

# Comparative Study on the Alternating Current Conduction and Dielectric Properties of Plasma Polymerized Monolayer and Bilayer Thin Films

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**Abstract:** The alternating current (ac) electrical conduction and dielectric properties of plasma polymerized pyrrole-N,N,3,5 tetramethylaniline (PPPy-PPTMA) bilayer composite thin films and a comparative study of those properties of PPPy monolayer, PPTMA monolayer and PPPy-PPTMA bilayer thin films have been discussed in this article. The monolayer and bilayer composite thin films were deposited by using a parallel plate capacitively coupled glow discharge reactor. To prepare the PPPy-PPTMA bilayer films, pyrrole monomer was used as the mother-material and TMA monomer was deposited in different deposition time ratio after the pyrrole films were formed. To study the ac electrical properties of PPPy-PPTMA bilayer composite thin film of different thicknesses the dielectric constant ( $\epsilon'$ ), the dielectric loss factor ( $\epsilon''$ ), and the ac conductivity ( $\sigma_{ac}$ ) were investigated as the function of frequency at room temperature. It was observed that the  $\epsilon'$  of bilayer thin films was decreased considerably with the increase of PPTMA content in the bilayer structure because PPTMA thin films has lower dielectric constant than that of the PPPy thin films, which was confirmed in the comparative study. This fact was explained by Maxwell-Wagner two-layered model and it was predicted that the grain size and the grain boundary capacitance were reduced with increasing PPTMA content in the bilayer structure which gives rise to a decrease in dielectric constant. The observed frequency dependence of the  $\epsilon'$  was attributed to the dielectric relaxation process and to interfacial or space charge polarization. The peak appearing at a characteristic frequency in the dielectric loss spectra suggested that the charge motion and polymer segmental motion were strongly coupled which indicated the presence of relaxing dipoles in the PPPy-PPTMA bilayer thin films. However, the PPPy-PPTMA bilayer thin films were found to have higher values of  $\epsilon'$  but lower values of  $\epsilon''$  at any particular frequency for a particular thickness which suggested that they have higher ability to polarize and hold charge and also can store more energy but rate of energy dissipation is lower than that of its components PPPy and PPTMA thin films. The ac conductivity of the bilayer thin film was found to have lower values than those of its component films over whole frequency range. It was predicted that during the formation of bilayer thin films, inhomogeneous and irregular complex polymer-polymer interface might be formed whose disorderness may cause a decrease in the conductivity of those films.

**Keywords:** Plasma Polymerization, Bilayer Thin Films, AC Conduction, Dielectric Properties

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## 1. Introduction

Electrical and electronic insulating materials, known as dielectrics, have the property of storing and dissipating electrical energy when subjected to electromagnetic field.

When exposed to an electric field, the electric charges in a dielectric material, including permanent and induced electric dipoles, can be moved, thus polarizing the material. The alternating current (ac) dielectric spectroscopic analysis measures two fundamental electrical characteristics of

materials, namely the capacitive (insulating) nature, which represents its ability to store electric charge and the conductive nature, which represents its ability to transfer electronic charge. Therefore, the ac measurements are important means for studying the dynamic properties e.g. the conductivity, dielectric constant, permittivity, loss factor etc. of a dielectric.

Because of good dielectric properties plasma polymerized thin films is found to be suitable dielectrics in integrated microelectronics and insulating layers for semiconductors. Thin films produced by plasma-polymerization are known to have free radicals or polar groups independent of the nature of monomers. They have permanent dipole moment and hence exhibit dielectric dispersion. This type of polymer thin films show very high dielectric constant and the dielectric loss. Therefore, these polymers are good candidates for the investigation of dielectric properties. The analysis of dielectric data over a wide temperature and frequency range provides deep insight into the nature of dominant polarization mechanism in polymer films, and therefore a dielectric study throws light on the molecular structure and relaxation behaviors of the polymers.

Many reports on the investigation of the structural, optical, direct current (DC) and alternating current (AC) electrical properties of plasma polymerized thin films are available in the literature but most of them dealt with single-layer thin films. Reports on the properties of bilayer thin films are relatively less abundant. Saravanan et al. [1] investigated on the dielectric constant and ac conductivity of plasma polymerized aniline thin films in a wide frequency range and found that the dielectric constant is considerably low in the high frequency range. The dielectric properties of rf plasma polymerized pyrrole (PPPy) thin film were studied in the frequency range from 1 kHz to 1 MHz at various temperatures by Sakthi Kumar and Yoshida [2]. They reported that the PPPy thin films have high dielectric constant with small variations against frequency and temperature, low dielectric losses, chemical inertness and also stability against environment and therefore these films could be considered as an ideal dielectric material. El-Nahass et al. [3] investigated the dependence of ac dielectric properties on the frequency of thermally deposited N-(p-dimethylaminobenzylidene)-p-nitroaniline (DBN) thin films. Both the dielectric constant and dielectric loss were observed to decrease with increasing frequency. Dielectric constant and conduction current of polyimides thin/ultrathin films of thicknesses 80–2000 nm were measured by Liang et al. [4] using a small electrode system. It was observed that the dielectric constant was decreased with decreasing film thickness, but the conduction current was found to be increased. Plasma polymerized polyaniline thin films were prepared and characterized by Joseph Mathai et al. [5]. Capacitance and dielectric loss were observed to be decreased with frequency and increased with temperature. The dielectric measurements of polymeraldine salt in an Al-polymeraldine salt-Al configuration as functions of frequency and temperature were done by Ram et al. [6]. The

analysis showed that the movement of charge carriers under the influence of an electric field gives rise to the space charge phenomenon, leading to interfacial polarization. The optical characterization and direct current electrical characterization of the plasma polymerized pyrrole-*N,N,3,5* tetramethylaniline (PPPy-PPTMA) bilayer thin films were studied by Kamal and Bhuiyan [7, 8]. The optical characterization and thickness dependent direct current electrical characterization of the PPPy monolayer thin films were also reported by Kamal and Bhuiyan [9, 10]. They also investigated the direct current electrical conduction mechanism of the PPPy monolayer thin films [11] and temperature dependence of DC electrical conduction in PPPy thin films [12]. The ac electrical characterization of PPPy thin films was also studied by Kamal and Bhuiyan [13].

The ac electrical conduction and the dielectric properties of PPPy-PPTMA bilayer composite thin films have been discussed in this article. The variation of dielectric constant, dielectric loss factor and ac electrical conductivity of PPPy-PPTMA bilayer thin films of different thicknesses were investigated as the function of frequency at room temperature. A comparative study of those properties of PPPy monolayer, PPTMA monolayer and PPPy-PPTMA bilayer thin films have been also done. The experimental results were discussed thoroughly in light of existing theory.

## 2. Theoretical Background

The dielectric constant,  $\epsilon'$ , which is used to characterize the dielectric properties, is an essential piece of information when designing capacitors and in other circumstances where a material might be expected to introduce capacitance into a circuit. It is the ratio of the permittivity of a substance,  $\epsilon$ , which is a measure of the ability of a material to be polarized by an electric field, to the permittivity of free space,  $\epsilon_0$ . It is also defined as the ratio of the field without the dielectric ( $E_0$ ) to the net field ( $E$ ) with the dielectric, or as the ratio of the amount of stored electrical energy when a voltage is applied, relative to the permittivity of a vacuum.

$$\epsilon' = \frac{\epsilon}{\epsilon_0} = \frac{E_0}{E} \quad (1)$$

$E$  is always less than or equal to  $E_0$ , so the dielectric constant is greater than or equal to unity. The larger the dielectric constant, the more charge can be stored in a material. Materials with high dielectric constants are useful in the manufacture of high-value capacitors because they are good at holding charge. High- $\epsilon'$  dielectrics are also used in memory cells that store digital data in the form of charge. A low- $\epsilon'$  dielectric, on the other hand, has a low ability to polarize and hold charge. Low- $\epsilon'$  dielectrics are very good insulators for isolating signal-carrying conductors from each other.

In an alternating (ac) field, the dielectric constant is a complex quantity,  $\epsilon^*$ , and is the combination of a real component, called the relative permittivity or dielectric

constant,  $\epsilon'$ , and an imaginary component, called the dielectric loss or dissipation factor,  $\epsilon''$ . This form, also called the complex dielectric permittivity, is defined as,

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (2)$$

A key issue is the variation of both  $\epsilon'$  and  $\epsilon''$  with respect to frequency and temperature for the ac measurements in plasma polymerized thin films, which would be presented in this article. Like dielectric constant ( $\epsilon'$ ), dissipation factor or loss factor ( $\epsilon''$ ) is also important electrical parameters, especially at high frequencies. As the frequency increases, the inertia of the charged particles tends to prevent the particle displacements from keeping in phase with the field changes. This leads to a frictional damping mechanism that causes power loss, because work must be performed to overcome these damping forces. Additionally, Ohmic losses due to free charge carriers are also included in the complex permittivity. It is customary to include the effects of both the damping and the Ohmic losses in the imaginary part of the complex permittivity,  $\epsilon^*$ : The dielectric loss factor can be written as

$$\sigma = \omega\epsilon'' \quad (3)$$

where  $\sigma$  is the conductivity and  $\omega$  is the angular frequency. Using equation (3) we can rewrite equation (2) as follows:

$$\epsilon^* = \epsilon' - j\frac{\sigma}{\omega} \quad (4)$$

On the basis of equation (4) a medium is said to be a good conductor if  $\sigma \gg \omega\epsilon'$  and a good insulator if  $\omega\epsilon' \gg \sigma$ . Thus, a material may be a good conductor at low frequencies, but may have the properties of a lossy dielectric at very high frequencies. In contrast, most dielectrics, including ceramics and polymers, exhibit low loss at low frequencies, but become lossy at high frequencies.

### 3. Experimental Details

In this study we have used two types of monomers to prepare plasma polymerized single-layer and bilayer thin films, namely, Pyrrole (Py) and N,N,3,5 Tetramethylaniline (TMA). The monomer pyrrole was collected from Aldrich-Chemie D-7924, Steinheim, Germany and The monomer N,N,3,5 Tetramethylaniline (TMA) was collected from BDH chemical limited, Germany.

The PPPy and PPTMA monolayer thin films and PPPy-PPTMA composite bilayer thin films were deposited on to chemically cleaned glass substrates at room temperature by using a capacitively coupled glow discharge plasma reactor. The vapor of the monomers was introduced in to the glow discharge reactor through a flow-meter (Glass Precision Engineering, Meterate, England, UK) at the flow rate of about 20 cm<sup>3</sup> (STP) / min. The glow discharge system consists of two parallel plate electrodes of stainless steel of diameter and thickness 0.09 and 0.001 m respectively placed

0.035 m apart. The glow discharge chamber was evacuated by a rotary pump (Vacuubrand GMBH & Co, 97877 Wertheim, Germany) and plasma was generated around the substrates with a power of about 30 W. Transparent light-yellow colored monolayer PPPy and PPTMA thin films of different thickness were deposited onto the glass substrates. To deposit the PPPy-PPTMA bilayer composite thin films, pyrrole-monomer has been used as the mother-material and TMA monomer has been deposited in different deposition time-ratios after the pyrrole thin films were grown. The deposition time-ratios of PPPy: PPTMA were (40min: 20min), (35min: 25min) and (30min: 30min) which have produced the bilayer thin films with thicknesses 500 nm, 450 nm and 400 nm respectively.

For electrical measurements the Al/ PPPy/ Al sandwich configuration were formed by using an Edward vacuum coating unit E-306A (Edward, UK) at a pressure of about 1.33×10<sup>-3</sup> Pa with an effective electrode area of about 10<sup>-4</sup> m<sup>2</sup>.

The ac measurement of PPPy thin films of different thicknesses was performed in the frequency range from 100 to 3×10<sup>6</sup> Hz and temperature range 298 - 423 K, by a low frequency (LF) Impedance analyzer, Agilent 4192A, 5 Hz - 13 MHz (Agilent Technologies Japan, Ltd. Tokyo, Japan).

The temperature was recorded by a Cr-Al thermocouple placed very close to the sample which was connected to a Keithley 197A digital microvoltmeter (DMV). To avoid oxidation, all measurements were performed in a vacuum of about 1.33 Pa.

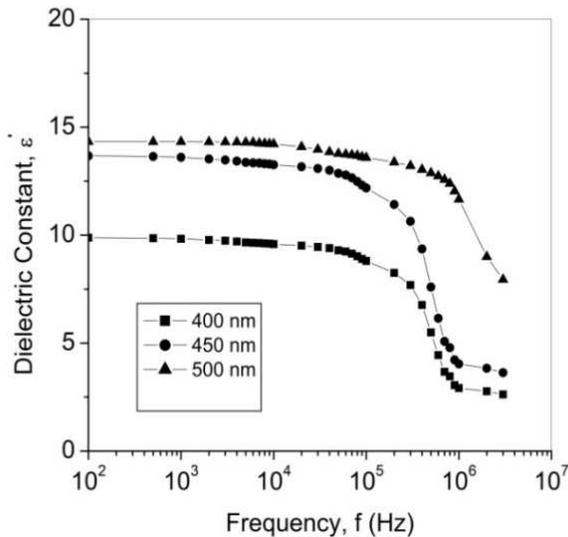
## 4. Results and Discussion

### 4.1. Variation of Dielectric Constant with Frequency

Figure 1 shows the variation of the dielectric constant  $\epsilon'$  of PPPy-PPTMA bilayer composite thin films for all compositions with frequency at room temperature. It is to be noted that, to prepare the PPPy-PPTMA bilayer films, pyrrole-monomer has been used as the mother-material and TMA monomer has been deposited in different deposition time ratio after the pyrrole films were formed. Therefore, the bilayer composite thin films have two components, namely, PPPy and PPTMA. The deposition time-ratios of (PPPy: PPTMA) were (40 min: 20 min), (35 min: 25 min) and (30 min: 30 min) and corresponding thicknesses of the bilayer thin films were 500 nm, 450 nm and 400 nm respectively. At room temperature, it is observed that the dielectric constant  $\epsilon'$  of bilayer thin films decreases considerably in the same frequency range with the increase of PPTMA in the bilayer structure, which could be explained by the fact that PPTMA thin films has lower  $\epsilon'$  than that of the PPPy thin films for the same thickness. This observation can also be stated in terms of PPPy component in the bilayer structure. Since PPPy thin films has higher  $\epsilon'$  than that of the PPTMA thin films for the same thickness, therefore, the increased proportion of PPPy component in the bilayer structure results in an increase of dielectric constant.

However, the decrease of dielectric constant  $\epsilon'$  of bilayer

thin films with the increase of PPTMA could also be explained by Maxwell-Wagner two-layered model [14]. A system may not be always homogeneous; there may be some region of non-uniformity and irregularities in the materials. Effects of dielectric properties attributable to material discontinuities are usually called Maxwell-Wagner effect. Complications also often arise at electrodes where contact with the specimen may be incomplete and where entities like discharged ions may form spurious boundary layers. This type of anomalous effect could give misleading results if they are not recognized or avoided.



**Figure 1.** Dielectric constant,  $\epsilon'$ , as a function of frequency of the PPPy-PPTMA bilayer composite thin films of different thicknesses at room temperature.

According to this model the dielectric function depends on the conductivity and permittivity of the two layers. Examining the effect of a field applied across a specimen of two different materials with dielectric constants  $\epsilon_1'$ ,  $\epsilon_2'$  and conductivities  $\sigma_1$ ,  $\sigma_2$  respectively, it was found that charges will accumulate in time at the interfaces between layers whenever  $\epsilon_1'\sigma_2 = \epsilon_2'\sigma_1$ .

The dielectric constant arises due to static dielectric permittivity,  $\epsilon_s$ , which can be given as

$$\epsilon_s = C_{gb} / C_0 \quad (5)$$

where  $\epsilon_s$  is the static dielectric permittivity,  $C_{gb}$  is the grain boundary capacitance and  $C_0$  is the capacitance in the free space. The above equation demonstrates that the dielectric constant mainly depends on the grain boundary capacitance. In the present case, probably, the grain size decreases with increasing PPTMA content in the bilayer structure resulting the reduction of grain boundary capacitance which gives rise to a decrease in dielectric constant.

However, all the phenomena of plasma polymerized bilayer thin films could not be explained by Maxwell-Wagner two-layered model. The strong possibilities of growing polymer-polymer inhomogeneous complex interface in

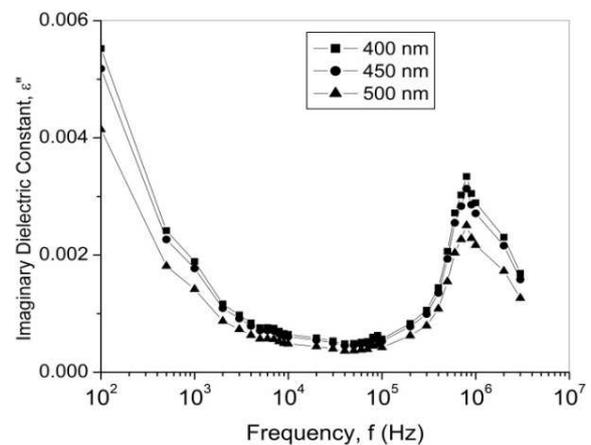
between two polymer thin films might affect the physical properties of bilayer structure.

From the figure 1, a general trend of decreasing  $\epsilon'$  with increasing frequency is observed; and the decrease in  $\epsilon'$  is very prominent at high frequencies. This is a similar behavior of  $\epsilon'$ - $f$  curves for PPPy thin films [13]. The decrease of  $\epsilon'$  with increasing frequency, however, is an expected behavior in most dielectric materials, and is usually attributed to the dielectric relaxation process. In a system of inhomogeneous structure,  $\epsilon'$  may arise due to interfacial and space charge polarization at frequencies from 100 Hz to few MHz. At lower frequency the dipole can respond rapidly to follow the field and dipole polarization has its maximum value, and therefore, higher values of dielectric constant and dielectric loss are usually observed in low frequency region. At higher frequencies, on the other hand, dipole polarization has minimum values, since the field cannot induce the dipole moment, and values of  $\epsilon'$  attain minimum values.

#### 4.2. Variation of Dielectric Loss Factor with Frequency

Figure 2 shows the variation of the imaginary part of dielectric constant or loss factor  $\epsilon''$  with frequency at room temperature for PPPy-PPTMA bilayer composite thin films for all composition of thicknesses about 400, 450, and 500 nm respectively at room temperatures.

For all samples, the loss factor has higher value at low frequency which may be due to the free charge motion within the materials. However, with the increase of PPTMA in the bilayer structure,  $\epsilon''$  increases in the lower frequency region reflect the enhancement of mobility of charge carrier.



**Figure 2.** Variation of dielectric loss factor,  $\epsilon''$ , as a function of frequency of the PPPy-PPTMA composite bilayer thin films of different thicknesses at room temperature.

From the figure 2, it is also observed that  $\epsilon''$  initially decreases with increasing frequency until a loss minimum is observed and then rises with frequency up to a sharp peak in the loss spectra, and thereafter decreases sharply with the increase of frequency. Since the appearance of peak in the loss factor is attributed to the relaxation phenomena of polymer, therefore there seem to be two relaxations exist in the lower and higher frequencies. The lower one seems to be

out of the range of the measurement frequency.

Dielectric relaxation is a result of the reorientation process of dipoles in the polymer chains, which show a peak in  $\epsilon''$  spectra. For polymeric materials the movement of ions from one site to another will perturb the electric potential of the surroundings. Motion of the other charges in this region will be affected by perturb potential. Such a cooperative motion of ions will lead to non-exponential decay or a conduction processes with distribution of relaxation time [15]. From the Figure of dielectric loss factor spectra, a relaxation peak is observed in the higher frequency range, suggests that charge motion and polymer segmental motions are strongly coupled manifesting as a single peak in the  $\epsilon''$  spectra.

It is already discussed that an increase in  $\epsilon''$  with increasing applied frequency is dominated by resistive losses since the mobile charges contained in the film cannot follow high-frequency electric fields. This loss of energy is associated with the degree of orientation of molecules in addition to the degree of internal friction of the films [16]. At higher frequencies, the very fast periodic reversal of the electric field occurs and no excess ion diffusion would become possible in the direction of the field. Above  $f_{max}$  the polar ionization decreases due to the charge accumulation results to a decrease in the value of the loss factor.

**4.3. Variation of ac Conductivity with Frequency**

Figure 3 represents the plot of the ac conductivity  $\sigma_{ac}$  as a function of the frequency for all the compositions for the PPPy-PPTMA composite bilayer thin films of thicknesses about 400, 450, and 500 nm respectively at room temperature.

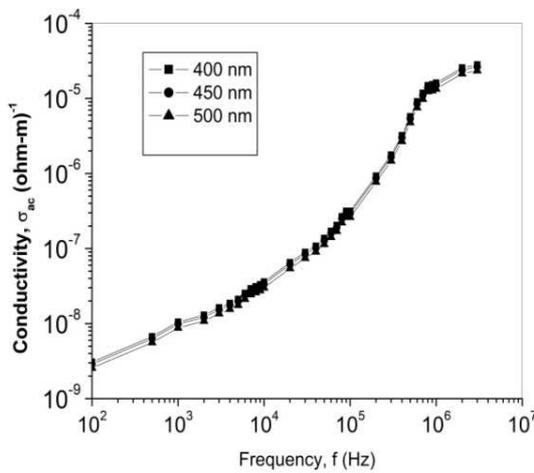


Figure 3. Plots of ac conductivity  $\sigma_{ac}$  as a function of frequency for the PPPy-PPTMA composite thin films of different thicknesses at room temperature.

From the figure it is observed that  $\sigma_{ac}$  increases as the proportion of PPTMA in the bilayer structure, as well with the decrease of thickness of the films in the same frequency range. This is a similar behavior of dc conductivity  $\sigma_{dc}$ . In another article [8] we calculated the dc conductivity of PPPy-PPTMA composite thin films of different compositions over a wide range of applied voltage and found that  $\sigma_{dc}$  is

increased in the composite bilayer films with the increase of PPTMA.

From the Figure 3 it is also seen that the ac conductivity  $\sigma_{ac}$  is linear function of the frequency; and like PPPy and PPTMA thin films, an increase of  $\sigma_{ac}$  is observed with increasing frequency. The dependence of ac conductivity,  $\sigma_{ac}$ , on frequency may be described by the power law [17]:

$$\sigma_{ac}(\omega) = A\omega^n \tag{6}$$

where A is a proportionality constant and  $\omega$  ( $=2\pi f$ , f is the linear frequency) is the angular frequency and n is the exponent, which generally takes the value less than or equal to unity for Debye type mechanism and is used to understand the conduction/relaxation mechanism in amorphous materials.

For physical convenience, the values of n are usually between 0.4 and 0.8 [17]. The values of n, however, for all the samples of PPPy-PPTMA bilayer thin films for all temperature and frequency ranges have been found to lie in between 0.726 to 0.938, which is close to the values of physical convenience. The types of results are usually attributed to the dielectric relaxations caused by the motion of charges or atoms. Such motion can involve hopping or tunneling between equilibrium sites [18]. By analyzing the observed behavior of the  $\sigma_{ac}$ -frequency relationship it can therefore be concluded that, the ac conduction mechanism may be due to the hopping of electrons between pairs of localized states at the Fermi level.

**4.4. Comparative Study of Dielectric Properties and ac Conductivity**

For a comparative study, the dielectric constant,  $\epsilon'$ , as a function of the frequency for the PPPy monolayer, PPTMA monolayer and PPPy-PPTMA bilayer composite thin films of thickness about 400 nm at room temperature are presented in Figure 4.

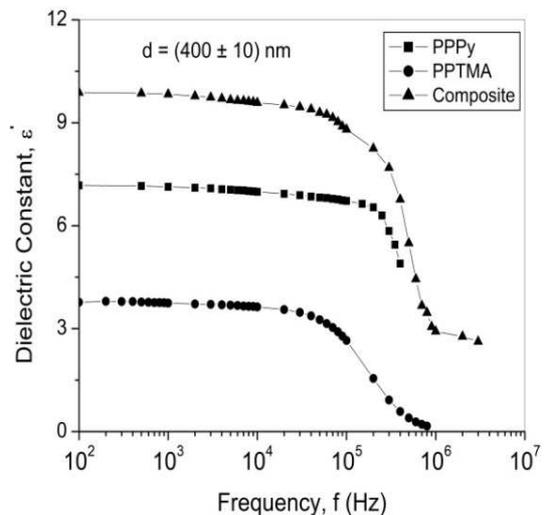
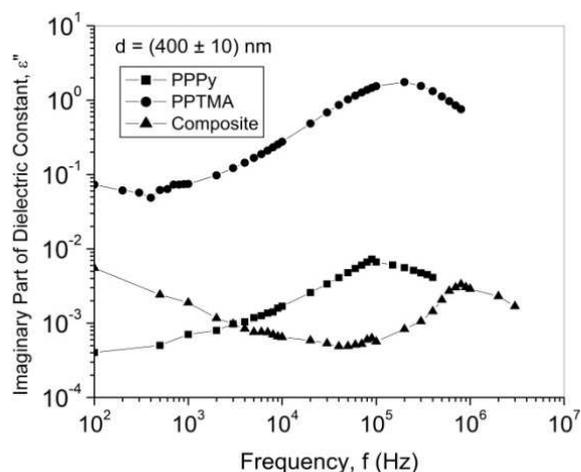


Figure 4. The dielectric constant,  $\epsilon'$ , as a function of the frequency for the PPPy, PPTMA and PPPy-PPTMA composite thin films of thickness about 400 nm at room temperature.

It is seen from the figure that the PPPy-PPTMA bilayer composite thin films have much higher value of  $\epsilon'$  compared to those of its component thin films.

It is known that a low- $\epsilon'$  dielectric has low ability to polarize and hold charge, a high- $\epsilon'$  dielectric, on the other hand, has a high permittivity and is good at holding charge. Generally, substances with high dielectric constants break down more easily when subjected to intense electric fields, than those materials with low dielectric constants. From the comparative study, it can thus be concluded that the PPPy-PPTMA bilayer thin films has higher ability to polarize and hold charge than that of its component thin films, and therefore the bilayer films could be more preferable dielectric for capacitors or for memory cells that store digital data in the form of charge.

In Figure 5, the dielectric loss factor,  $\epsilon''$  as a function of the frequency for the PPPy monolayer, PPTMA monolayer and PPPy-PPTMA composite bilayer thin films of thickness about 400 nm at room temperature has been plotted.



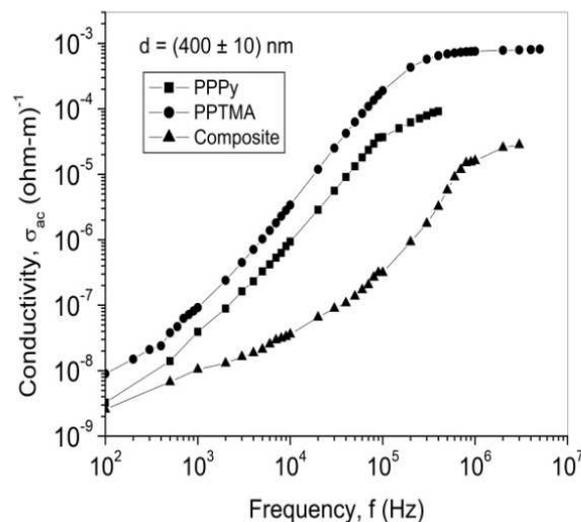
**Figure 5.** The dielectric loss factor,  $\epsilon''$  as a function of the frequency for the PPPy, PPTMA and PPPy-PPTMA composite thin films of thickness about 400 nm at room temperature.

Comparing Figures 4 and 5, it could be seen that PPTMA thin film has lower values of  $\epsilon'$  but higher values of  $\epsilon''$  compared to other thin films at any particular frequency. PPPy-PPTMA bilayer composite thin film, on the other hand, show opposite character, i.e., bilayer film has higher values of  $\epsilon'$  but lower values of  $\epsilon''$ . Since  $\epsilon'$  is a measurement of energy stored per cycle and  $\epsilon''$  is the energy dissipated per cycle, therefore from this observation it could be concluded that in the bilayer thin films more energy is stored but rate of energy dissipation is lower than that of its component thin films.

The loss spectra characterized by peak appearing at a characteristic frequency for all the samples suggest the presence of relaxing dipoles in all the samples. The strength and frequency of relaxation depend on characteristic property of dipolar relaxation. It is seen that the high frequency relaxation peak shifts to the higher frequency, and at the lower frequency side, a relaxation peak seems to appear just below the lowest frequency used in this study. Thus it can be concluded that both the loss peaks were shifted towards higher

frequency in the bilayer composite thin films compared to its components. The shifting of loss peaks towards the higher frequency is an indication of reducing the relaxation time in the bilayer thin films. This behavior may be due to an increase in the amorphous content in the bilayer structure.

Figure 6 shows the ac conductivity  $\sigma_{ac}$  as a function of the frequency for the PPPy monolayer, PPTMA monolayer and PPPy-PPTMA bilayer composite thin films of thickness about 400 nm at room temperature.



**Figure 6.** The ac conductivity  $\sigma_{ac}$  as a function of the frequency for the PPPy, PPTMA and PPPy-PPTMA composite thin films of thickness about 400 nm at room temperature.

It is seen that the bilayer composite thin film has lower  $\sigma_{ac}$  than those of its component films over whole frequency range. This is a similar behavior of dc conductivity  $\sigma_{dc}$ . In another communication [8] it is discussed that PPPy-PPTMA composite thin films have lower values of  $\sigma_{dc}$  than that of its component films for a certain thickness.

The total conductivity of the composite thin films, however, depends on the microscopic and macroscopic conductivities. The microscopic conductivity depends upon the doping level, conjugation length or chain length etc., whereas the macroscopic conductivity depends on the inhomogeneities in the composites, compactness of pellets, orientation of microparticles etc. In the present system, the individual thin films were deposited one over the other to prepare the PPPy-PPTMA bilayer composite thin films, which may give rise to a system with polymer-polymer complex interface, i.e., the interface between the PPPy and PPTMA thin films may not be homogeneous and therefore there are some possibilities of presence of irregularities in the interface. It should be noted that in most inhomogeneous polymeric systems, the electronic conductivity is affected by this interface. So the microscopic conductivities remain almost the same but the physical (macroscopic) properties viz. compactness and molecular orientations, may significantly vary due to the complex polymer interface. This disorderliness causes to decrease the compactness and molecular orientations leading to a decrease in resultant conductivity.

## 5. Conclusions

From the characteristics of the dielectric constant  $\epsilon'$  as a function of frequency for PPPy-PPTMA bilayer composite thin films, it is observed that at the low frequencies, the dielectric constant for all the samples are almost independent of frequency, but at high frequencies the decrease in  $\epsilon'$  is very prominent. The decrease of  $\epsilon'$  with frequency is usually attributed to the electrical relaxation processes and multi-component contribution of polarizability of the polar materials. The observed frequency dependence of the dielectric constant in this study is probably due to the interfacial or space charge polarization, which is usually found in sandwich type configurations. The other relaxation processes can also be superimposed with this polarization; e.g. the orientational polarization of molecular chains. Since the orientation polarization depends upon the molecular arrangement of dielectric and at higher frequencies, the rotational motion of the polar molecules of dielectric is not sufficiently rapid for the attainment of equilibrium with the field. The orientational polarization is therefore decreased which in turns results in a decrease of dielectric constant with increasing frequencies.

It is observed that the loss factor  $\epsilon''$  increases with the frequency up to a characteristics frequency  $f_{\max}$  with a sharp peak and after that decreases. The loss spectra characterized by peak appearing at a characteristic frequency for all the samples suggest the presence of relaxing dipoles in all the samples and the behavior has been attributed to structural rearrangement of the molecule, the  $\alpha$ -relaxation process, connected with segment motion in polymers.

The variation of the  $\sigma_{ac}$  with the frequency shows a common pattern of linear behavior, i.e. the ac conductivity  $\sigma_{ac}$  is linear function of the frequency. The results have been attributed to the relaxations caused by the motion of electrons or atoms, which could involve hopping or tunneling between equilibrium sites. By analyzing the observed behavior of the  $\sigma_{ac}$ - $f$  relationship it has been therefore concluded that, the ac conduction mechanism may be due to hopping mechanism.

In a comparative study of the dielectric properties PPPy, PPTMA and PPPy-PPTMA bilayer composite thin films of nearly same thickness of about 400 nm, it is seen that the bilayer composite thin film has higher value of  $\epsilon'$  compared to those of its component thin films. This result implies that bilayer thin films has higher ability to polarize and hold charge than those of its component thin films, and therefore the bilayer films could be more preferable dielectric for capacitors or for memory cells that store digital data in the form of charge. Moreover, since bilayer film has higher values of  $\epsilon'$  but lower values of  $\epsilon''$  at a particular frequency, therefore it has been concluded that in the bilayer thin films more energy is stored but rate of energy dissipation is lower than that of its component thin films. It is also observed that the dielectric loss peaks of bilayer thin films shift towards the higher frequency, which is an indication of reducing the relaxation time. This behavior may be due to an increase in the amorphous content in the bilayer structure.

The  $\sigma_{ac}$  of the bilayer composite thin film has been found

to have lower values than those of its component films over whole frequency range, which is a similar behavior of  $\sigma_{ac}$ . During the formation of bilayer thin films by plasma polymerization, a system with polymer-polymer complex interface might be grown up in between the PPPy and PPTMA thin films. This interface may not be homogeneous and therefore there are some possibilities of presence of irregularities in the interface and in most inhomogeneous polymeric systems, the electronic conductivity is affected by this interface. It is known that the total conductivity of the composite thin films depends on both the microscopic and macroscopic conductivities. The microscopic conductivity depends upon the doping level, conjugation length or chain length, etc. whereas the macroscopic conductivity depends on the inhomogeneities in the composites, compactness of pellets, orientation of microparticles etc. Therefore in this system the resultant conductivity may significantly vary due to the complex polymer-polymer interface, and the disorderness of the interface may cause a decrease in the conductivity of the bilayer thin films.

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