Magnetic field driven dielectric relaxation in non-magnetic composite medium: A low temperature study

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HIGHLIGHTS

• Dielectric relaxation is observed in PANI and functionalized MWCNT composites by applying magnetic field.
• PANI/fMWCNT composites are an inhomogeneous and highly mismatched conductive material at low temperature.
• Dielectric relaxation frequency shifts by varying space charge polarization at interface of PANI/fMWCNT and temperature.
• Negative dielectric loss is observed below the dielectric relaxation frequency.
• Relaxation frequency does not shift with increasing magnetic field.

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ABSTRACT

The frequency dependence of dielectric constant for composites of polyaniline (PANI) and multi-walled carbon nanotube (MWCNT) with different degree of functionalization is studied at low temperature (down to 4.2 K) and magnetic field (up to 3 T) applied both in parallel and perpendicular direction of ac electric field. A relaxation phenomenon is observed in all the MWCNT/PANI composites by applying magnetic field in both the directions, below $10^3$ Hz. However, PANI does not show any relaxation peak with applied magnetic field in either direction. The relaxation peak frequency does not depend on the strength of magnetic field but it varies with temperature and degree of functionalization of MWCNT in composites. This relaxation phenomenon occurs due to the inhomogeneity of the medium of two highly mismatched conductive materials at low temperatures. The results are explained in the light of Parish and Littlewood theory about magnetocapacitance in nonmagnetic composite.

1. Introduction

The coupling between magnetization and dielectric constant is a very well-known phenomenon in multiferroics which have potential application in magnetic field sensors, multi-state memory devices [1] and so on. This coupling is manifested by several ways in different materials. For instance, BaTiO$_3$–CoFe$_2$O$_4$ composite exhibits the magnetoelastic coupling by the strong elastic interaction between these two phases [2]. The external magnetic field affects the magnetization, and thus influences the dielectric properties of these materials, known as magnetodielectric (MD) effect. However, MD effect can be observed without the coupling between these two. The interfacial polarization [3] at the grain boundaries can also induce the MD effect. There are few reports where the interfacial polarization and magnetic field give the dielectric relaxation [4]. For example, La$_{2/3}$Ca$_{1/3}$MnO$_3$ shows the magnetic field dependence of the dielectric constant above ferromagnetic to paramagnetic transition temperature, which is manifested by the interfacial polarization [5]. Anomalous dielectric relaxation is observed in doped silicon by applying magnetic field perpendicular to the ac electric field [6]. This effect is differentiated from usual Debye like dielectric relaxation which occurs due to parallel magnetic field and is explained by the effect of Lorentz force on charge polarization. Parish and Littlewood have proposed that dielectric relaxation can be observed in inhomogeneous medium without magnetism, where the inhomogeneity gives rise to magnetic field dependent dielectric relaxation due to the mixing between real and imaginary part of the dielectric constant [7].

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2. Methods and characterization

The MWCNT (multiwalled; average outer diameter: 10 nm, inner diameter: 4 nm; denoted as fMWCNT) is functionalized by concentrated 
H₂SO₄ (98%; Molarity: 18) and HNO₃ (vol. ratio 3:1). The MWCNT was immersed into the mixture of concentrated acids and stirred for different hour. Then it was washed with DI water and neutralized the pH, and dried in vacuum oven. The degree of functionalization is varied by changing the duration (hour; denoted by h; we have prepared particularly 6 h, 48 h and 96 h) of functionalization using acids [10]. Composites of 10 wt % MWCNT and fMWCNT with PANI are prepared by following the in-situ polymerization technique [11]. In this process, we added 2 ml aniline monomer with 40 ml 1 M HCl and required amount of MWCNT/fMWCNT to make 10 wt percentage composites and sonicated for 1 h to obtain well dispersed suspensions. Then 400 mg Ammonium per sulfate (APS) with 20 ml 1 M HCl solution was added dropwise into the above suspension at room temperature.

The composites are collected in powder form and then the samples were made in the form of pallet with radius 10 mm and thickness 1.35 mm for the measurement of impedance spectroscopy. The dielectric measurements are performed keeping the samples in between two silver plates, and putting inside the Janis cryostat equipped with superconducting magnet. During the measurement, the magnetic field is applied in both perpendicular and parallel directions of applied ac electric field by altering the orientation of the sample with respect to the external magnetic field. The dielectric measurements are performed by using Agilent 4294A high precision impedance analyzer.

2.1. SEM

Scanning electron microscopic (SEM) image of 96 h fMWCNT/PANI composite is shown in Fig. 1. We can observe that PANI is adsorbed on the surface of fMWCNT. The PANI coated fMWCNT is distributed randomly in the system. The connectivity among fMWCNT and PANI gives the high conductivity of the composites.

The samples are also characterized using Raman and FTIR spectroscopy which are discussed in Ref. [12]. In summary, the Raman peak intensity at 1337 cm⁻¹ (corresponds to C–N⁺⁺ bond stretching) is increased in fMWCNT/PANI composite compared to MWCNT/PANI composite and enhancement of peak intensity corresponding to C–N stretching in FTIR spectra indicate that more number of polaron formation and polar interaction due to functionalization of MWCNT increases in the composites. The polar interaction between fMWCNT and PANI increases significantly with the increasing duration of functionalization.

X-ray photo emission spectroscopy (XPS) measurement indicates that chemical functionalization attaches different functional groups (−C=listen –O, –COOH) on the surface of MWCNT and their percentage varies with the variation of degree of functionalization [10,11].

3. Results and discussions

The study of dielectric properties of materials give the great insight about the microscopic charge relaxation in grains and grain boundaries. The effect of magnetic field in dielectric properties provide the information about multiferroic behaviour of the materials. The real and imaginary parts of dielectric constant are calculated from measured impedance by using the formula; real part ε’ = 1/C₀(1/Z’² + Z’’²) and imaginary part ε” = 1/C₀(1/Z’²) where C₀ = A/2πt is the geometrical capacitance of the sample, A: Area and t is the thickness. In Fig. 2, the
variation of real part of dielectric constant ($\varepsilon'$) with frequency is shown for PANI at different temperatures by applying magnetic field parallel to the current. The error of this measurement is 0.08% in this frequency range (Taking a typical value; at $T = 50$ K and magnetic field $0 T$, $\varepsilon'$ will be 17887.483 ± 14.3). We can observe that $\varepsilon'$ decreases with increasing frequency and is constant at high frequency. The decreasing behaviour represents the dipolar relaxation in the system. The dipolar relaxation frequency shifts towards higher value with increasing temperature. All the curves for different applied magnetic field merge with one another at a constant temperature indicating there is no effect of magnetic field in dielectric properties and the electrical polarization behaviour of PANI.

The variation of $\varepsilon'$ with frequency is shown in Fig. 3 for different degree of functionalized fMWCNT/PANI composites by applying magnetic field in the parallel direction of ac electric field at temperature 30 K. We can clearly observe that a relaxation in $\varepsilon'$ appears due to the magnetic field in all the composites at low frequency ($< 10^3$ Hz). However, this relaxation behaviour is not present in the absence of magnetic field ($H = 0$ T). This behaviour is completely dissimilar to the PANI. The relaxation frequency does not vary with increasing magnetic field for composites at constant temperature; however, it shifts towards higher frequency with increasing the degree of functionalization of MWNT in different composites. The relaxation peak frequency increases from 63 Hz to 160 Hz when the duration of functionalization increases from 0 h to 96 h. The functionalization of MWCNT enhances the interfacial polarization and increases the boundness (attachment of charge carrier with other atom, related to the spring constant of potential which holds the charge in place) of charge carrier between fMWCNT and PANI [13]. The enhanced boundness of charge carriers help to relax fast with applying magnetic field and relaxation frequency shifts towards higher value. This coupling of dielectric constant and magnetic field is not due to the presence of magnetic relaxation of either PANI or fMWCNT, since PANI manifests the paramagnetism [14] and MWCNT shows diamagnetic behaviour at low temperature [15]. In our case, the interfacial polarization between fMWCNT and PANI is affected by the magnetic field and give rise to the dielectric relaxation at low frequency.

This magnetic field relaxation behaviour in composites can be explained by Parish and Littlewood theory. At low temperature, PANI becomes highly resistive but MWCNT is very conducting (conductivity difference $\approx 10^7$–$10^8$ S/cm). The mismatch of conductivity of two dissimilar dielectric medium creates interfacial polarization which is affected by the magnetic field. PANI contains relatively high and low conductive regions depending on the doping. The charge transport between these high and low conductive regions creates the electrical polarization and shows the finite dielectric constant. At low temperature, PANI behaves like a homogeneous system of almost similar conductive regions. In this case, external magnetic field does not affect the dielectric constant and no relaxation is observed at low frequency. At high temperature the electrode polarization might contribute to the dielectric relaxation phenomenon and induce magnetic field dependence. For proper comparison, we have used same silver plate electrodes for pure PANI and the composites. However, magnetic field dependence is not observed in pure PANI. Hence, contribution from electrode towards magnetic field dependent relaxation can be ruled out.

The electrode polarization (EP) increases significantly for conducting samples due to the piling up highly mobile charge carriers at the interface of electrode and sample. These charge carriers are deflected by Lorentz force, when we apply static magnetic field. This deflection hinders the piling up charges at the interface of electrode and samples. Therefore, the dielectric constant (electric polarization) decreases by applying magnetic field (suppress EP), and it is observed in transformer oil-based magnetic nanofluid thin layer [16]. However, the magnetic field driven dielectric relaxation is not observed due to the electrode polarization. The EP is highly controlled by the electrode work function, conductivity difference between electrode and sample, electrode area and topography, and type of contact [17]. In our case, the dielectric constant decreases by applying magnetic field (below relaxation frequency) which is similar to the previously reported results. In addition, the dielectric relaxation arises by applying magnetic field which is not due to the electrode polarization effect. It is the bulk property of the composites and relaxation can be explained by PL theory qualitatively.

The variation of $\varepsilon'$ with frequency of 96 h fMWCNT/PANI composite is shown in Fig. 4 for different temperatures. The relaxation behaviour is observed at all the temperatures and relaxation frequency shifts towards lower frequency with increasing temperature. The thermal energy of charge carrier increases when temperature increases and deflect longer distance due to enhanced Lorentz force, and charge carriers take longer time to relax with magnetic field i.e. the relaxation process becomes slow. With increasing temperature, $\varepsilon'$ shows negative value by applying magnetic field below the relaxation frequency. The space charge are separated by magnetic field, and these charges can not follow the vibration frequency of ac electric field and shows opposite phase. Hence, the negative value increases with increasing magnetic field.

In Fig. 5 the relaxation behaviour of $\varepsilon'$ is shown at 30 K by varying the magnetic field. The difference between dielectric constant with magnetic field and without magnetic field, for both real and imaginary parts ($\Delta \varepsilon' = \varepsilon'(H) - \varepsilon'(0)$ similarly, $\Delta \varepsilon''$) are plotted in Fig. 5 (a) and (b), respectively. It is important to note that the relaxation frequency is not shifted with increasing magnetic field, but the width and height of the peak are increased. It can be speculated that the magnetic field excites more number of charge carriers to relax at the same frequency, and does not change the relaxation time of the charge carrier.

The variation of dielectric loss tangent ($\tan \delta$) with frequency and applied magnetic field is shown in Fig. 6 (a). Dielectric loss is calculated as $\tan \delta = \frac{\varepsilon''}{\varepsilon'}$. We can observe that $\tan \delta$ value decreases sharply at the relaxation frequency and shows negative below this frequency [see the inset graph]. This is contrast to the usual dielectric relaxation where the dielectric loss decreases with increasing frequency with positive value throughout the frequency range. The negative dielectric loss can be explained by proposition of Axelrod et al. for space charge polarized systems [18,19]. In our case, the applied magnetic field separates...
positive and negative space charge which are accumulated at the interface of fMWCNT and PANI, and store energy. This energy is released due to the recombination of these charges by applying ac electric field at low frequency. Applied high value of magnetic field increases the separation and decreases the recombination probability, hence less negative tanδ is observed for increasing magnetic field and therefore reduces the conductivity.

The ac conductivity, \( \sigma_{ac}(\omega) = \omega \varepsilon_0 \varepsilon \tan \delta \), is plotted in Fig. 6 (b). The ac conductivity and tanδ decrease sharply with increasing magnetic field at the resonance frequency. The space charges are separated by the applied magnetic field which decreases the hopping probability of the free charges in the composite.

The dielectric relaxation behaviour of PANI and fMWCNT/PANI composites is also measured by applying magnetic field in the perpendicular direction of applied ac electric field and plotted in Fig. 7. No relaxation peak is observed for PANI at low frequency for applying magnetic field up to 5 T. The MWCNT/PANI exhibits relaxation and the peak intensity increases with increasing magnetic field. However, the relaxation peak frequency does not shift position with magnetic field similar to the applied field in parallel direction. The relaxation behaviour of MWCNT/PANI composite in the both parallel and perpendicular direction imply the inhomogeneity of the composite system is distributed isotropically in all directions e.g. 3D nature of the system. The MWCNT makes network in the PANI and creates interfacial polarization which are isotropically distributed in 3D fashion. We can also observe that another relaxation appears at higher frequency for perpendicular field. This indicates the higher energetic relaxation in the system.

Our result is very dissimilar to the doped silicon and RGO composites with different polymers. In doped silicon, Brook et al. observed the anomalous dielectric relaxation for perpendicular direction however it is usual Debye like for parallel field [6]. They have explained that polarized charge carriers feel the Lorentz force due to applied magnetic field in perpendicular direction and modify the polarization. The relaxation peak frequency shifts with increasing magnetic field for a constant temperature. In our case, there is no shift in relaxation peak by increasing magnetic field, and can’t be explained completely by considering this model. On the other hand, Parish and Littlewood (PL) proposed that there is possibility to observe the dielectric relaxation [we have mentioned here ‘relaxation’ as it takes place at low frequency though PL used the term ‘resonance’] in 2D inhomogeneous medium and interface between different conductive materials [7, 20] by applying magnetic field without magnetism present in the system. The dielectric relaxation is observed due to the mixing of real and imaginary part of the dielectric response occurred by inhomogeneity of the medium. The relaxation peak is observed for the condition \( \beta \tau = 1 \), where \( \beta = \mu H \) (\( \mu \) is the mobility of charge carrier and H is magnetic field) and \( \tau = \rho \varepsilon / \omega \) (\( \rho \) is resistivity). Considering the resistivity variation with temperature is like \( \rho = \rho_0 \exp(\Delta/kB) \); \( \Delta \) is activation energy, the relaxation condition modifies to \( \ln(\omega_\tau) = \frac{1}{kT} \). Assuming no variation of dielectric constant with temperature, modified relaxation condition predicts that the relaxation peak shifts towards higher frequency with increasing temperature for a constant magnetic field, and it should shift towards lower frequency with increasing magnetic field for a constant temperature.

In case of our sample, the dielectric resonance peak shifts towards lower frequency with increasing temperature for a constant magnetic field which is the opposite behaviour of the prediction. PL model also tells that the dielectric resonance enhances for the current flow in the perpendicular direction of the magnetic field. In the MWCNT/PANI composites, MWCNT is distributed in all the direction (3D nature) and finds the perpendicular current flow at the interface with respect to the magnetic field for which we have observed the dielectric relaxation for both parallel and perpendicular direction.

**Fig. 4.** Variation of real part of dielectric constant with frequency for 96 h fMWCNT/PANI composite applying magnetic field at different temperature (a) 4.2 K, (b) 10 K, (c) 20 K and (d) 30 K. The relaxation shifts towards lower frequency with increasing temperature.

**Fig. 5.** The difference between with and without applying magnetic field of (a) real and (b) imaginary parts of dielectric constant as a function of frequency for 96 h fMWCNT/PANI composites at 30 K.
4. Conclusion

In summary, we studied the dielectric properties of non-magnetic fMWCNT/PANI composite with varying functionalization, temperature and magnetic field. We have found that the magnetic field has significant effect on the origin of dielectric relaxation. The dielectric relaxation is observed for all the composite at low frequency in the presence of magnetic field. The results are explained with the essence of 2D PL theory. However, it’s not fully explained by this theory. An extended version of this theory in 3-dimension is required to understand the magnetic field dependent dielectric relaxation. Interestingly, the dielectric relaxation due to inhomogeneity of the system is studied extensively in this fMWCNT/PANI system. We believe this study will help to pave the way of this phenomenon in other similar composite systems.

CRediT authorship contribution statement

Krishna Prasad Maity: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. Ananya Patra: Investigation, Validation, Writing – review & editing. Narendra Tanty: Investigation, Validation, Writing – review & editing. V. Prasad: Supervision, Funding acquisition, Writing – review & editing.

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.

Data availability

Data will be made available on request.

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