMA/ PS blends were prepared by the casting solution procedure. Solutions of PMMA/PS were first prepared by dissolving mixtures of (10/0, 8/2, 6/4, 4/6, 2/8, and 0/10) (w/w%) in Chloroform HPLC with 99.8% purity with continuous stirring and heating at a temperature of 60°C for approximately three days. The polymer solution was then cast onto glass dishes to form samples with thickness = 0.85 mm. The cast films were dried under ambient conditions for 24 h and then placed in an oven at 70 °C for 24 h to remove residual solvent.

2.3 Irradiation Procedure

The prepared blend 2/8 (PMMA/PS) was exposed to 10 kGy, 25 kGy, and 50 kGy by ^{60}Co source of gamma facility. (γ cell type 4000A, ^{60}Co source) performed at National Center for Radiation Research and Technology, Atomic Energy Authority, Cairo, Egypt. This unit was manufactured by the Indian Atomic Research Center. The dose rate was about 6.5 kGy/h. The sample was irradiated with these different doses at room temperature and ambient humidity.

2.4 Electrical and Mechanical Measurements of the PMMA/PS blends

The PMMA/PS blends' electrical conductivity was determined according to ASTM D257, and measurements were performed using a Keithley 2636b. Dielectric properties were measured with a Hioki 3532-50 LCR Hitester in the frequency range from 500 Hz to 5 MHz. For static tension properties, the PMMA/PS blends were tested using Triton Instruments, operating in the static tension mode with preload force 0.01 N, load rate of 0.2/min, and maximum force 2 N. Dynamic mechanic analysis (DMA) was performed on a Triton Instruments, operating in the tension mode at an oscillation frequency of 1 Hz.

Data were collected from room temperature to 155 °C at a scanning rate of 10 °C/min. The cross-link density was calculated from the storage modulus curve in the rubbery region using the following equation [7].

$$\upsilon = E'/(3\,R\,T) \qquad (1)$$

Where υ is the cross-link density, E' is the storage modulus in the rubbery region, R is the gas constant, and T is the temperature.

3 Results and Discussion

3.1 Electrical properties of PMMA/PS blends

Figure 1 shows the DC electrical conductivities (σ) for PMMA/PS blends. The pure PS (sample 0-10) and the pure PMMA (sample 10-0) exhibit approximately the same low DC electrical conductivities of 1.6 × 10^{-6} S/m and 1.8 × 10^{-6} S/m, respectively. The highest DC electrical conductivities are shown in blends 4-6 and 2-8 of 3.5 × 10^{-6} S/m and 3.1 × 10^{-6} S/m, respectively.

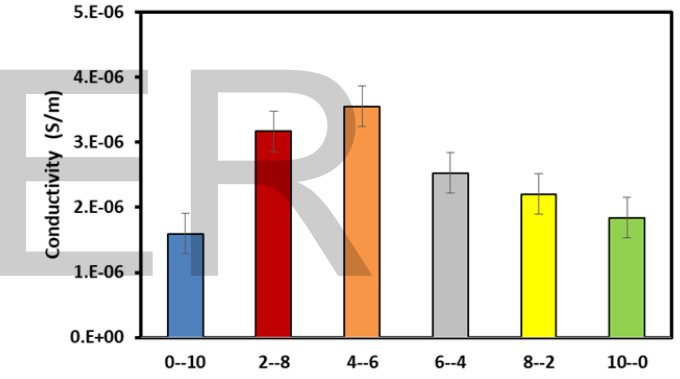

Fig. 1. The electrical conductivities of PMMA/PS blends.

The complex dielectric constant as a function of frequency (f) is represented by the equation; ε*(f) = ε'(f)-iε"(f). The real part ε' is the relative dielectric constant and the imaginary part ε" is the dielectric loss. The relationship between the imaginary and the real part (ε"/ ε') is called the "dissipation factor" and denoted by tan δ, which referring to the angle between the voltage and the charging current.

The change in the dielectric permittivity, ε', and the dielectric loss, ε", versus frequency of all PMMA/PS blends is shown in Figure 2 (a, b) at room temperature. Dielectric permittivity and dielectric loss reach high values in the low-frequency region, decreasing with increasing the frequency. This behavior demonstrates a relaxation process attributable to an interfacial polarization, known as the Maxwell-Wagner-Sillars effect, which is a phenomenon of accumulation of charges on interfaces in heterogeneous media [8].

Also, Figure 2 (a, b) shows that the (2-8) PMMA/PS blend exhibited the highest dielectric constant and the dielectric loss that approximately 1150 and 7871 at frequency 500 Hz, respec-

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tively. While (10-0) PMMA/PS blend exhibited the lowest dielectric constant and the dielectric loss, that approximately 33 and 5 at frequency 500 Hz, respectively.

Figure 3 demonstrate the AC conductivity as a function of the frequency of the PMMA/PS blends. The values of conductivity indicate a broad frequency dispersion. Conductivity decreases with frequency in the low-frequency range for the blending material of significant content of PS (0-10, 2-8 and 4-6), while conductivity increases steadily with frequency in the high-frequency range. Conductivity increases with frequency in blends with large content of PMMA (10-0, 8-2 and 6-4), and shows an exponential dependence on frequency. Due to migration of charge carriers, AC conductivity sums up all dissipative processes, including dipolar effects and real Ohmic conductivity[9]. At low frequencies, the alternation of the field is sluggish, causing charges inside the composite to drift over large distances. High margins on this motion are applied to the insulating nature of the host material, resulting in low conductivity values. The field's alternation becomes rapid as frequency increases, and charges do not move over long distances. Charges may, however "hop" between adjacent conductive sites, thus contributing to the total conductivity

3.2 The effects of gamma-ray irradiation on PMMA/PS blend

3.2.1 Dielectric properties

The change in the dielectric permittivity, ε', and the dielectric loss, ε", versus frequency of PMMA/PS blend of 2-8 composition is shown in Figure 4 (a, b) at room temperature before and after gamma-ray irradiation doses of 10 kGy, 25 kGy and 50 kGy. The reason for choosing the PMMA/PS blend of 2-8 composition is that having the highest dielectric permittivity and AC conductivity.

Figure 4 (a, b) shows that the dielectric constant and the dielectric loss are significantly affected by gamma-ray doses. As gamma-ray doses increase, the dielectric constant increases and remains constant over all frequencies' range. The maximum ε' was found to be approximately 3106 at a 50 kGy dose of gamma irradiation; this may be due to dipoles' orientation owing to high gamma irradiation doses causing orientation polarizations yielding higher dielectric values.

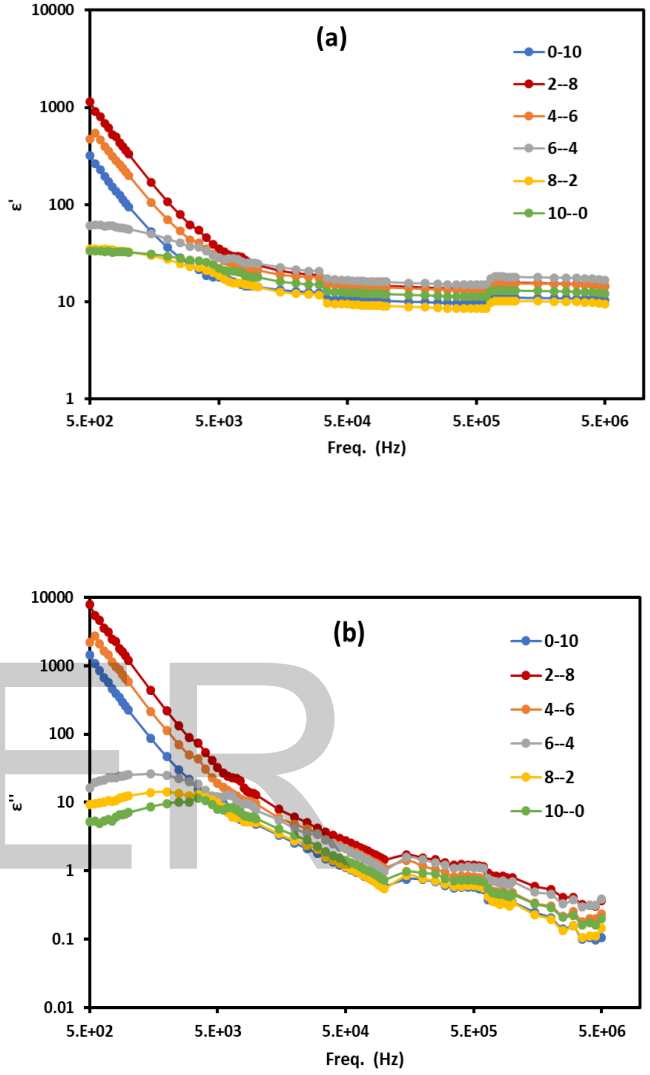

Fig. 2. The frequency dependence of (a) dielectric permittivity, ε', and (b) the dielectric loss, ε" of PMMA/PS blends.

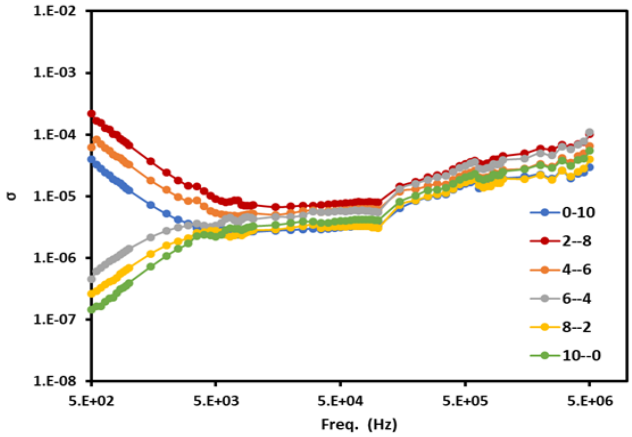

Fig. 3. The frequency versus AC conductivity of PMMA/PS blends

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ISSN2229-5518

It can also be observed that the dielectric loss remains almost constant over all frequencies' range after irradiation, and has lower values at high frequencies before exposure to gamma doses.

AC conductivity as a function of frequency for the PMMA/PS blend of 2-8 composition before and after gamma-ray irradiation doses of 10 kGy, 25 kGy and 50 kGy is shown in Figure 5. It can be observed that, after irradiation the conductivity increases exponentially with frequency, and the highest conductivity is recorded after irradiation with 50 kGy specially at high frequencies.

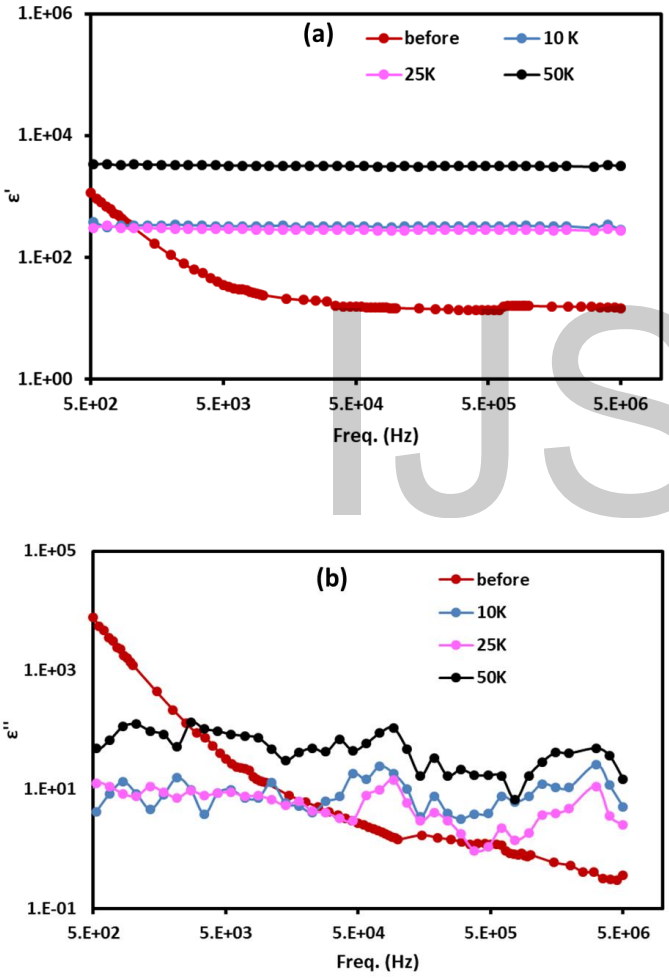

Fig. 4. The frequency dependence of (a) dielectric permittivity, ε', and (b) the dielectric loss, ε" of 2-8 blend before and after gamma-ray irradiation doses of 10 kGy, 25 kGy and 50 kGy.

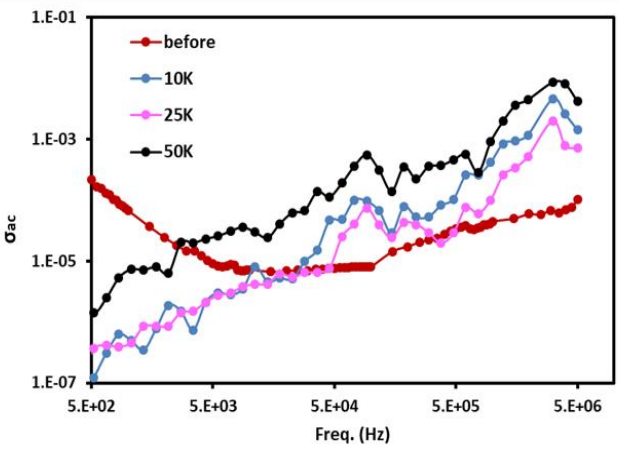

Fig. 5. The frequency dependence of AC conductivity of 2-8 blend before and after gamma-ray irradiation doses of 10 kGy, 25 kGy and 50 kGy.

3.2.2 MECHANICAL PROPERTIES

Mechanical properties of the PMMA/PS blend of 2-8 composition before and after gamma-ray irradiation doses of 10 kGy, 25 kGy and 50 kGy are shown in Figure 6 (a, b). The stress-strain relationship observed at room temperature and the change in elastic modulus (E) versus gamma-ray irradiation doses are shown in Figures 6(a) and 6(b), respectively. The results show a strong influence of the gamma-ray doses on the mechanical properties of 2-8 blend, a gradual increase of material stiffness by increasing the dose up to 25 kGy, and a sharp decrease in the material stiffness for blend irradiated with 50 kGy. Moreover, the elastic modulus increases from 272 KPabefore irradiation to 373 KPa and 449 KPa with increasing the gamma-ray doses from 10kGy to 25 kGy and drops to 164 KPa at 50 kGy, indicating that the elastic modulus increases by 20% and 65% at 10kGy to 25 kGy compared with the non-irradiated blend, respectively and decreases by 40% at 50 kGy compared with the non-irradiated blend. After certain gamma radiation doses, this opposite tendency is attributed to two opposing phenomena: the photo cross-linking and photo-degradation that instantaneously takes place under gamma radiation. At lower doses, a combination reaction stabilizes free radicals and result in photo cross-linking between the molecules, increasing the elastic modulus. Inversely, the backbone of the chain may lead to break at a higher dose. Polymers are then degraded into small fragments, causing a decrease in the elastic modulus [10].

The influence of temperature on the storage modulus and loss modulus at frequency 1 Hz for the PMMA/PS blend of 2-8 composition before and after gamma-ray irradiation doses of 10 kGy, 25 kGy and 50 kGy are shown in Figure 7(a,b) and the data are registered in Table 1. As the temperature increased, the storage modulus decreased and displayed three distinct areas; the first glassy region which has high modulus values due to limitation of segmental mobility, the second transition region with a decrease in modulus values representing glass transition temperature T_g and the third rubbery re-

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ISSN2229-5518

gion, with low modulus values because of energy dissipation due to high mobility of polymer chains [11].

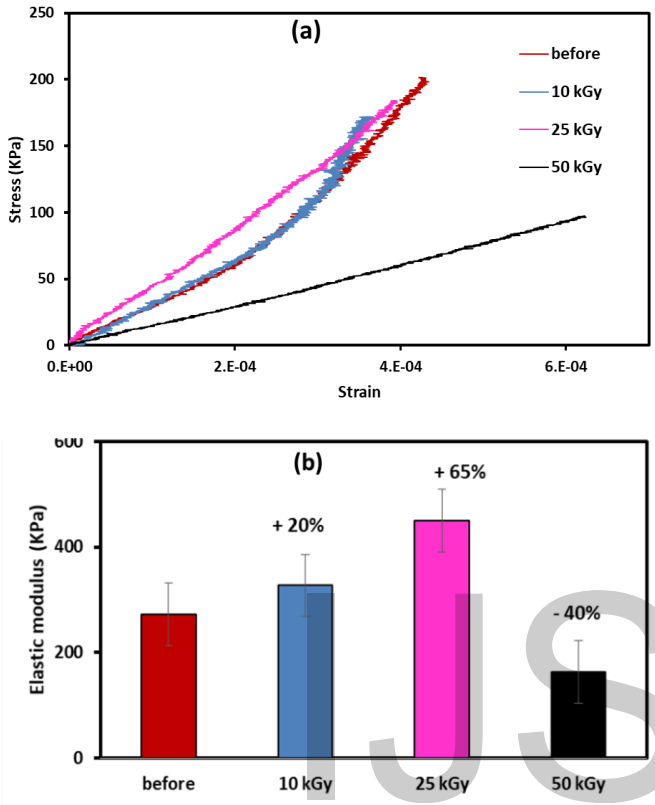

Fig. 6. (a) The stress-strain relationship and (b) the change in elastic modulus versus the gamma-ray irradiation doses for 2-8 blend.

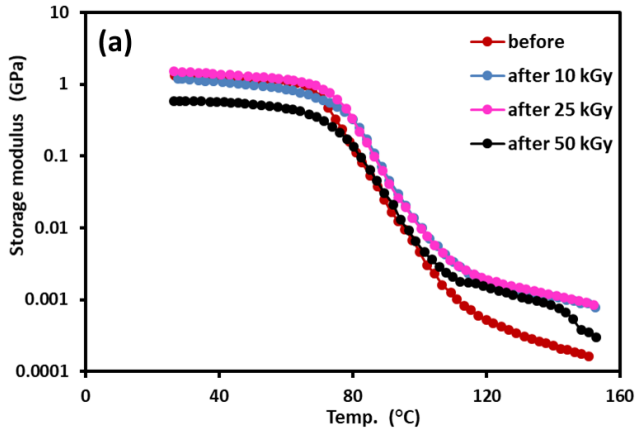

Fig. 7. (a) Storage modulus versus temperature for 2-8 blend before and after gamma-ray irradiation doses of 10 kGy, 25 kGy and 50 kGy.

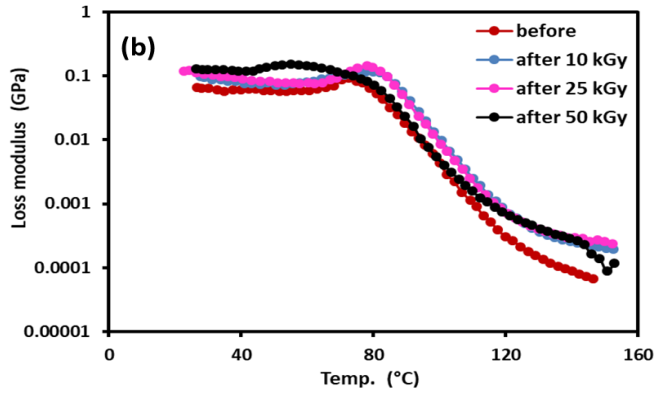

Fig. 7. (b) Loss modulus versus temperature for 2-8 blend before and after gamma ray irradiation doses of 10 kGy, 25 kGy and 50 kGy.

Table 1: DMA data for 2-8 blend before and after ɣ-ray irradiation doses of 10 kGy, 25 kGy and 50 kGy.

	Storage modulus (GPa) at 26 °C	Loss modulus (GPa) at 26 °C	Glass transition temp. (°C)	Crosslinking density ×10^{-5} (mol/cm3)
Before	1.34	0.065	72.6	1.51
10 kGy	1.2	0.097	77.6	8.51
25 kGy	1.53	0.111	78.1	9.27
50 kGy	0.54	0.129	55.1	3.35

It was also found that the storage modulus was increased with increasing of gamma-ray irradiation dose (at 10 kGy and 25 kGy) and then decreased at 50 kGy. According to the elasticity theory [7], the change in storage modulus indicated the change of the polymer's cross-link density. The higher value of storage modulus indicated the higher cross-link density of materials. Therefore, the cross-linking reaction should be predominating during the gamma-ray irradiation with 10 kGy and 25 kGy. As listed in Table 1, cross-linking density increase by 563% at 10 kGy and 613% at 25 kGy compared with the non-irradiated blend, respectively, and decreases again at 50 kGy to 221% compared with the non-irradiated blend.
Glass transition temperature also increased after gamma-ray irradiation doses of 10 kGy, 25 kGy, which was due to the cross-linking formation. Even after the 50 kGy the decrease in the cross-link values was observed, confirming the bond cleavage.

To further understand the effect of cross-linking density on the mechanical properties of 2-8 blend before and after gamma-ray irradiation doses, FTIR analysis was performed. FTIR is utilized to observe chemical group changes before and after gamma-ray radiation.

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ISSN2229-5518

In Figure 8, the most intense bands are the $-CH_3$ and $-CH_2-$ stretching (3000-2830 cm^{-1}), the carbonyl $-C=O$ stretching (1726 cm^{-1}), and the $C-O-C$ symmetric stretching (1142 cm^{-1}). The characteristic peaks of the functional groups have been recognized; the bending vibrations of the CH2, CH3, and OCH3 groups are bands between 1400 and 1500 cm^{-1}. The bands between 1250 and 980 cm^{-1} are linked to the stretching vibrations of the $C-O-C$ group. The high-intensity band at 1142 cm^{-1} is the $C-O-C$ group's symmetric stretching vibration. By irradiation, the peak heights decreases which could confirm that there is a chain split[12, 13]. The absorbance intensity corresponding to the carbonyl and the $C-O-C$ groups decreases, reaching a minimum value at 50 kGy. The methyl groups (2945, 2920 cm^{-1}) shift to low wave-numbers, which indicates cross-linking processes at the applied gamma-ray. The extreme decrease in the band at 1726 cm^{-1} indicates breaking the acrylate carboxyl group due to chain scission leading to a decrease in cross-linking bonds [13].

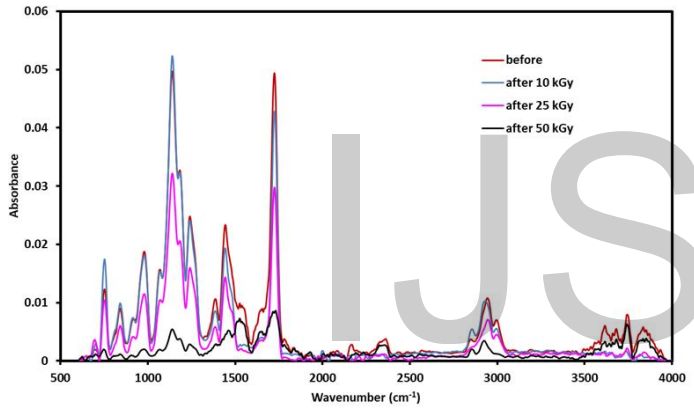

Fig. 8. Fourier Transform Infrared (FTIR) spectra of 2 -8 blend before and after gamma-ray irradiation doses of 10 kGy, 25 kGy and 50 kGy.

4 Conclusion

The dielectric and mechanical properties, and AC conductivity have been successfully employed to study the modifications induced in the structural properties of PS/PMMA blends due to gamma irradiation. Such techniques pointed out that the gamma radiation dose up to 25 kGy increases the interaction of PS and PMMA molecules and more compact structure are formed through cross-linking, which resulted in an increase in the average molecular mass. The presence of PS polymer in the blends affords protection against radiation degradation and the blend (2-8) considered to be high radiation resistant material that improved the mechanical properties especially at low dose of 25kGy.On the other hand, the gamma radiation disintegrate molecules and increases the number of dipoles, so that the higher radiation dose produces a larger permittivity[14]. This blend can be used as an electronic component in the printed circuits where devices may be exposed to gamma or x-ray radiation.

References

[1] G. M. Nasr , R. M. Ahmed et al., Electrical Properties of Gamma-Irradiated ST/MMA Copolymers, International Journal of Polymeric Materials, vol.,56, pp. 371–386, 2007.

[2] M. M. Magida, A. Abou Elfadl, S. A. Nouh. "Modifications induced in natural rubber due to vinylacetate versatic ester copolymer blend concentration and gamma radiation" , Polymer Bulletin, 2019.

[3] S. K. J. Al-Ani, Y. Al-Ramadin,, M. S Ahmad, et al.., J. Polymer Testing ,vol.18, 611 1999.

[4] B. R Basett,. and A. F.Yee, , J. Polym. Compos. 11 ,1990.

[5] Ali A. Alhazime, Nesreen T. El-Shamy, Kaoutar Benthami, Mai Barakat and Samir A. Nouh, "Effect of gamma radiation on the structural, thermal and optical properties of PMMA/$Sn_{0.75}Fe_{0.25}S_2$ nanocomposite", J. Poly. Eng., DOI: https://doi.org/10.1515/polyeng-2020-0197 .

[6] Mahasin F. Hadi Al-Kadhemy "Effect of gamma ray on optical characteristics of (PMMA/PS) polymer blends", J Theor Appl Phys vol.11, pp.201–207, 2017.

[7] L.E. Nielsen, Cross-linking: Effect on physical properties of polymers. J. Macromol. Sci. C Polym. Rev., vol. 3, pp.69–103, 1969.

[8] Mittal V, "Characterization Techniques for Polymer Nanocomposites" (Wiley Online Library) ,2012.

[9] A. C. Patsidis , K. Kalaitzidou &; G. C. Psarras , Graphite nanoplatelets/polymer nanocomposites: Thermomechanical, dielectric, and functional behavior,Journal of Thermal Analysis and Calorimetry, vol. 116, pages41–49 ,2014.

[10] K.Z.M. Abdul Motaleb, Rimvydas Milašius and Abdul Ahad, Influence of Gamma Radiation on Mechanical Properties of Jute Fabric-Reinforced Polymer Composite, Fibers vol.8, pp.58,2020.

[11] Kevin P. Menard , Dynamic Mechanical Analysis-A Practical Introduction. CRC press, Taylor & Francis Group, second edition, 2008.

[12] R. Huszanka, E. Szilágyi, Z. Szoboszlai, Z. Szikszai." Investigation of chemical changes in PMMA induced by 1.6 MeV He+ irradiation by ion beam analytical methods (RBS-ERDA) and infrared spectroscopy (ATR-FTIR)", Nuclear Inst and Methods in Physics Research B., 2018. doi.org/10.1016/j.nimb.2018.05.016

[13] S. A. Nouh, K. Benthami , A. Abou Elfad, Huda A. El-Nabarawy. Modification Induced by Gamma Irradiation in Polystyrene/Poly(methyl methacrylate) Blends. Intern. Polymer Processing XXXII ,2017.

[14] K.Shinyama and S.Fujita,IEEE Transactions on Dielectrics and Electrical Insulation,8,pp.538, 2001..