

## Effect of plasma irradiation on the electrical characteristics of the PMMA-PS/Al<sub>2</sub>O<sub>3</sub> nanocomposites

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A nanocomposite consisting of (PMMA/PS) polymeric blend was prepared with the nanomaterials (Al<sub>2</sub>O<sub>3</sub>) by the casting method. The structural and dielectric characteristic were studied. The optical microscope photos demonstrated high homogeneousness and fine dispersal of Al<sub>2</sub>O<sub>3</sub> NPs inside the blend polymer films, as well as the formation of charge transfer complex. The FTIR indicate to a physical interference between the polymer matrix and nanoparticles. SEM images showed agglomeration of small and close packed group of elliptical particles on the surface of the polymeric matrix as a result of adding different number of Al<sub>2</sub>O<sub>3</sub> NPs. The insulator constant and the insulator loss of the (PMMA-PS/Al<sub>2</sub>O<sub>3</sub>) nanocomposites reduce with the rise in frequency, while the A.C electrical conductivity increases with increase of the frequency. The insulator constant, insulator loss and A.C electrical conductivity of (PMMA-PS/Al<sub>2</sub>O<sub>3</sub>) nanocomposites rises with raising of Al<sub>2</sub>O<sub>3</sub> nanoparticles concentrations. The dielectric constant, dielectric loss and A.C electrical conductivity after irradiation have high values compared before irradiation which attributed to the plasma interact with the molecular of these nanocomposites. As a results of their improved electrical conductivity after irradiation, polymeric nanocomposites have been proposed for use in electronic devices, sensors, and batteries.

(Received March 5, 2023; Accepted May 17, 2023)

*Keywords:* PMMA, PS, Al<sub>2</sub>O<sub>3</sub>, Nanocomposites, Dielectric characteristics

### 1. Introduction

Polymer nanocomposites have garnered a lot of interest in the scientific and industrial communities over the past 20 years not only because they combine a number of fascinating qualities like small weightiness, cost effectiveness, and affluence of combination, but also since they have multi-faceted, multi-functional abilities that are appropriate for a variety of requests [1]. Polymer or copolymer nanocomposites have nanoparticles dispersed throughout the polymer matrix. From a fundamental and technological standpoint, it is anticipated that the distinctive properties of polymers and nanoparticles combined in special, well-designed composites will provide materials of significant interest [2]. Similarly, nanoparticles have a significant effect on the matrix due to their high surface-to-bulk ratio, resulting in some special assets that aren't created at one of the pure materials. The effect of nanoparticles on the properties of a polymer matrix has to be further studied in order to improve predictions of the final features of the composite [3]. Recently, composites of polymer and ceramic filler have drawn attention because of their appealing electronic and electrical properties [4]. Poly (methyl methacrylate, or PMMA) is distinguished by its ease of synthesis, electrical act, high transparency, small index of refractive, inflexibility, good mechanical assets, and favorable thermal parameters. It has a lot of appeal and benefits in a wide range of modern applications because of these characteristics [5]. Amorphous polymer with large side groups is polystyrene (PS). general objectives at room temperature, polystyrene is rigid, hard, and transparent. It is also a thermoplastic substance that resembles glass and can soften and deform when heated. It is soluble in cyclohexane, chlorinated hydrocarbons, and aromatic hydrocarbon solvents [6,7]. Many people are using aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) because of its strong dielectric strength, remarkable stability, resistance to harsh conditions, and high

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<https://doi.org/10.15251/DJNB.2023.182.669>

transparency down to 250 nm [8]. Because of their diverse requests, such as antibacterial and biomedical requests, the photo-physical characteristic of these dyes in various solid matrices, such as polymers, have sparked important interest [9]. Plasma reactively alters the physicochemical characteristics of material surfaces through interaction. It is simpler for various sorts of reactions to add or remove particles to or from the surface thanks to plasma treatment [10] It stands out as a capable strategy to change the cellulose's physicochemical characteristic. In terms of price, time, and energy, it is vastly superior than the aforementioned pretreatment techniques [11]. In addition, different wet-chemical pretreatments, plasma action propositions a greener and more environmentally responsible method of dissolving cellulose because it produces no chemical waste, albeit the technology's scalability presents a problem in its application to industrial processes [12]. This paper aims to study effect of gold plasma irradiation on the dielectric characteristics of the PMMA/PS/Al<sub>2</sub>O<sub>3</sub> nanocomposites

## 2. Materials and method

Poly methyl methacrylate (PMMA)/ Polystyrene (PS) doped with aluminum oxide nanoparticle (Al<sub>2</sub>O<sub>3</sub> NPs) has been prepared by casting method. The blend film (70%PMMA/30%PS) was prepared by dissolving of 1 gm in chloroform (30 ml). The fabricated of nanocomposites by adding of the Al<sub>2</sub>O<sub>3</sub> NPs to solution (PMMA/PS) with content 2, 4, 6 and 8 wt. % and then casting on glass betri dish. After prepared this nanocomposite, the gold plasma irradiated (Ar gas). The structural characteristics of (PMMA-PS/Al<sub>2</sub>O<sub>3</sub>) nanocomposites examined by the "Fourier Transformation Infrared Spectroscopy (FTIR) with range wavenumber (500-4000) cm<sup>-1</sup>", scanning electron microscopic (SEM) using a Hitachi SU6600 variable and Optical microscope (OM) provided by Olympus (Top View, type Nikon-73346). The dielectric characteristics were studied at range (f=100 Hz to 5 × 10<sup>6</sup> Hz) by LCR meter type" (HIOKI 3532-50 LCR HI TESTER)". The insulator constant,  $\epsilon'$  is given by [13]:

$$\epsilon' = C_p d / \epsilon_0 A \quad (1)$$

wherever,  $C_p$  is capacitance of substance, thickness (d in cm),  $A =$  (in cm<sup>2</sup>). Insulator loss,  $\epsilon''$  is planned by [14]:

$$\epsilon'' = \epsilon' D \quad (2)$$

wherever, D: dispersal factor. The A.C electrical conductivity is determined by [15]:

$$\sigma_{A.C} = 2\pi f \epsilon' D \epsilon_0 \quad (3)$$

## 3. Result and discussion

The optical microscope images of the pure (PMMA/PS) composite and variant content of aluminum oxide nanoparticle (Al<sub>2</sub>O<sub>3</sub> NPs) and exposed to the argon plasma gas are shown in fig. (1). At low concentrations of Al<sub>2</sub>O<sub>3</sub> NPs, it can be noted that the formation of small pits on the surface of the nanocomposites as a result of exposure to Argon plasma gas, and when we reach a concentration of 8 wt.% Al<sub>2</sub>O<sub>3</sub> NPs, it notes that these pits increase due to the rise in the interface of the plasma with the surface of the sample.

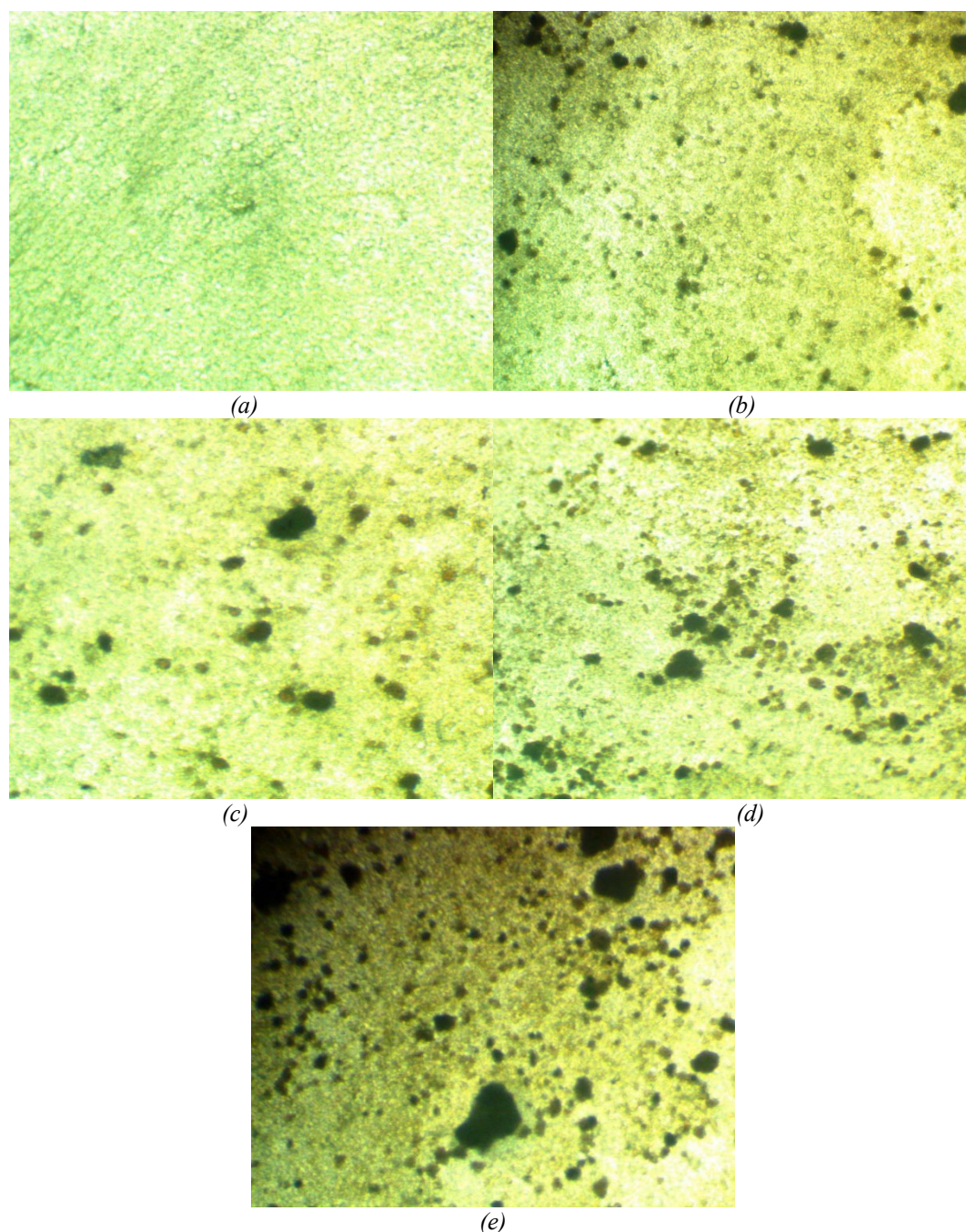


Fig. (1). Photomicrographs ( $\times 10$ ) for (PMMA/PS/ $\text{Al}_2\text{O}_3$ ) nanocomposites: (a) for pure (b) for 2wt.%  $\text{Al}_2\text{O}_3$  NPs, (c) for 4wt.%  $\text{Al}_2\text{O}_3$  NPs, (d) for 6wt.%  $\text{Al}_2\text{O}_3$  NPs and (e) for 8wt.%  $\text{Al}_2\text{O}_3$  NPs.

FTIR spectra of (PMMA/PS/ $\text{Al}_2\text{O}_3$ ) nanocomposites are shown in fig. (2) at wavenumber range (500-4000)  $\text{cm}^{-1}$ . FTIR studies of nanocomposites show the interactions in nanocomposites. FTIR spectra of (PMMA/PS) polymer reveals absorption band at 2984.45  $\text{cm}^{-1}$  corresponding to the  $\text{CH}_3$  bending vibration and the band 1723.34  $\text{cm}^{-1}$  owing to the  $\text{C}=\text{O}$  stretching vibration. Band at 1435.14  $\text{cm}^{-1}$  corresponding to the  $\text{CH}_3$  stretching vibration. The absorption band at 1143.71  $\text{cm}^{-1}$  attribute to the symmetric stretching vibration of  $\text{C}-\text{O}$ . The bands 984.77  $\text{cm}^{-1}$ , 697.33  $\text{cm}^{-1}$  and 749.08  $\text{cm}^{-1}$  matching to the  $\text{C}-\text{C}$  bending and stretching vibration respectively [16]. After adding  $\text{Al}_2\text{O}_3$  nanoparticles to the polymers (PMMA/PS) as shown in image (from B to E) from fig. (2) leads to the displacement of some of the bonds and not emergence of new peaks therefore, there is no interaction between  $\text{Al}_2\text{O}_3$  nanoparticle and the PMMA/PS polymer matrix. these results agree with the researchers [17,18].

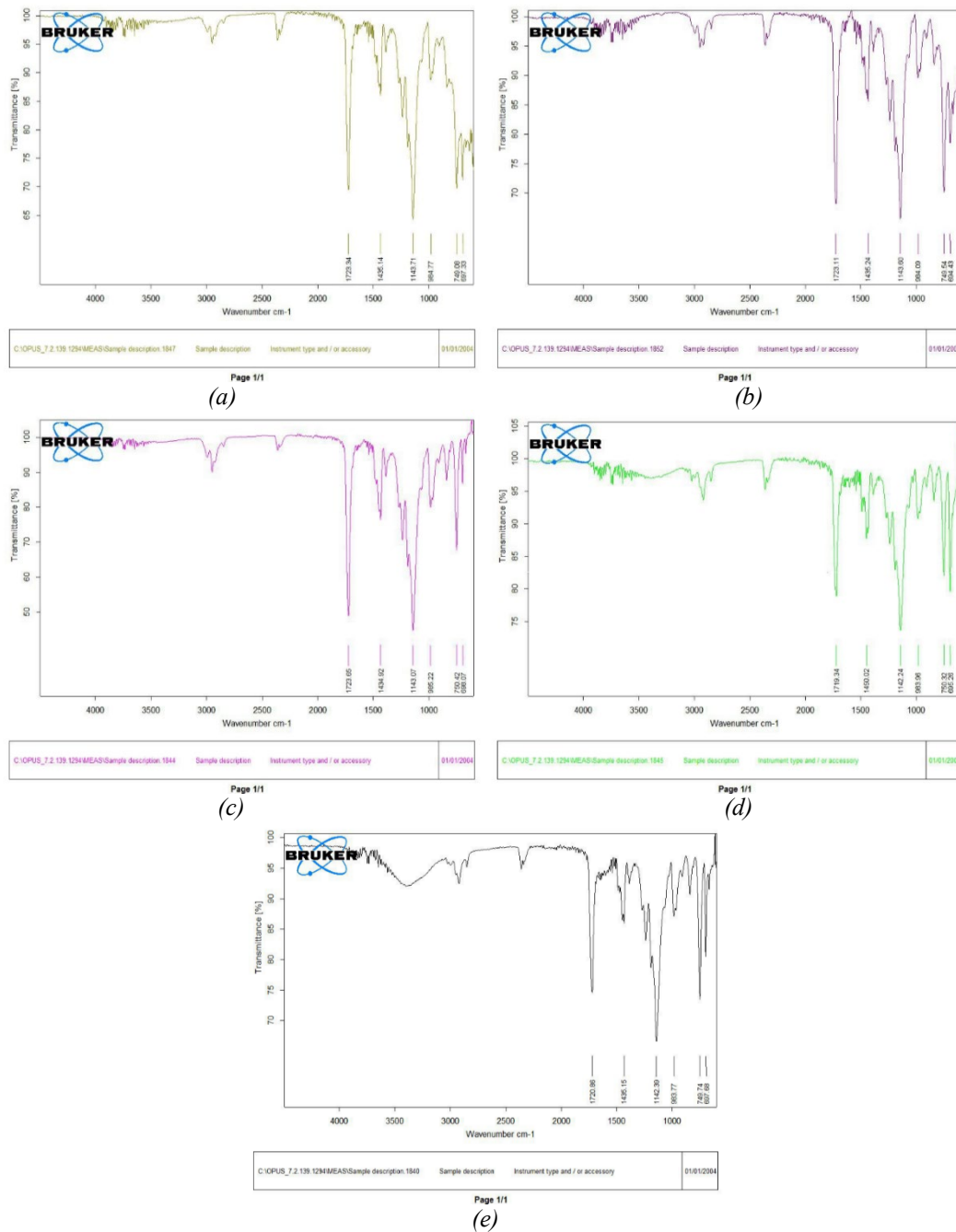


Fig. (2). FTIR spectra of (PMMA/PS/Al<sub>2</sub>O<sub>3</sub>) nanocomposites: (a) for pure (b) for 2wt.% Al<sub>2</sub>O<sub>3</sub> NPs, (c) for 4wt.% Al<sub>2</sub>O<sub>3</sub> NPs, (d) for 6wt.% Al<sub>2</sub>O<sub>3</sub> NPs and (e) for 8wt.% Al<sub>2</sub>O<sub>3</sub> NPs

Scanning electron microscopy (SEM) was tested to study the compatibility between various components of the polymer and nanomaterials. The surface morphology for samples of PMMA-PS/Al<sub>2</sub>O<sub>3</sub> nanocomposites was examined using an SEM, as shown in Fig. (3), with a scale of 200 nm and exposed to the argon plasma gas. From Fig. (2), it can be noted that the formation of craters results from surface exposure to the argon plasma gas, and when we reach a concentration of 8 wt.% Al<sub>2</sub>O<sub>3</sub> NPs, the formation of grooves [19]. Treatments using reactive gases like argon are known to produce this effect. These processes involve the chemical interaction of energetic plasma particles with the sample species, which removes them and creates volatile

byproducts including water vapor, carbon monoxide, and carbon dioxide that are subsequently pumped out of the reactor. Moreover, polar groups, which, if not removed from the system, may persist in the discharge and be reincorporated into the sample, may be created when the removed species recombine. This result agrees with [20].

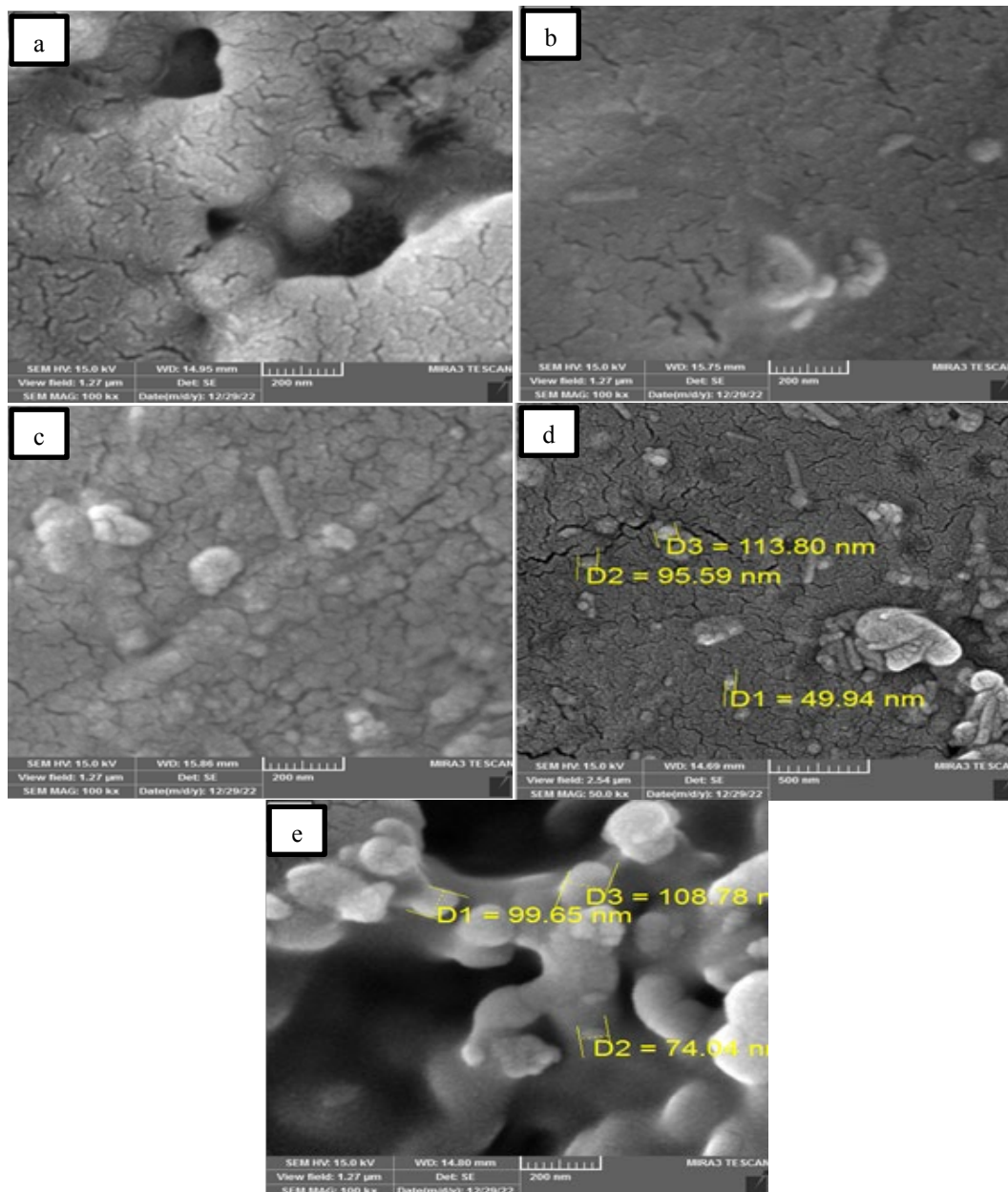


Fig. (3). SEM of (PMMA/PS/Al<sub>2</sub>O<sub>3</sub>) nanocomposites: (a) for pure (b) for 2wt.% Al<sub>2</sub>O<sub>3</sub> NPs, (c) for 4wt.% Al<sub>2</sub>O<sub>3</sub> NPs, (d) for 6wt.% Al<sub>2</sub>O<sub>3</sub> NPs and (e) for 8wt.% Al<sub>2</sub>O<sub>3</sub> NPs

Equation (1) was calculated the dielectric constant ( $\epsilon$ ). The dependence of insulator constant of (PMMA/PS/Al<sub>2</sub>O<sub>3</sub>) nanocomposites with frequency before and after irradiation plasma are shown in Figs. (4 and 5). It is obvious that the dielectric constant decreases as the electric field frequency rises. This could be as a result of the samples' dipoles' propensity to align themselves with the directions of the applied electrical fields and with respect to total polarization, space charge polarization is decreasing. Space charge polarization is the most significant form of polarization at low frequencies, and as frequency rises, it becomes fewer significant, while the  $\epsilon$  increasing with increasing concentration of Al<sub>2</sub>O<sub>3</sub> NPs are shown in Figs. (6 and 7). Both an

increase in the charge carriers of the (PMMA-PS/Al<sub>2</sub>O<sub>3</sub>) nanocomposites and interfacial polarization within the nanocomposites in the applied field's alternating electric field might be used to explain these characteristics [21]. Also, it notes that the dielectric constant has high value after irradiation compare before irradiation which, may be due to interaction plasma with molecules which give more energy that effect on the dielectric constant of this nanocomposites. This result agrees with researcher [22].

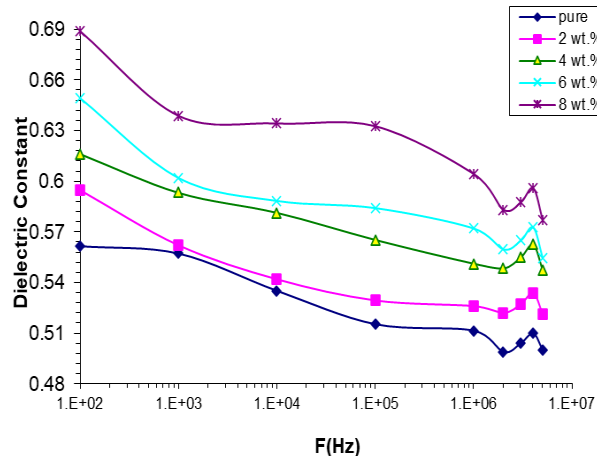


Fig. (4). The dielectric constant with the frequency of (PMMA/PS/Al<sub>2</sub>O<sub>3</sub>) nanocomposites before irradiation plasma

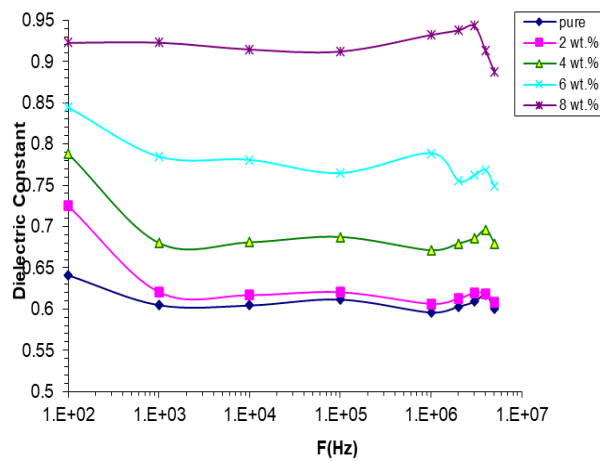


Fig. (5). The dielectric constant with the frequency of (PMMA/PS/Al<sub>2</sub>O<sub>3</sub>) nanocomposites after irradiation plasma

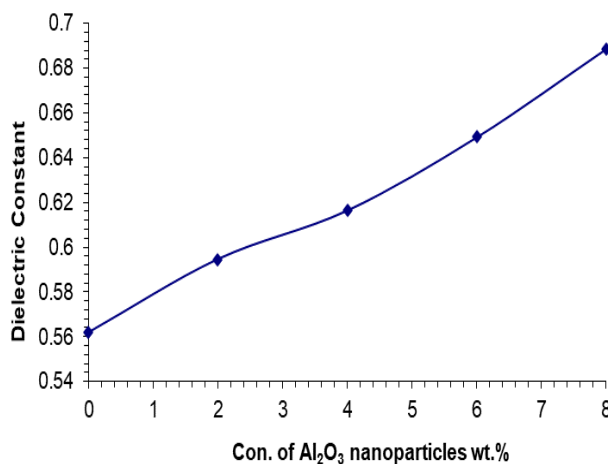


Fig. (6). The dielectric constant with Al<sub>2</sub>O<sub>3</sub> NPs concentration of (PMMA/PS/Al<sub>2</sub>O<sub>3</sub>) nanocomposites before irradiation plasma

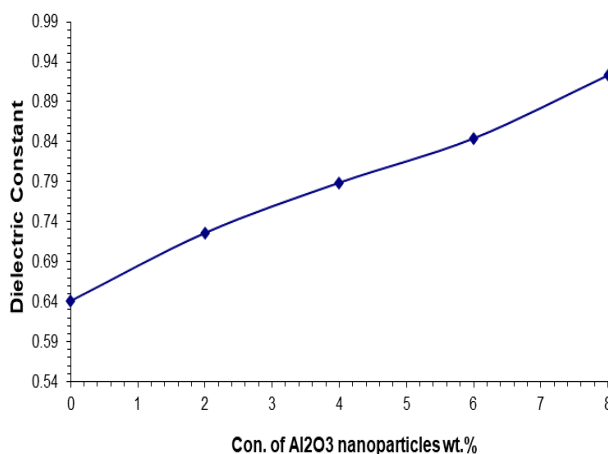


Fig. (7). The dielectric constant with Al<sub>2</sub>O<sub>3</sub> NPs concentration of (PMMA/PS/Al<sub>2</sub>O<sub>3</sub>) nanocomposites after irradiation plasma

The dielectric loss ( $\epsilon''$ ) was calculated from eq. (2). The dependence of dielectric loss on electric field frequency of (PMMA-PS/Al<sub>2</sub>O<sub>3</sub>) before and after irradiation plasma are shown in Figs. (8 and 9). The  $\epsilon''$  increased with increasing frequency. This is due to a decline in the contribution of space charge polarization. With rise content of Al<sub>2</sub>O<sub>3</sub> NPs, the  $\epsilon''$  of (PMMA-PS/Al<sub>2</sub>O<sub>3</sub>) nanocomposites rises before and after irradiation plasma are explain in Figs. (10 and 11), which ascribed to the rise of the number of charge carriers. At small contented of NPs, it creates as a cluster and at high contented reach to 8%, its formation a network inside the nanocomposites [23]. Also, it can be noted that the dielectric loss has value larger after irradiation plasma compared before irradiation plasma, which attributed to that the plasma give energy to this molecule that effect to the dielectric loss of this nanocomposites. This result is deal with scientists [24].

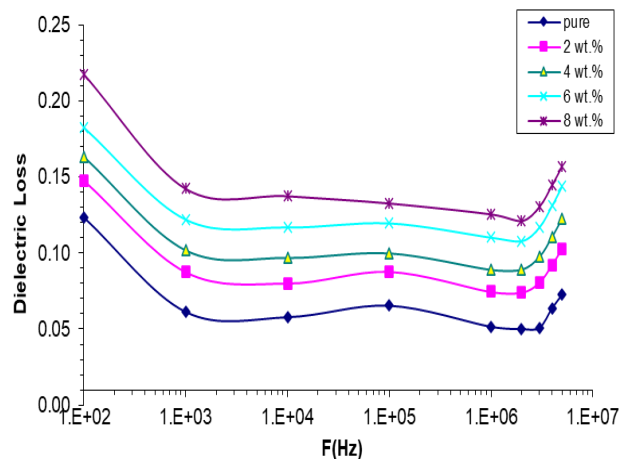


Fig. (8). The dielectric loss with the frequency of (PMMA/PS/Al<sub>2</sub>O<sub>3</sub>) nanocomposites before irradiation plasma

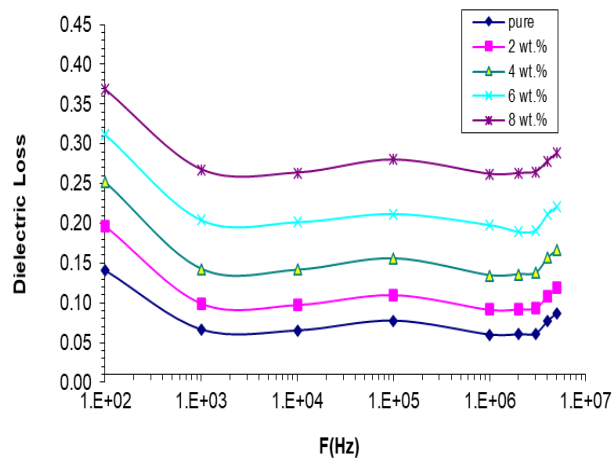


Fig. (9). The dielectric loss with the frequency of (PMMA/PS/Al<sub>2</sub>O<sub>3</sub>) nanocomposites after irradiation plasma

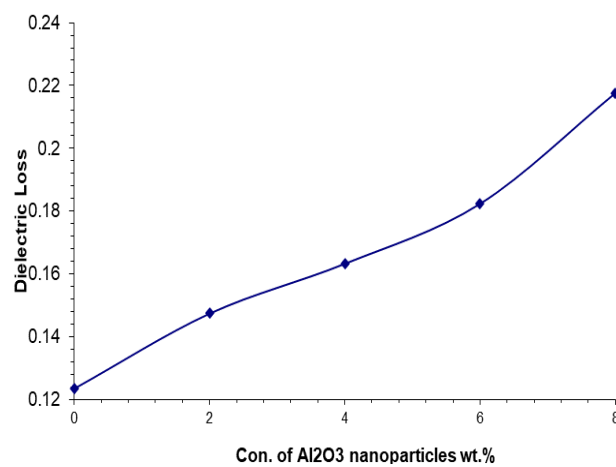


Fig. (10). The dielectric loss with Al<sub>2</sub>O<sub>3</sub> NPs concentration of (PMMA/PS/Al<sub>2</sub>O<sub>3</sub>) nanocomposites before irradiation plasma



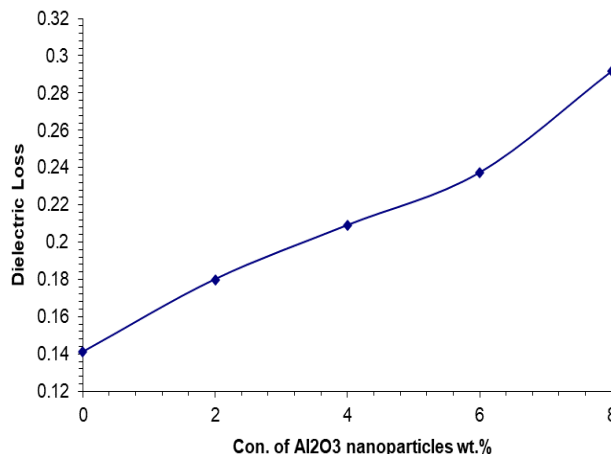


Fig. (11). The dielectric loss with Al<sub>2</sub>O<sub>3</sub> NPs concentration of (PMMA/PS/Al<sub>2</sub>O<sub>3</sub>) nanocomposites after irradiation plasma

The A.C conductivity was calculated from relation (3). The dependence of A.C electrical conductivity on electric field frequency for (PMMA-PS/Al<sub>2</sub>O<sub>3</sub>) nanocomposites before and after irradiation plasma are shown in Figs. (12 and 13). The A.C conductivity dramatically rises with raising electric field frequency for all samples. This results from both the hopping motion of charge carriers and space charge polarization, which takes place at low frequencies [25]. Also, the Figs demonstrate how the conductivity rises with a rise in the weight percentage of Al<sub>2</sub>O<sub>3</sub> NPs in the plasma before and after irradiation (14 and 15). Because of the regular arrangement of charge carriers in the polymer matrix and the action of the space charge, this phenomenon is caused. Also, it should be noted that the A.C conductivity increased after plasma irradiation compared to before plasma irradiation, indicating that the plasma had an impact on the conductivity of these nanocomposites. This is consistent with the researcher's conclusions [26].

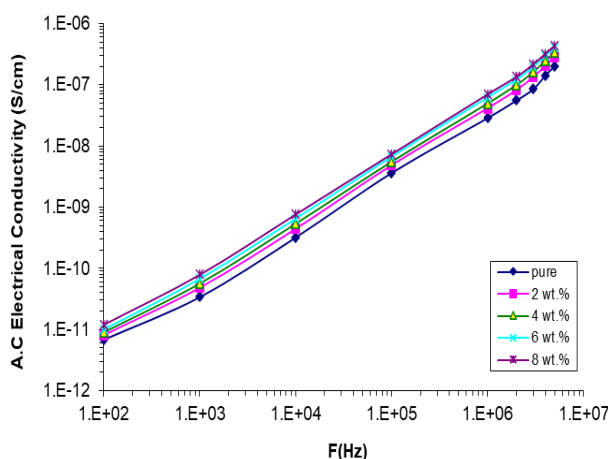


Fig. (12). The A.C electrical conductivity with the frequency of (PMMA/PS/Al<sub>2</sub>O<sub>3</sub>) nanocomposites before irradiation plasma

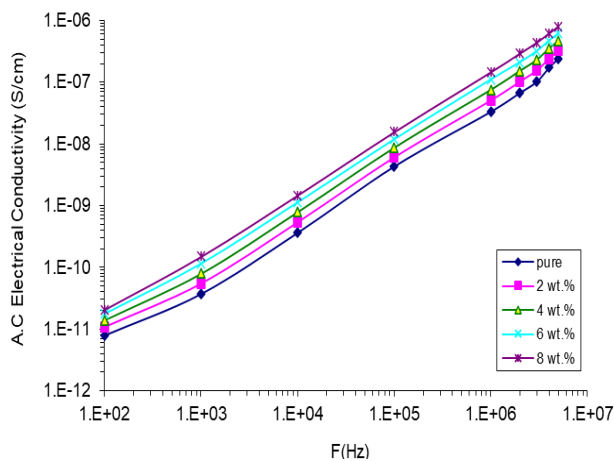


Fig. (13). The A.C electrical conductivity with the frequency of (PMMA/PS/Al<sub>2</sub>O<sub>3</sub>) nanocomposites after irradiation plasma

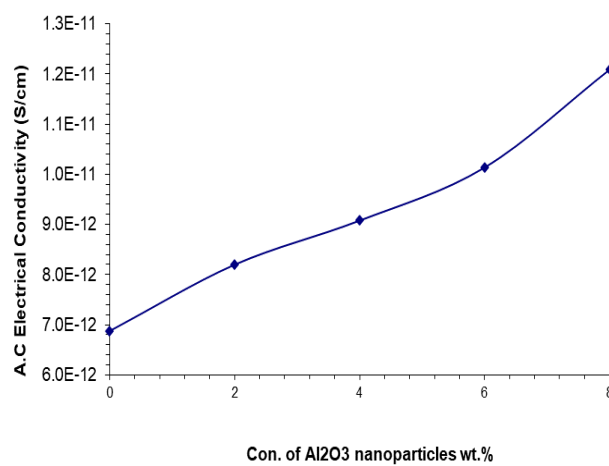


Fig. (14). The A.C electrical conductivity with Al<sub>2</sub>O<sub>3</sub> NPs concentration of (PMMA/PS/Al<sub>2</sub>O<sub>3</sub>) nanocomposites before irradiation plasma

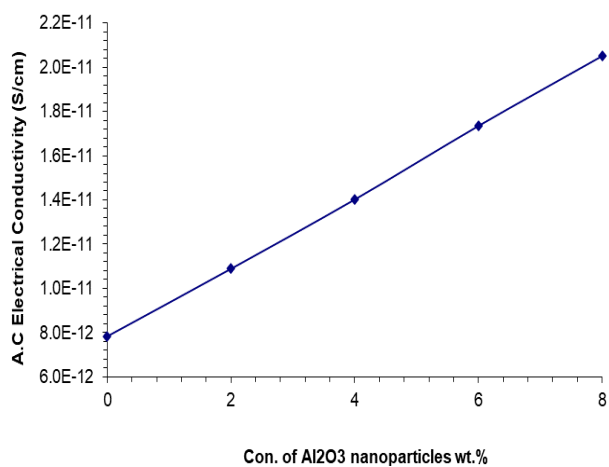


Fig. (15). The A.C electrical conductivity with Al<sub>2</sub>O<sub>3</sub> NPs concentration of (PMMA/PS/Al<sub>2</sub>O<sub>3</sub>) nanocomposites after irradiation plasma

#### 4. Conclusion

The summarized as followed: The successful of casting method to prepare the (PMMA/PS/ Al<sub>2</sub>O<sub>3</sub>) nanocomposites. The optical microscope photos demonstrated high homogeneousness and fine dispersal of Al<sub>2</sub>O<sub>3</sub> NPs inside the blend polymer films, as well as the formation of charge transfer complex. FTIR exhibited that when combined, the polymer and the nanoparticles exist in a physical superposition. SEM images showed agglomeration of small and close packed group of elliptical particles on the surface of the polymeric matrix as a result of adding different number of Al<sub>2</sub>O<sub>3</sub> NPs.

The (PMMA/PS/Al<sub>2</sub>O<sub>3</sub>) nanocomposites' dielectric constant and dielectric loss increase with frequency, although the electrical conductivity for alternating current (A.C.) increases with frequency. PMMA/PS/ Al<sub>2</sub>O<sub>3</sub> nanocomposites' dielectric constant, dielectric loss, and AC electrical conductivity all rise when Al<sub>2</sub>O<sub>3</sub> nanoparticle concentrations rise. The insulator constant, insulator loss and A.C electrical conductivity after irradiation have high values compared before irradiation which attributed to the plasma interact with the molecular of these nanocomposites.

#### Acknowledgments

Acknowledgment to University of Babylon.

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