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Study of Dielectric Relaxation and Surface Morphology of Pure and Malachite Green Doped Polysulfone by Dielectric and Scanning Electron Microscope (SEM) Spectroscopy

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Abstract - In the present investigation, enhancement of dielectric constant and lowering of dielectric losses has been observed, as the amount of doping element malachite green increases in host polymer Polysulfone(PSF). The modification in surface morphology of Polysulfone on adding malachite green has been investigated by Field Emission Scanning Electron Microscope (FE-SEM) spectroscopy. The dielectric constant and dielectric loss factor of pure and malachite green doped Polysulfone (PSF) was measured in the temperature range (30°-90°C) at various frequencies from 500 Hz to 20 kHz. The dielectric properties have been observed to be governed by dipolar polarization fully and interfacial polarization partially. An appreciable change has been observed in properties associated with surface and texture of PSF, due to addition of malachite green. The SEM images of doped samples represent the formation of small clusters in the original PSF matrix. This activity suggests the formation of Charge Transfer Complexes (CTC) between the donor and acceptor molecules, implying that the electrical characteristics of the Polysulfone polymer have improved.

Index Terms - Polysulfone; Malachite Green; Dielectric Spectroscopy, Scanning Electron Microscope (SEM) Spectroscopy, Charge Transfer Complex (CTC)

1. INTRODUCTION

A dielectric material is a non-metallic material with specific resistance high, a temperature coefficient of resistance negative and with large insulation resistance. The dielectric is an electrical insulator that can be polarized when it comes in contact with an applied electric field. The demand for suitable insulating material in the electronic industry is increasing day by day. The thin layer of dielectric material of high permittivity is sandwiched between conducting material of opposite polarity increasing the charge storage capacity of an electronic device. This type of device can provide energy backup for a very long time. Polymers have long been known as insulating materials and are often used to insulate cables and electrical devices. They are also called dielectrics[1]. The use of polymers as dielectrics is becoming increasingly important. Polymers are one of the key elements in energy harvesting and storage devices due to their unique properties such as high breakdown strength, flexibility, ease of processing, and low cost, in comparison with traditional ceramic and metallic materials. The trend to utilize polymers in designing the most efficient dielectric devices is increasing rapidly. The dielectric technique measure and analyses the behavior of the physical properties of the dielectric material as a function of either the time they are exposed to a constant external field or the frequency of an external alternating electric field[2] . Dielectric studies in polymers provide vital information on the molecular configuration of a system; for example, movement of dipoles, losses of energy, segmental motion, conduction mechanism, latent heat, etc. It is therefore important that their dielectric behavior should be fully understood.

The dielectric behavior of a polymer is determined by the charge distribution and also by the statistical motion of polar groups. Dielectric relaxation is the momentary delay (or lag) in the molecular polarization concerning a changing electric field in a dielectric medium. Dielectric measurements of polymers generally show α and β relaxation processes. The α process is associated with the reorientation of the dipoles along the main chain which takes place around and above the glass transition temperature.

The scanning electron microscope (SEM) is a type of electron microscope that uses a high-energy beam of electrons to scan the sample surface in a raster pattern to obtain an image. The SEM produces images of high resolution, which means that closely spaced features can be examined at high magnification and large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. SEM is most widely used for revealing information about the microstructures and orientation of the samples.

The goal of this study is to look into the dielectric relaxation behaviour of pure and malachite green doped Polysulfones. The dielectric spectroscopy is used for the study of the dielectric relaxation mechanism and field emission scanning electron microscope (FE-SEM) spectroscopy is done to understand the structural modification that occurs in Polysulfone by introducing malachite green. The dielectric material of high dielectric constant and permittivity is suitable to design charge storage electronic devices.

2 EXPERIMENTAL DETAILS

2.1. Material

2.1.1. Polysulfone: For this experiment, polysulfone was employed as the host polymer. Polysulfones are a type of thermoplastic polymer that comes in a variety of shapes and sizes. These polymers are notable for their hardness and temperature stability. They contain the aryl-SO2-aryl subunit, which is distinguished by the presence of a sulfone group. Union Carbide first introduced polysulfones in 1965. A typical polysulfone is made by reacting a diphenol with bis(4-chlorophenyl)sulfone and then removing sodium chloride to make a polyether.Polysulfone is a rigid, high-strength, translucent material that maintains its qualities between 100 and 50 degrees Celsius. It has a glass transition temperature of 185 degrees Celsius. In a pH range of 2 to 13, polysulfone is extremely resistant to mineral acids, alkali, and electrolytes.

$$n\ HOC_6H_4OH + n(ClC_6H_4)_2SO_2 + n\ Na_2CO_3 \rightarrow [OC_6H_4OC_6H_4SO_2C_6H_4]_n + 2nNaCl + nH_2O + n\ CO_2.$$

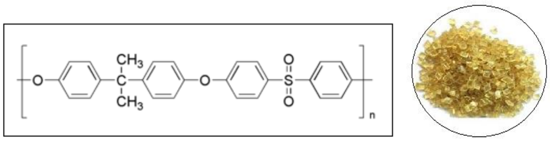

Fig.1

Structure of Polysulfone

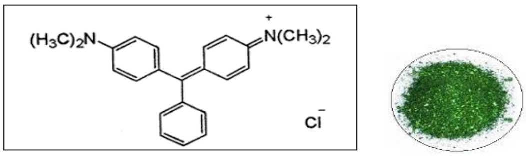

Fig.2

Structure of Malachite Green

2.1.2. Malachite Green: Malachite green is a dyestuff that is made up of an organic molecule with a low molecular weight. 4-[4-(Dimethylamino) phenyl](phenyl) methylidene-N is the IUPAC designation for this compound. The chromatic version of malachite green, which is a green dye, is the most well-known. A high absorption band at 621 nm (extinction coefficient of 105 M1cm1) is responsible for the cation's bright green colour. The leuco malachite green (LMG) is made by combining benzaldehyde with dimethylaniline.

$$C_6H_5CHO + 2\ C_6H_5N(CH_3)_2 \rightarrow C_6H_5CH(C_6H_4N(CH_3)_2)_2 + H_2O$$

2.2 Sample preparation

For the preparation of foil samples, the isothermal immersion technique was used. For the creation of the pure sample, 4 gm of pure polysulfone was dissolved in 50 ml of chemically pure solvent Dimethylformamide(DMF) in a glass beaker. To obtain a homogenous and transparent solution, the solution was maintained for 24 hours. The solution was then put over a mercury-floating glass plate that had been optically planed. To obtain the desired samples, the solvent was allowed to evaporate in a high-temperature oven for 24 hours. After that, any leftover solvent was removed by outgassing at ambient temperature for another 12 hours at 10-5torr. After then, the plate was progressively taken out of the solution. The resulting samples were clear, uniformly smooth, and easily peeled from the glass surface. The doped sample was made by dissolving 10 mg of malachite green, 50 mg of malachite green, and 100 mg of malachite green in 4 g of pure polysulfone in 50 ml of Dimethylformamide (DMF). Using the same technique as before, this solution was turned into a doped sample. Green in colour, uniformly smooth, and easily removed from the glass surface, the doped samples were a success. As a result, both pure and doped samples were created.

2.3 Dielectric Technique

Dielectric studies in polymers provide vital [4-9] information on the molecular configuration of a system; for example, movement of dipoles, losses of energy, segmental motion, conduction mechanism, latent heat, etc. It is therefore important that their dielectric behavior should be fully understood. The molecular motion affects the dielectric behavior, charge storage, and charge transport properties of polymers[10] . The LCR measuring technique has been effectively used to investigate molecular movements and relaxation behaviour in polymeric materials. This technique has been used to characterise homopolymers and copolymers, as well as to examine the effect of plasticizers and additives, among other things, 11 on polymer dielectric relaxation behaviour[11]. At various temperatures, measurements were taken in the frequency range of 500 Hz to 20 kHz. Pure and malachite green doped polysulfone samples were measured for dielectric losses and dielectric constants. The sample was placed between two stainless steel electrodes with brass plating. The assembly was placed in a thermostatic furnace and kept at the proper temperature.

2.4 Field Emission Scanning Electron Microscope (FE-SEM) Spectroscopy

The scanning electron microscope (SEM) is a type of electron microscope that uses a high-energy beam of electrons to scan the sample surface in a raster pattern to obtain an image. The SEM produces images of high resolution, which means that closely spaced features can be examined at high magnification and large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. SEM is most widely used for revealing information about the microstructures and orientation of the samples. FE-SEM provides 2 nm resolutions, 3 to 6 times better than conventional SEM, and minimized sample charging and damage. The field emission process itself depends on the work function of the metal, which is affected by adsorbed gases. Due to this reason, a very high vacuum is required [12-19].

3. RESULT AND DISCUSSION

The measurement of dielectric constant and dielectric losses of pure Polysulfone (PSF) and malachite green doped PSF samples are observed in the temperature range 30^0C -80^0C and frequency from 500 Hz to 20 kHz range. The various results obtained during the measurement process are illustrated in the following summarised points. The variation of dielectric constant as a function of temperature (ranging from 30^0C -80^0C at various fixed frequencies i.e. 500 Hz to 20 kHz is represented in Figures 3 to 6 respectively. For both pure and doped PSF samples, the dielectric constant drops with increasing frequency. It's also obvious that when the temperature rises, the dielectric constant rises with it. The value of the dielectric constant is found higher for doped samples with the highest doping ratio. The estimated value of the dielectric constant was found 7.896 for the pure PSF sample at a minimum frequency 500 Hz and at the highest temperature 80^0C. The dielectric constant observed 8.096, 9.696 and 12.212 for samples of PSF doped with 10mg, 50 mg and 100 mg of malachite green respectively at a lower frequency 500Hz and at the highest temperature 80 ^{0}C. It is clear that the dielectric constant increases as the temperature rises, as well as as the impurity ratio in the pure PSF rises.

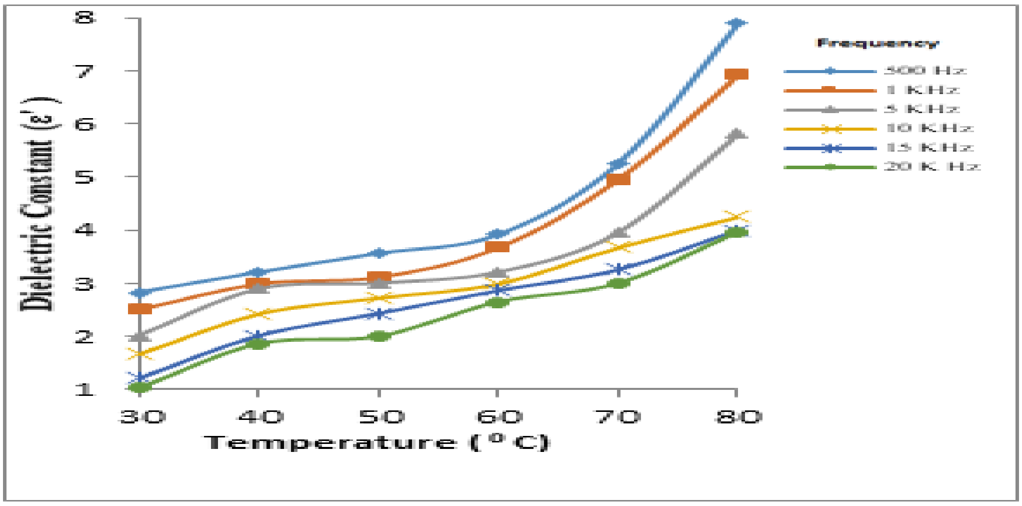

Fig.3
Dielectric Constant Vs Temperature at different frequencies for pure PSF

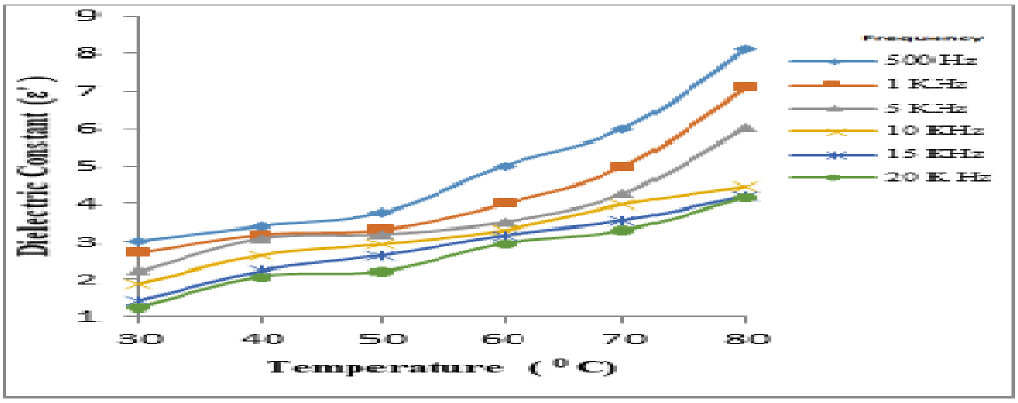

Fig. 4
Dielectric Constant Vs Temperature at different frequencies for PSF doped with 10 mg of Malachite Green.

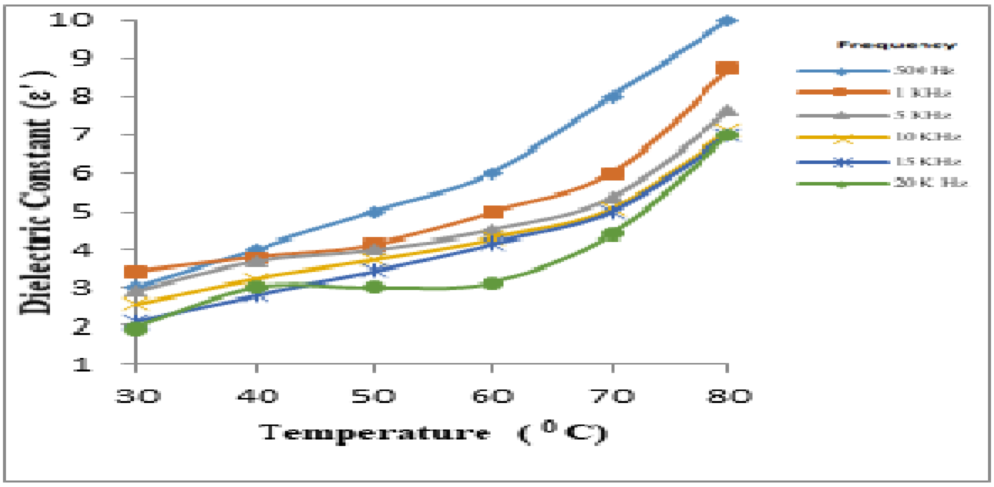

Fig. 5
Dielectric Constant Vs Temperature at different frequencies for PSF doped with 50 mg of Malachite Green.

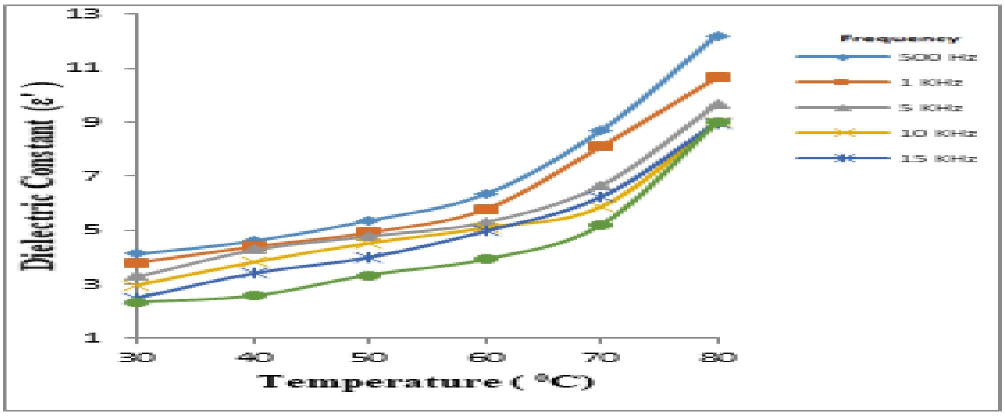

Fig. 6

Dielectric Constant Vs Temperature at different frequencies for PSF doped with 100 mg of Malachite Green.

The increase in temperature stimulates the thermal expansion of material which increases the available free volume and the mobility of the molecular units and thus reduces the relaxation time. The increase in the value of the dielectric constant with temperature is a characteristic of polar polymers. At lower temperatures, the dipoles are almost frozen-in. Hence they find themselves unable to orient in the direction of the applied field. The increase in the dielectric constant with the rise in temperature is may be due to the effect that as temperature increases, the mobility of polar molecules also increases. The molecular motion of the chain units available in the structure of the polymer is modified when subjected to the electric field with increasing temperature, producing increase in the polarization of the sample. The improvement in the degree of polarization is bringing modification in the dielectric property of the material and may be due to this trend the value of the dielectric constant increases.

Because molecules are immobile at temperatures below the glass transition temperature, the number of dipoles that allow them to orient with the field is reduced. The mobility of molecules increases as the temperature rises. As a result, a greater number of dipoles align themselves in the field's direction. Excitation of charge carriers, which are likely to be present inside the specimen at the defect sites, is another method for increasing the dielectric constant with temperature. The amorphous-crystalline interfaces may act as charge carrier trapping centres. The polarisation of the system is increased by molecular chains with varying motilities of the amorphous-crystalline zones adjusting themselves.This molecular alignment of the chain may also contribute to the observed increase in dielectric constant with temperature. This behavior has been observed in the entire temperature range of the present investigation (more appreciable at lower frequency) for all pure and doped malachite green samples. Interfacial and trapped charge carriers are also expected to contribute to the total polarization as the polymer system normally contains a large number of trapping sites. Polarization due to such charge carriers is more significant at higher temperatures. The contribution of interfacial space charges can also be considered in the heterogeneous system and may be responsible for the improvement in the value of the dielectric constant with an increase in temperature.

The variation of the value of dielectric losses as a function of temperature ranging from 30^0C -80^0C at various fixed frequencies i.e. 500 Hz to 20 kHz are represented in Figures 7 to 10 respectively. These curves show that the value of dielectric losses increases as temperature increases. The value of dielectric loss for the pure PSF sample is found 0.1484 at 30^oC, and 0.5662 at 80^oC temperature when subjected to an alternating electric field of a higher frequency 20 KHz. The Dielectric loss for doped samples found 0.423, 0.3263 and 0.169 at 80^oC temperature with respect to frequency 20 kHz for doing ratio 10 mg, 50 mg and 100 mg of malachite green respectively. It is evident that the value of dielectric loss at fixed temperature and at fixed frequency decreases as the doping amount of malachite green increases in pure PSF as compared to pure PSF.

In polymers, the dielectric loss behaviour may be attributed to the deformation of polymer chains The other important mechanism for dielectric losses in polymers is considered to be internal motions or the local movements of the molecular chains of the polymers. These segmental motions are particularly noticeable at the polymer's glass transition temperature (Tg). Such segmental motions are evident at high temperatures, particularly at the polymer's glass transition temperature. These motions, however, become less prominent at low temperatures.However, at low temperatures, these motions become less significant. The dielectric losses caused by the dipole mechanism reach their maximum at a certain definite temperature. This may also be attributed to thermal agitation (which decreases the polarization) thermal expansion (which decreases the ratio of the number of molecules to the effective length of the dielectric) and to the vigorous motion of the polymer chain.

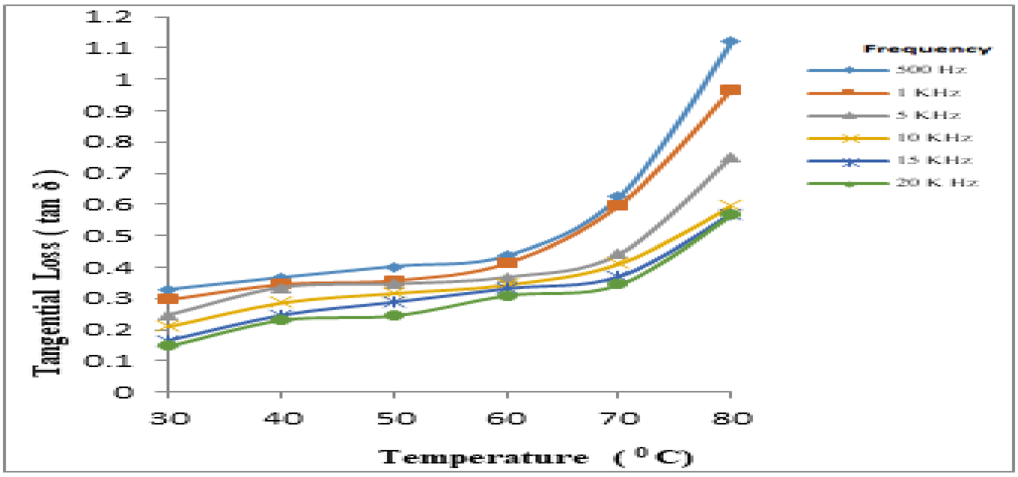

Fig. 7

Tangential Losses Vs Temperature at different frequencies for pure PSF.

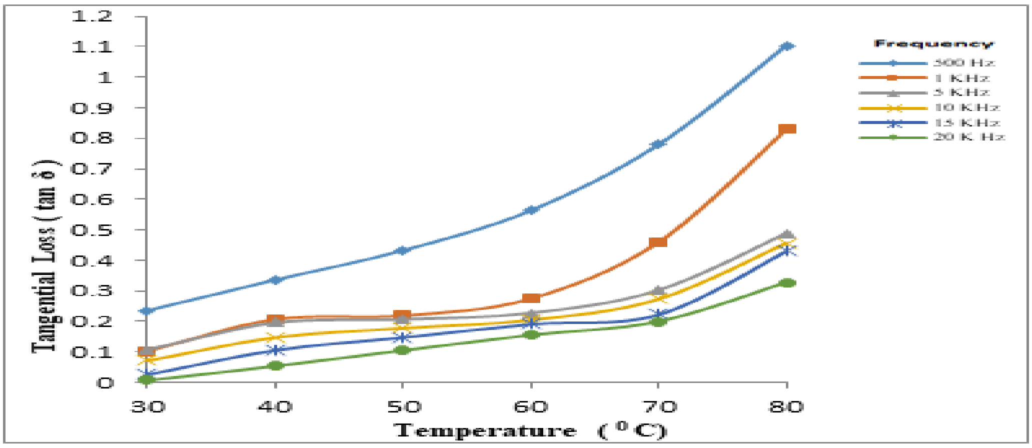

Fig. 8

Tangential Losses Vs Temperature at different frequencies for PSF doped with 10 mg of Malachite Green.

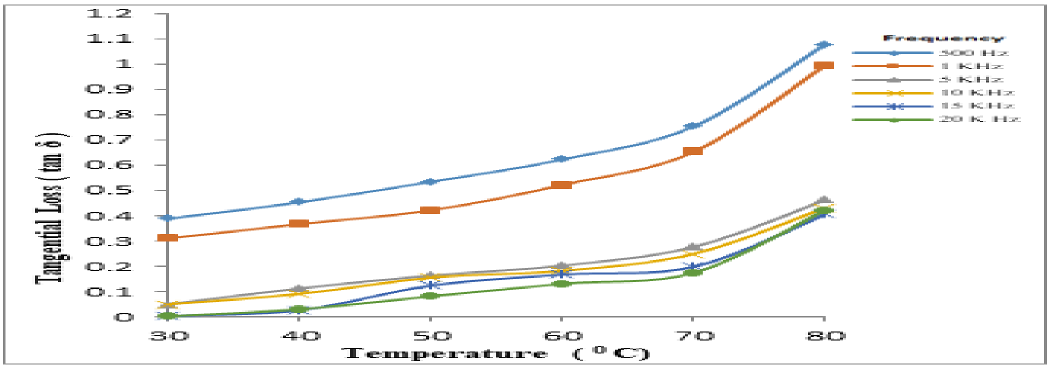

Fig. 9

Tangential Losses Vs Temperature at different frequencies for PSF doped with 50 mg of Malachite Green

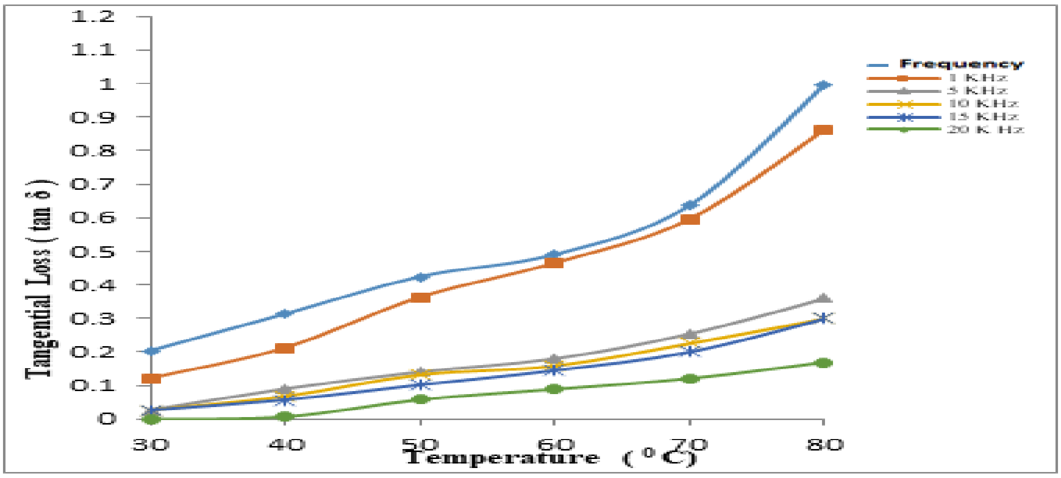

Fig. 10

Tangential Losses Vs Temperature at different frequencies for PSF doped with 100 mg of Malachite Green

Field Emission Electron Microscope (FE-SEM) spectroscopic studies were carried out to understand the influence of the addition of dopant malachite green on surface morphological features and compatibility between various phases of dopant and its iteration interfaces with the original matrices of pure PSF. PSF has an annular shape with porous sections between the molecular chains, as shown by SEM pictures of pure PSF and doped PSF with varying doping ratios. The amorphous phase of Polysulfone is confirmed by SEM investigation. The presence of malachite green is partially filling the original porous areas of pure PSF, as shown in the results above. The addition of malachite green to pure PSF alters the polymer grain formation process, changing the pore size and shape. Figures 11 to 14 show the SEM micrographs of pure and malachite green doped PSF that were taken.

The addition of malachite green to a polymer matrix results in a significant change in the surface characteristics and texture of PSF. Figures 12 to 14 show that malachite green doped PSF samples had proper solubility and enhanced smoothness. The creation of tiny clusters in the original PSF matrix is depicted in SEM images of doped samples. On doping malachite green, the surface roughness and crystalline texture appear to reduce, assisting in the production of a smooth texture on the surface. PSF has a globular structure with porous zones between the globes, according to SEM pictures of pure and malachite green doped PSF samples of various ratios. The amorphous phase of malachite green is also observed to partially cover the original porosity spaces of the pure PSF, influencing the size or perfection of the polymer crystal. Malachite green appears to influence the polymer grain formation process by modifying the size and shape of the pores when added to the PSF matrix.

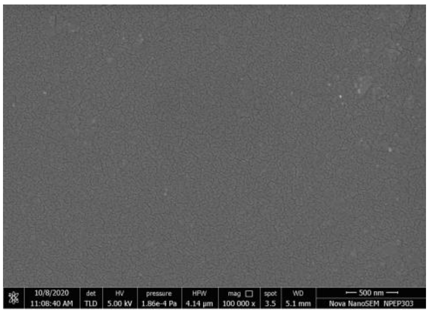

Fig. 11

FE-SEM image of pure PSF (Polysulfone)

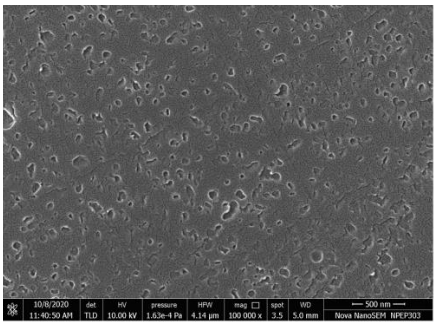

Fig. 12

FE-SEM image of PSF doped with 10 mg of Malachite Green

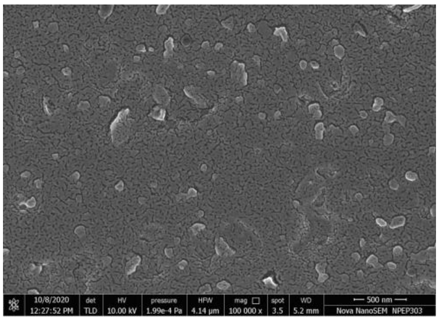

Fig. 13

FE-SEM image of PSF doped with 50 mg of Malachite Green

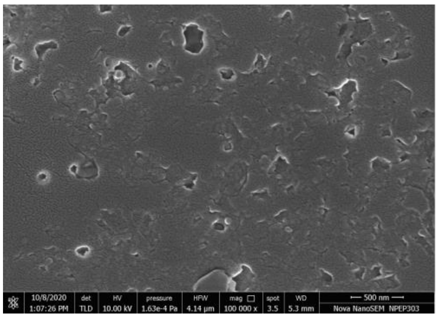

Fig. 14

FE-SEM image of PSF doped with 100 mg of Malachite Green

4. Conclusion

The dielectric spectroscopic approach can be used to investigate how material polarisation changes in the presence of a time-varying electric field. Because the various mechanisms that cause polymer polarisation are efficient at different frequencies, it is seen as a frequency-dependent process. This approach can also be used to detect changes at the molecular level or in the vicinity of molecules, as well as changes in intra- or intermolecular interactions. The net influence of some internal fields within the polymer, as well as the external ac field, is suggested by the variation in dielectric constant and losses. Lower losses with a wider frequency range are suggested by dipole-dipole interactions between the distinct groups or many-body interactions.The increase in dielectric constant and losses due to malachite green impregnation in PSF matrix may be due to the formation of charge-transfer complexes. Malachite green has an amino group-containing an unshared pair of electrons which may be responsible for CTC formation. Malachite green is a cationic dye with a triphenylmethane structure. Because the dye is cationic, the coloured ion is positively charged. The dye's cationic nature suggests it's an electron giver, whereas PSF is more likely to receive electrons. When mixed with PSF under the right conditions, malachite green is very likely to form donor-acceptor complexes.. The Scanning Electron Microscope spectroscopic techniques are done for detailed analysis of high-resolution images and collection of quantitative compositional information of pure and doped samples. These results help to record the activity of electrons of each atom present in compound samples across the surface and detect secondary or backscattered electron signals. Therefore, it is expected that the present study involving the use of malachite green in PSF will bring some new dimensions in the polymer study.

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