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Polymer - silicate nanocomposites: Package material for nanodevices as an EMI shielding

M. Nasreen Taj^a, B. DarukaPrasad^b, N. Rama Rao^c, H. Nagabhushana^d, K.S. Anantharaju^e, M.V. Murugendrappa^f

^a Department of Electrical and Electronics Engineering, HMS Institute of Technology, Tumakuru 572104, India

^b Department of Physics, BMS Institute of Technology and Management, Avalahalli, Bangalore 560064, India

^c Department of Electrical and Electronics Engineering, BMS Institute of Technology and Management, Bangalore 560064, India

^d C.N.R. Rao Centre for Advanced Materials Research, Tumkur University, Tumakuru 572 103, India

^e Department of Chemistry, Dayanand Sagar College of Engineering, Shavige Malleshwara Hills, Kumaraswamy Layout, Bangalore 560078, India

^f Department of Physics, BMS College of Engineering, Basavanagudi, Bangalore 560019, India

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ABSTRACT

Strontium silicate nanoparticles were filled in the organic matrix of poly ethylene glycol, polyvinyl alcohol and polyvinyl pyrrolidone polymers. Different weight percentages were selected for the preparation of thin films on the glass substrate using spin coating technique. Prepared polymer nanocomposite films were characterized for their structural analysis and compositional details using powder X-ray diffraction. Amorphous polymer films with intense diffraction peaks at around 43.8° and 73° exhibited the crystalline phase when doped with strontium silicate in polymer blend matrix. Structural information shows the stable existence of crystalline nanoparticles in the polymer matrix. Dielectric and electrical properties of these samples were studied in the frequency range from 100 Hz to 5500 Hz. Dielectric constant decreased with increase in frequency and changed to different values based on the loading of different weight percentage of nanoparticles. With increase in frequency, the dipolar ordering of polymer-polymer decreased and strengthens the polymer-nanoparticles interaction. Polyvinyl alcohol with 3-wt% of poly ethylene glycol showed the low dielectric constant and dielectric loss as less than 0.03 confirms their improved dielectric properties. Hence, this composition can be used as a better insulating polymeric nanodielectric material which finds application in packaging of nanoscale electronic devices to have better electromagnetic shielding.

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1. Introduction

There is a huge demand for the Multifunctional materials to meet the fast growing technological needs [1–7] Silicates (SiO₂) based nanomaterials (NMs) [8–10] have showed better role in the fields of optoelectronics [11,12], electrical insulation [13,14], advance battery [15,16], and fuel cells [17] applications because of their physical and chemical stability. Further, silicates are cheap and available in enormous; further in nano-regime, different properties exhibited were because of increased surface to volume ratio and the quantum confinement effects. Because of their ability to convert near IR-light into strong visible light [18], they can be used

in phosphor based lamps [19], Solar cells [20], Biological imaging and Medical-Dosimetry [21]. Thin films of nanocomposites (NCs) blended with both organic and inorganic compounds are in demand for the effective insulation of small-scale devices during packaging. Inorganic and organic materials based polymer nanocomposite (PNC) films where the polymer matrix filled with NMs significantly changes the strength, morphology etc helps in tailoring the various requirements in the fields of automobile, coatings, packaging materials, electronics and optical devices, aerospace, EMI shielding, drug delivery, sensors, medical and consumer devices etc. [22]. Polymers having high dielectric constant can be used for applications such as film capacitors, artificial muscle, while the ones with low dielectric constants are used in the field of capacitors and dielectric material with low dielectric

E-mail address: darukap@bmsit.in (B. DarukaPrasad)

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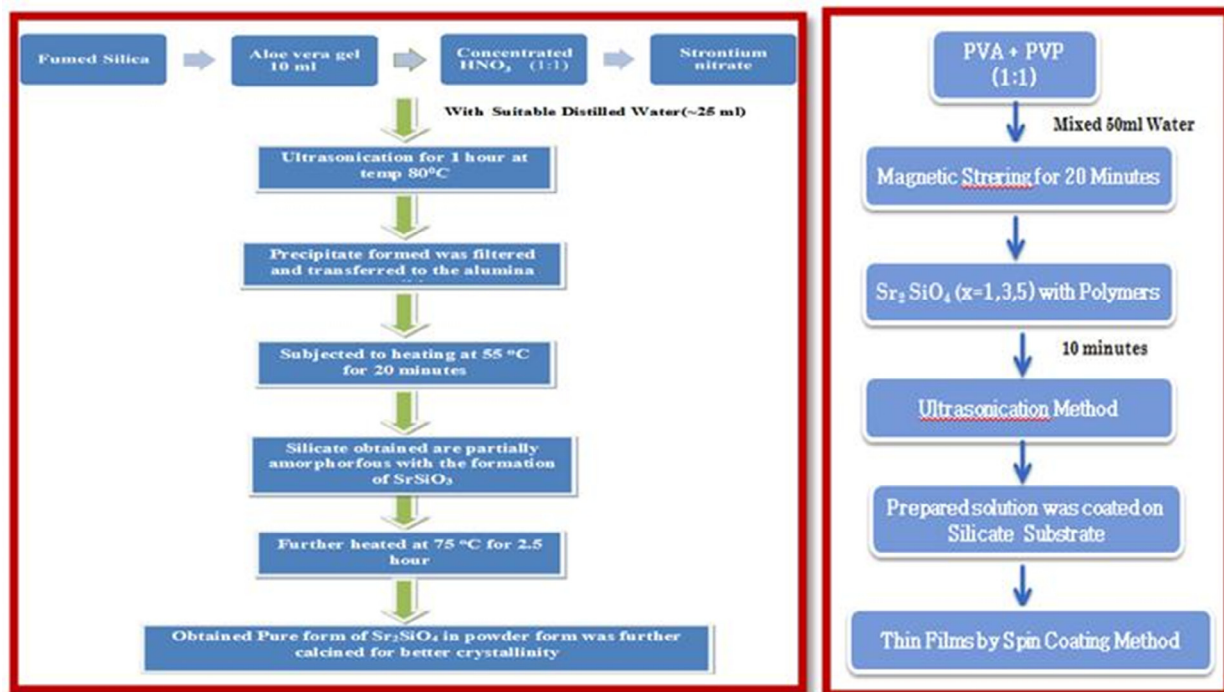


Fig. 1. Flow charts for the preparation of Strontium silicate NPs and the thin film of polymer- PNCs.

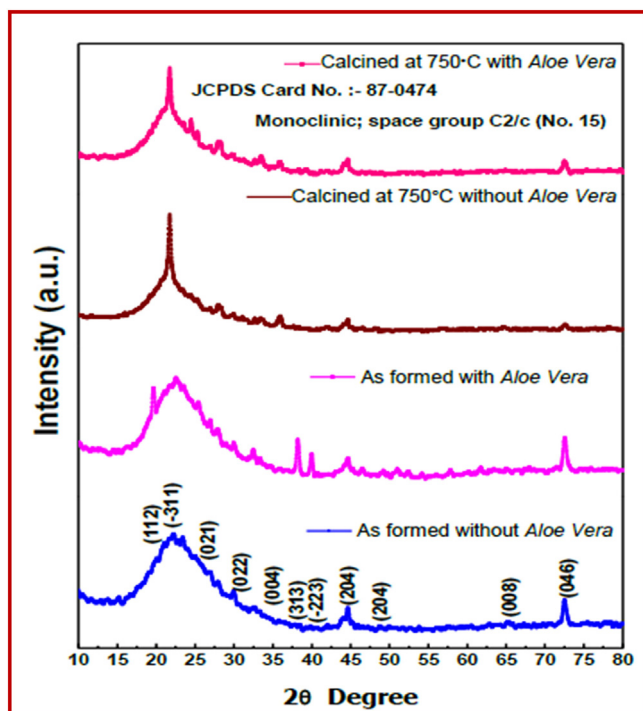


Fig. 2. PXRD profiles for the prepared Sr₂SiO₄ NPs with and without A.V. gel.

constants are used in the field of capacitors and dielectric material. Particular interest is on the application of polymers as insulating materials for high-voltage apparatus such as transformers, electrical machines and underground cables. Ionic radii of Sr²⁺ is 1.18 Å whereas for Si⁴⁺ is 0.4, hence doping of Sr²⁺ makes the SiO₂ matrix stronger and stable due to increased ionic radii, then helps the polymer composites also to behave differently. Polyethylene glycol

(PEG) has hydroxyl groups with electron donors which can be taken as advantage to enhance the further stronger in the prepared PNCs to make them better insulating material. This article reports the morphological, structural and dielectric properties of the Polyvinyl alcohol and poly vinyl propylene films prepared by the modified ultrasonication followed by spin coating method. Incorporated strontium silicate NPs with different weight percentage to these polymer matrices were studied comparatively and concluded with the best composition for the EMI Shielding application.

2. Experimental methods

PNC materials with varied Sr₂SiO₄ (1 to 5 wt%) named as PPO, PP1, PP2 and PP3 and PNCs with varied PEG (1 to 5 wt%) and fixed 3 wt% of Sr₂SiO₄ NCs named as PPP0, PPP1, PPP2 and PPP3. Method of preparation was adopted based on the reported literature elsewhere along with slight modifications in the percentage of composition [23,24]. Solution combustion method followed by ultrasonication for the NPs preparation. Samples were subjected to calcination at 700 °C which can be claimed as the low temperature synthesis compared to the other reported same type of samples. Later, the polymers blend was prepared by taking the equal Wt% of different polymers. For the polymer liquid of specific concentration, NPs of 3 wt% was mixed and coated the same on glass substrate. All the chemicals procured are of analytical grade from sigma Aldrich. Stoichiometric quantities of fumed silica and strontium nitrate were mixed using magnetic stirrer along with concentrated nitric acid and 10 ml of Aloe Vera Gel. Further, the samples were mixed with 25 ml of distilled water and kept for ultrasonication at 80 °C for 1 h. white precipitate formed were transferred to alumina crucible at 55 °C for 20 min to obtained partially amorphous silicates to get pure crystalline material again the samples were heated to 75 °C at 2.5 h to obtained pure form of strontium silicate powder. Then two equal weight of amount organic polymers (50/50 wt%) PVA (polyvinyl alcohol) and PVP (polyvinyl

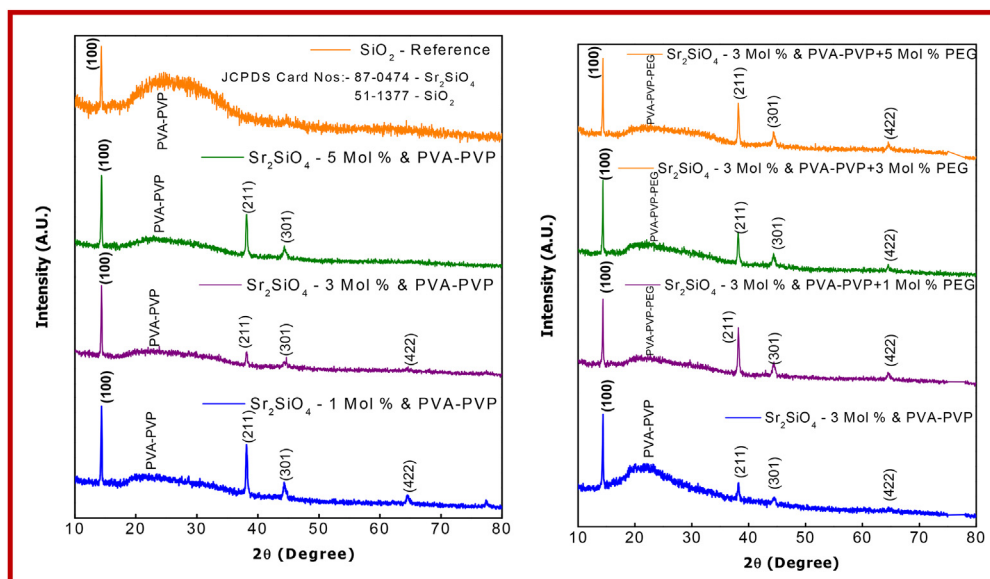


Fig. 3. PXRD patterns of the prepared thin film composites of Sr_2SiO_4 : PVA-PVP (a) with varying wt% of Sr_2SiO_4 NPs and without PEG and (b) with 3 wt% of Sr_2SiO_4 and varying wt% of PEG.

pyrrolidone) mixed with 50 ml of distilled water using magnetic stirrer for 20 min then add strontium silicate Sr_2SiO_4 , wt% $x = 0, 1, 3$ and 5 ultrasonication for 10 min prepared samples were coated on silicate substrate by spin coating method. Another samples were prepared by adding another organic polymer PEG (Poly ethylene glycol) at $x = 0, 1, 3$ and 5 coated on silicate substrate by spin coating method. The prepared PNC films heated for 100°C for one hour prior to characterization. Detailed preparation technique was as showed in the flow charts of Fig. 1. Crystallographic information of these thin films was characterized by X-ray diffraction (XRD) measurements in the 2θ range from 10° to 80° with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) by using a PAN analytical X'pert X-ray diffractometer. Dielectric and ac conductivity over the frequency range from 20 Hz to 1 MHz were obtained using Wayne Kerr 6500B Impedance analyzer. For obtaining these spectra, frequency dependent capacitance values of the PNC film loaded dielectric test fixture were measured in parallel circuit

Table 1

Estimated crystallite parameters of Sr_2SiO_4 NPs.

Samples name	Average particle size D (nm) Scherrer's method	Micro-strain ϵ
Sr_2SiO_4 as prepared & without <i>Aloe vera</i> gel	237	1.01
Sr_2SiO_4 as prepared & with <i>Aloe vera</i> gel	176	1.02
Heat treated Sr_2SiO_4 as prepared & without <i>Aloe vera</i> gel	67	1.10
Heat treated Sr_2SiO_4 as prepared & with <i>Aloe vera</i> gel	47	1.12

mode (Cp-Rp) at 1 V of source voltage. The dielectric and electrical spectra of the PNC films were determined at a fixed temperature (30°C) for the Sr_2SiO_4 ; 3 wt% containing PNC film. The measurement accuracy of the Cp and Rp values in the test frequency range (20 Hz to 1 MHz) is greater than 99.9%.

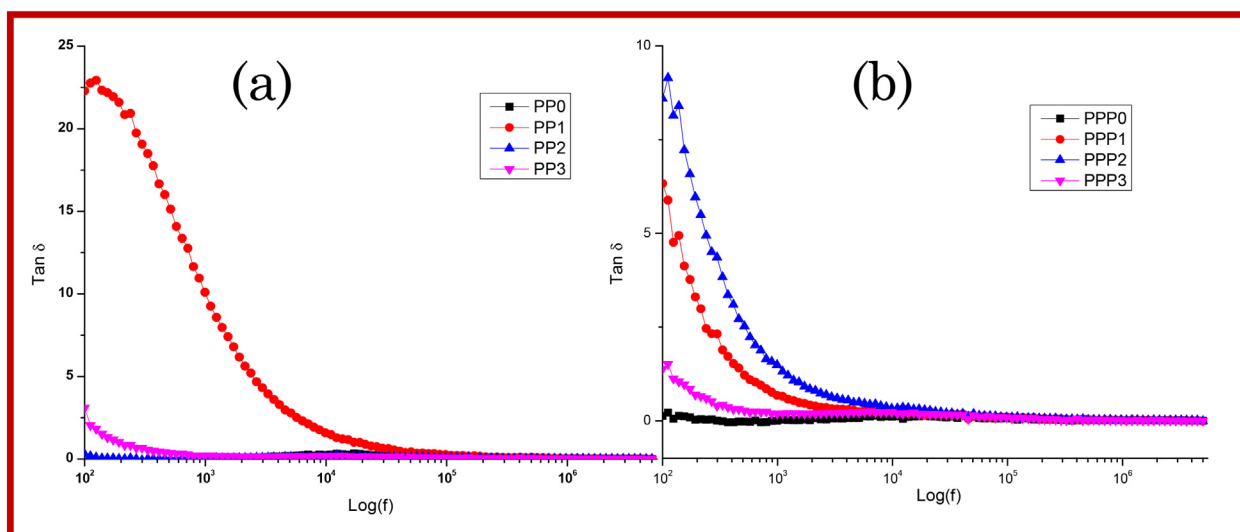


Fig. 4. Variation of dielectric loss (a) with varying wt% of Sr_2SiO_4 NPs and varying wt% of PEG with the fixed 3 wt% of Sr_2SiO_4 NPs.

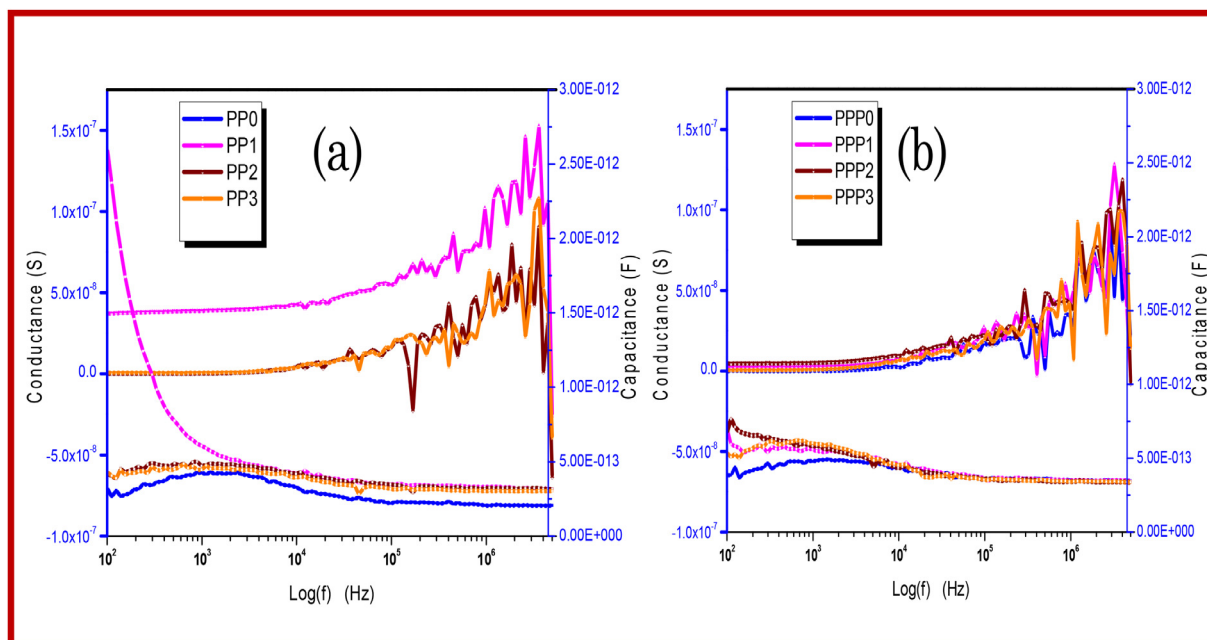


Fig. 5. Variation of conductance and capacitance (a) with varying wt% of Sr₂SiO₄ NPs and varying wt% of PEG with the fixed 3 wt% of Sr₂SiO₄ NPs.

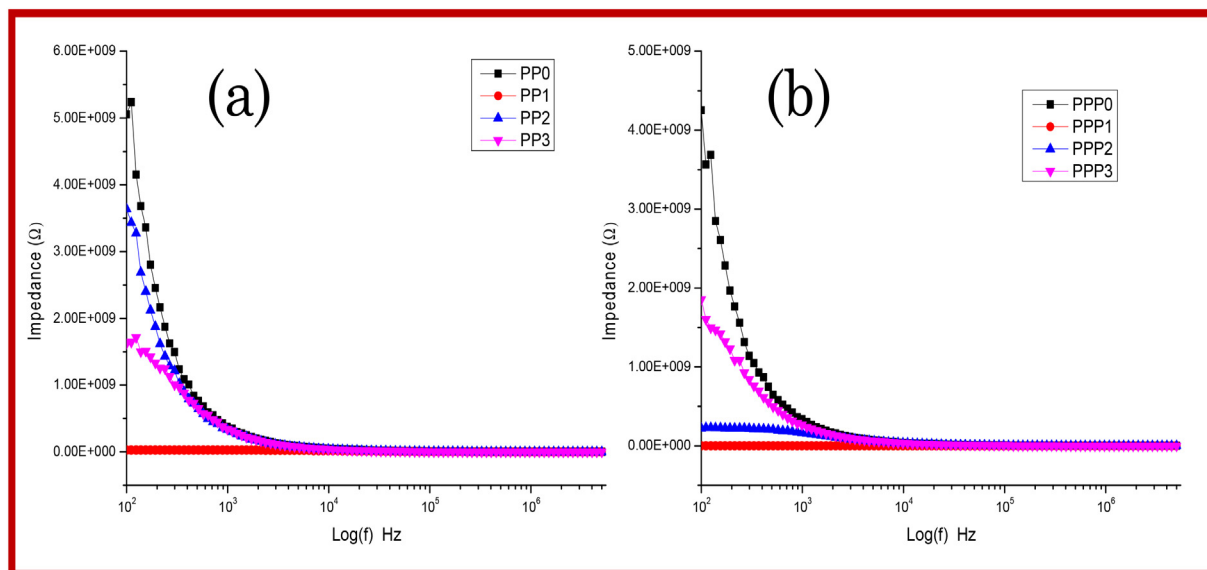


Fig. 6. Impedance variation for the prepared samples (a) with varying wt% of Sr₂SiO₄ NPs and varying wt% of PEG with the fixed 3 wt% of Sr₂SiO₄ NPs.

3. Results and discussion

Fig. 2 shows the PXRD patterns of the Sr₂SiO₄ NPs confirms the formation without any impurities. Further, the use of A.V. gel helped in decreasing the crystallites size and also replacing the organic fuels with A.V. gel makes the preparation technique as green approach. A.V. gel consists of many polysaccharides such as pectin; cellulose etc., helps the dispersion of NPs in the matrix of these polysaccharides and protein chains more effectively to obtain chemically arranged regular patterns / superstructures. Prepared samples confirmed as Sr₂SiO₄ matches with the JCPDS card no. 87-0474 obtained by using Crystallographica search match version 2.0.2.0 of Oxford Cryosystems software. Fig. 3(a) shows the XRD pattern for the SiO₂ as a reference substrate with JCPDS card no. 51-1377 and (PVA-PVP)-x wt% Sr₂SiO₄ NC films (PP0 – PP4)

and Fig. 3(b) shows the XRD patterns for the (PVA-PVP)-3 wt% Sr₂SiO₄ – x wt% of PEG (1–5 wt%) PNC films. According to the literature [22], the semicrystalline PVA-PVP-PEG film exhibits broad peak in the range of 19° to 23.5° corresponding to little changes in the PVA peaks positions, their intensities, and widths with the incorporation of Sr₂SiO₄ NPs in the blend polymer matrices. The values of crystallographic parameters such as crystallite size 'D' and microstrain obtained with Williamson-Hall method were tabulated in Table 1. It can be noted that the D values for NPs prepared using A.V. gel is less compared to NPs prepared without A.V. gel.

The frequency dependence of dielectric loss tangent ($\tan(\delta) = \epsilon''/\epsilon'$) of the (PVA-PVP)-x wt% Sr₂SiO₄ films at 3 wt% of Sr₂SiO₄ nano-filler and also at various concentrations of PEG were shown in Fig. 4. The highest $\tan(\delta)$ for the sample with 1 wt% of Sr₂SiO₄ and with the incorporation of PEG of 3 wt% to the NC again brings

the $\tan(\delta)$ value to higher due to increased hydroxyl ions concentration and also the proper dispersion of Sr_2SiO_4 NPs (Fig. 4(a)). The trend shows the smooth variation in the profiles with increase in frequency follows the Koop's Model [23]. At lower frequency, the dipoles able to follow the applied frequency perturbations, but at higher frequencies, the dipoles not able to follow the increased frequency of perturbations. Hence, it leads to decrease in dielectric constant and also the dielectric loss tangent. But the obtained loss tangent is very high for the prepared samples compared to reported data in the literature confirms the potentiality of the samples towards the electrical insulation applications [23,24].

The linear increase in $\tan\delta$ values of these PNC films with the decrease of frequency in the lower frequency region of the spectra is attributed to dominant contribution of the interfacial polarization (IP) effect (i.e., the Maxwell–Wagner effect) which is commonly exhibited in the composite and hybrid dielectrics. Further, the dispersion behaviour of $\tan\delta$ values with the increase of filler concentration in the PNC films reveals that the interaction of Sr_2SiO_4 NPs with the polymer chains initially promotes the parallel dipolar alignments of the functional groups present in the polymers repeat units when the loading of Sr_2SiO_4 NPs is raised up to 3 wt%, but at 5 wt% Sr_2SiO_4 , the polymer–nano particle interactions were progressively less effective in the enhancement of dielectric polarization which may be due to some aggregation of nano filler particles. It can be read from Fig. 4 that at a fixed Sr_2SiO_4 concentration the increase in $\tan\delta$ values is about 23 to 8, when the frequency value is in the range of 100 Hz to 500 Hz. The low values of $\tan\delta$ at 1 MHz for these PNC films confirm that the prepared materials can be a potential candidate for the low-permittivity nanodielectrics commonly used in the design of advanced flexible microelectronic devices, and also in the fabrication of energy storing capacitor at radio frequencies as demonstrated for numerous PNC materials on the basis of their low $\tan\delta$ values above 100 kHz.

The spectra of complex electrical conductivity ' σ ' and capacitance ' C ' with respect to a.c. are depicted in Fig. 5. Order of the ' σ ' and ' C ' are in the range of 1.4×10^{-7} to 3.8×10^{-8} and 0.1 to 0.07 μF at 100 Hz and at higher frequency the capacitance increases to the order of $1 \times 10^6 \mu\text{F}$. Fig. 6 shows the variation of impedance to the order of $1 \times 10^9 \Omega$ at 100 Hz which is the highest value as reported from this publication. Further, it is noticed that on the logarithmic scale the $\tan(\delta)$ and impedances values decrease almost linearly with the increase of frequency, whereas the ' σ ' obeys the power law relation separately in the low and high frequency regions of these PNC films. The high impedance values of the prepared samples confirms that the energy loss per cycle in these materials is relatively small, and therefore these films can be used as nano dielectric and insulator in the fabrication of energy storing devices and in electronic packing applications.

4. Conclusions

Strontium silicate nanoparticles were prepared by solution combustion followed by ultrasonication method. Polymer nanocomposites films were prepared by spin coating method on the glass substrate. Addition of strontium silicate had a significant influence on the properties of the selected polymers blended matrix. Prepared samples showed semi-crystalline nature and the crystalline phase was observed due to strontium silicate nanoparticles. Powder X-ray diffraction patterns indicates that the selected polymers mixture were compatible and exhibit miscible structure. The frequency dependent dielectric loss of these samples initially decreased with the loading of nanoparticles up to 3 wt% and after

that it remains constant with further increase of nanofiller concentration. This relates to the changes in the dipolar ordering of polymer–polymer structures. The dielectric loss values at radio frequencies range remains much lower than 0.03, confirming the suitability and can be used as low-permittivity flexible polymeric nanodielectrics. Electrical conductivity was found in the order of 10^{-12} S/cm indicating their high electrical insulation behaviour. For the further confirmation of the nanolevel of the samples, SEM and TEM analysis were under progress. Therefore, prepared materials could be used for the insulation purpose in the packaging of Nano devices.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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