Room-Temperature Ferromagnetic $\text{Sr}_3\text{YCo}_4\text{O}_{10+\delta}$ and Carbon Black-Reinforced Polyvinylidene Fluoride Composites toward High-Performance Electromagnetic Interference Shielding

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Supporting Information

ABSTRACT: In this study, we fabricated composites of conducting carbon black (CB), room-temperature ferromagnetic $\text{Sr}_3\text{YCo}_4\text{O}_{10+\delta}$ (SYCO) and polyvinylidene fluoride (PVDF) by the solution mixing and coagulation method for the first time. During the nucleation process of PVDF, the presence of SYCO and CB individually facilitates the crystallization of polar $\beta$ and semipolar $\gamma$ phases along with the nonpolar $\alpha$ phase in PVDF. The dc electrical conductivity of PVDF raised from $1.54 \times 10^{-8}$ to $9.97$ S/m with the addition of 30 wt % of CB, and it is nearly constant with respect to the SYCO content. The PVDF/CB/SYCO composites (PCS) possess high permittivity and its variation is in accordance with the content of polar phases in PVDF. Moreover, the complex permittivity and permeability spectra from 10 MHz to 1 GHz indicate that the dielectric loss dictates over magnetic loss in these composites. The electromagnetic interference shielding effectiveness (EMI SE) of PCS composites is higher than that of PVDF/CB and PVDF/SYCO composites in the 8.2–18 GHz region. Addition of SYCO in the PVDF/CB matrix enhances shielding by dominated absorption with minimal reflection. The analysis of the shielding mechanism suggests that in addition to conducting and magnetic losses due to CB and SYCO, respectively, the synergy among CB, SYCO, and PVDF promotes shielding by matching the input impedance to that of free space, enhancing multiple internal reflections from SYCO and subsequent absorption by CB, eddy current losses, dielectric damping losses, interfacial polarization losses, and so forth. These different mechanisms result in an enhanced EMI SE of 50.2 dB for the PCS-40 composite for a thickness of 2.5 mm.

INTRODUCTION

Ever since the electronic revolution, electronic devices have become an indispensable part of common man’s life. The rapid increase in the usage of such devices as well as instruments dealing with electromagnetic (EM) waves generates a serious issue of EM interference (EMI). Scientists have turned their attention toward EMI as the devices began to grow smaller and smarter. Presently, with respect to the necessity and application, different frequencies in the microwave frequency bands are allocated for various purposes, especially for communication. As a result of the extensive use of such EM devices, tremendous amount of unwanted energy is radiated into the surroundings. Because of this, all the organisms as well as the devices are engulfed into the exposure to this radiation atmosphere. Owing to this long-term exposure to such radiation, adverse biological effects like breaking of DNA, weakening of biological immune system,¹ leukemia, cancer²,³ and so forth and technological effects like malfunctioning of devices, information leakages and so forth are encountered. Shielding is one of the best remedies to avoid or rather reduce the problem of EMI, mainly, as its effectiveness depends on the performance of the material used as shield and because it can be finely tuned or tailored by availing current advanced technologies.⁴–⁸

The underlying criteria for choosing an effective shielding material rely not only on its ability to safeguard the devices from external stray signals but also on its capability to optimize the emissions from the devices to a lower value. These can be achieved either by reflecting and/or absorbing the EM energy. Reflection, which occurs prior, is the result of significant interactions of EM signals with the charge carriers present in the shielding materials. On account of this, the shielding...
materials are expected to be electrically conducting. Absorption, which is considered as an ecofriendly way to shield EM radiation occurs as soon as the signals enter into the shield, as a consequence of the interaction of the radiation with the electric and magnetic dipole fences in them.\(^8\) In order to enter the radiation into the material, it should have a matching input impedance to that of free space impedance. Generally, the EM energy attenuation inside the materials mainly arises due to the dielectric loss, magnetic loss, and their synergistic effect. The dielectric loss depends mainly on the conductivity loss and relaxation loss. Under an alternating EM field, the dipoles present in the defective sites and interfaces undergo oscillation and results in relaxation loss. In heterostructure, dipoles present in the defective sites and interfaces undergo oscillation and results in relaxation loss. Under an alternating EM field, the dipoles present in the defective sites and interfaces undergo oscillation and results in relaxation loss. Under an alternating EM field, the dipoles present in the defective sites and interfaces undergo oscillation and results in relaxation loss. Under an alternating EM field, the dipoles present in the defective sites and interfaces undergo oscillation and results in relaxation loss.

\[ \delta_p \] polar and antipolar analogs of \( e \) due to the dielectric loss, magnetic loss, and their synergistic effect losses. In addition to these, multiple internal reflections that occur at the interfaces or defect centers within the material also contributes to EMI shielding. However, most of the materials, which suffice the requisiteness of necessary electric and magnetic properties, lack mechanical flexibility which withholds their direct usage in EMI shielding applications. Under such circumstances, addition of suitable polymer materials provides the mechanical flexibility, compressibility and so forth and additionally, helps to mold the shield into desired shapes. The polymer selection is solely based on one’s requirement. Thus, an efficient composite material can be fabricated by adding one or more filler materials having appropriate electric and magnetic properties into a suitable polymer matrix.

Innumerable combinations were studied with different permutations of polymers, conducting materials, and magnetic materials intending special applications. Among the choice of polymers, polyvinylidenefluoride (PVDF) is a technologically predominant thermoplastic with largest piezo- and pyroelectric coefficients along with outstanding chemical and thermal resistivity. Insulating and nonmagnetic PVDF is widely used for EMI shielding applications by adding suitable fillers bearing these properties because these are the imperative requirement for EM wave attenuation. PVDF exists in five polymorphic forms \((\alpha, \beta, \gamma, \delta, \text{and} \varepsilon)\), of which \(\alpha, \beta, \text{and} \gamma\) are the most important forms. A nonpolar \(\alpha\) phase with a monoclinic unit cell is the commonly existing phase with trans-gauche (TGTG) chain conformation while the highly polar \(\beta\) phase which crystallizes to an orthorhombic unit cell has all trans (TTTT) conformation. The semipolar \(\gamma\) polymorph formed under high pressure and temperature also has an orthorhombic unit cell but has \(T_{\alpha}GT_{\gamma}G\) chain conformation. The remaining two phases \(\delta\) and \(\varepsilon\) are the polar and antipolar analogs of \(\alpha\) and \(\gamma\) forms, respectively.\(^9\)\(^-\)\(^11\)

Recently, active research studies are being carried out to nucleate PVDF in the \(\beta\) polymorphic phase, following its polar nature which makes it suitable for piezoelectric, pyroelectric, and dielectric applications. Incorporation of organically modified nanoclay,\(^9\) graphene sheets,\(^12\) functionalized multi-walled carbon nanotubes,\(^9\)\(^14\) metal nanoparticles,\(^15\)\(^16\) and ferrite nanoparticles into the PVDF matrix is often traced out methods for achieving \(\beta\) crystallization. For the first time, Deepa et al. studied the effect of particle size of a double perovskite compound \(La_{0.5}Sr_{0.5}CoO_3\) \((\text{LSCO})\) on the phase crystallization of PVDF and the resulting dielectric properties of PVDF/LSCO composites.\(^17\) Even though there were studies on the variation of dielectric properties with PVDF phase change,\(^18\) its influence on EMI shielding is not investigated so far.

The prime concern for a good magnetic filler always goes to ferrite materials owing to their better magnetic loss. There have been extensive studies on the EMI shielding performance of ferrite-added polymer composites and to investigate their size and shape dependence on shielding.\(^19\)\(^-\)\(^24\) Most of them reveal dominated microwave absorption mechanism rather than reflections hence are useful for microwave absorbing materials applications like in radar stealth technology. The fabrication of hybrid composites of conducting and magnetic materials is a widely adopted strategy to optimize microwave absorption performance and bandwidth. There are many reports on graphene-based hybrid materials incorporated with different ferrite materials. NiFe\(_2\)O\(_4\) clusters in nitrogen-doped graphene\(^25\) and Fe\(_3\)O\(_4\) magnetic filler-incorporated reduced graphene oxide \((\text{rGO})\) composites\(^26\) are examples for such hybrid materials showing effective microwave absorption with improved bandwidth. Even though the cobalt containing oxygen deficient perovskite family includes members having comparable magnetic properties, their EMI shielding property is least explored. Dijith et al.\(^27\) studied microwave shielding properties of an oxygen deficient compound \(La_{0.5}Sr_{0.5}CoO_{3-\delta}\)—epoxy composites for microwave shielding applications. One of the main factors which limits their application is their lower curie temperature, and hence, such materials are not suitable for applications at room temperature.\(^28\) Cao et al.\(^29\) synthesized a flower-like Co\(_3\)O\(_4@\)rGO/\(\text{SiO}_2\) composite showing high-temperature MA performance. In most of the magnetic and conducting materials containing composites, in addition to the conducting and magnetic loss, their synergy also promotes microwave absorption. The compound Sr\(_3\)YCo\(_4\)O\(_{10+x}\) \((\text{SYCO})\) is found to be exhibiting ferromagnetism with highest transition temperature \((T_c = 335\ \text{K})\) compared to other cobalt oxide perovskites.\(^30\)\(^-\)\(^33\) In this, A sites are occupied by Sr\(^{2+}\) and Y\(^{3+}\) ions while B sites are occupied by Co ions. The various spin states of Co ions owing to various oxidation states, surrounding crystal field, coordination number, and type of neighbouring ions are the undisputed cause for the observed magnetism in this class of compounds.\(^34\) In the present study, effective microwave absorbing composite materials were fabricated by reinforcing PVDF with cost-effective conducting carbon black \((\text{CB})\) and magnetic SYCO by simple solution mixing and coagulation procedure. The microwave absorption enhancement of the composite material with the addition of SYCO and its underlying mechanism were investigated. Also, the role of SYCO and CB incorporation in the phase crystallization of PVDF and its effect on EMI shielding is also discussed in detail.

## RESULTS AND DISCUSSION

### Structure and Morphology

The crystal structure of the synthesized compound and fabricated composites was studied using X-ray diffraction \((\text{XRD})\) and the patterns are given in Figure 1. The diffraction peaks observed at 33.0°, 40.8°, 47.4°, 59.1°, 69.5°, and 79.1° are, respectively, assigned to the reflections from \((204), (224), (008), (228), (408),\) and \((604)\) planes of SYCO \((\text{ICDD}: 01-078-4256)\). No reflections corresponding to other phases were observed in the XRD patterns indicating good crystallinity and phase purity of the compound. The patterns can be indexed based on the tetragonal crystal structure with the \(14/mmm\) space group.
having refined lattice parameters \(a = 7.645(4) \, \text{Å}\) and \(c = 15.348(5) \, \text{Å}\). After fabricating composites by mixing SYCO in the PC matrix, the relative intensity of the PVDF and CB peaks shows a gradual decrease while that of SYCO shows a gradual increase. This suggests the effective incorporation of SYCO into the PC matrix without any loss that may occur during the coagulation process.

The surface morphology and uniformity of the filler dispersion in the matrix were studied using field-emission scanning electron microscopy (FESEM) analysis. The surface morphology of SYCO (Figure S1) shows that it forms an agglomerated structure with irregular grains. SEM images of a few PCS composites are presented in Figure 2. The connected networks formed by CB are clear from the surface and fracture surface images of PC, PCS-10, and PCS-40 composites (Figure 2a–f). There is no particle agglomeration observed on the surface of the composite PCS-10 and is uniform. However, in the case of maximum SYCO-loaded composite PCS-40, the top surfaces contain SYCO particles in cluster forms. The fractured surface of the entire studied composite indicates an almost uniform dispersion of the filler in the polymer matrix. Here, in the case of filler materials with higher tendency to form aggregates, rapid coagulation is an effective method for solvent removal because it can avoid the settling down of particles that may occur during solvent evaporation.

XPS analysis shows the presence of Co\(^{2+}\) and Co\(^{3+}\) ions as the surface states in the SYCO lattice with Co\(^{3+}\)/Co\(^{2+}\) molar ratio 0.53. The spectra are given in Figure S2. The temperature dependence of magnetization and its isothermal field response are studied using vibrating sample magnetometer (VSM). The response curve (Figure S3a,b) indicates that the compound exhibits ferromagnetism with a high transition temperature of 335 K. The detailed analysis of the XPS spectra and VSM response curve are provided in the Supporting Information.

Identification of Electroactive Phases. Fourier transform infrared spectroscopy (FTIR) and wide-angle X-ray scattering (WAXS) techniques are often used to identify the crystallized phases in PVDF. However, it is difficult to distinguish \(\alpha\) and \(\gamma\) phases from WAXS patterns. Likewise, some FTIR modes are similar for both \(\beta\) and \(\gamma\) phases. Hence the combination of these two techniques is essential to identify the exact phase determination in PVDF.

The XPS patterns of melt blended PVDF, PC, PCS-30, and PVDF with 30 wt % of SYCO (S: 30 wt %) are shown in Figure 3. The diffraction peaks observed are around 17.9°, 18.5°, 20.2°, and 26.5° 2\(\theta\) angles. The intense reflection peak around 20° is common for \(\alpha\), \(\beta\), and \(\gamma\) phases of PVDF. For the pure \(\beta\) form, only one peak at 20.3° is reported and is attributed to the combined reflections from its (110) and (200) planes.\(^{17,35}\) The observed peak around 26.5° is a characteristic reflection of the \(\alpha\) phase and is present in all the composites. In CB-containing composites, this peak shows a broadening due to the superposition of XRD from (200) planes of CB, which is around 25.6°.\(^{36}\) Out of the two other reflections, one at 17.9° is due to (100) \(\alpha\) planes and other at 18.5° may be due to (020) \(\alpha\) and/or \(\gamma\) planes.\(^{7}\) There are SYCO reflections at 11.7°, 21.0°, and 23.4° (ICDD: 01-078-4256) in composites containing SYCO.

The composites were characterized using attenuated total reflectance FTIR spectroscopy. The individual contribution of SYCO and CB on the PVDF nucleation is shown in Figure 4a. For melt-blended PVDF, the strong absorption bands at 483,
530, 613, 761, 795, and 976 cm\(^{-1}\) stem from the \(\alpha\) phase.9,10,13,18,35,37,38 The absorptions at 613 and 761 cm\(^{-1}\) are due to CF\(_2\)-bending and skeletal-bending motions in PVDF and at 795 and 976 cm\(^{-1}\) correspond to CH\(_2\) rocking motion. The signature absorption band of polar \(\beta\) and semipolar \(\gamma\) phase at 840 cm\(^{-1}\) (CH\(_2\) rocking and CF\(_2\) stretching motion) shows an increase in intensity with SYCO addition from 20 to 40 wt % and also with the CB content. However, it has been recently accepted that for \(\gamma\) PVDF, this band will be appeared as a shoulder band of 833 cm\(^{-1}\).35 Another band, which also represents \(\beta\) and \(\gamma\) phases is at 510 cm\(^{-1}\), shows an increase with SYCO addition but no considerable variation with the CB content. The intensity of absorption at 1232 cm\(^{-1}\) corresponding to the \(\gamma\) phase increased with SYCO and CB and also the absorption at 1275 cm\(^{-1}\) arises due to CH\(_2\) wagging motion, which solely characterizes the \(\beta\) phase increased with CB and SYCO. These observations along with reduction in intensity of \(\alpha\) absorption bands at 530, 613, 761, and 795 cm\(^{-1}\) with filler loading also suggests that these two fillers individually facilitate polar \(\beta\) phase and semipolar \(\gamma\) phase nucleation in PVDF.

Mechanical Properties. Figure 5a shows the stress–strain curve for the PCS composites studied at room temperature. The Young’s modulus, elongation at break, tensile strength, and toughness of the materials are calculated from the stress–strain plots and are shown in Figure 5b–d. The Young’s modulus of the composites increases with the SYCO content, that is, the stress required to produce unit strain in the composites increases as the filler content increases. This may be because of the more compact nature of the composites with higher filler loading occurred during hot-pressing. From the bar diagram, it can be identified that the tensile strength of the composites increases with the SYCO content, however, the elongation at break decreases with the concentration of SYCO. These observations are also due to the stiffness of the composites. The decreasing value of toughness with the SYCO content may be attributed to the lack of interface regions capable to transfer the applied stress throughout the composites.9 The decreased value of Young’s modulus of PVDF compared to other reports may be due to the processing condition like pressure, temperature, and time duration.

Electrical Conductivity. The electrical conductivity of a material has a positive role in its EMI shielding efficiency. When the content of a conducting filler reaches electrical percolation threshold, it forms a conducting network. Here, the conductivity of the composites results from CB and it is essential to determine whether the conductivity is maintained even after the addition of SYCO. To explore this, the room-temperature dc conductivity is studied and is shown in Figure 6. The dc conductivity value of pure PVDF is 1.54 \(\times\) 10\(^{-8}\) S/m and is increased to 9.97 S/m with the addition of 30 wt % of CB (PC) and is maintained almost unchanged with the SYCO content. When 40 wt % of SYCO is added (PCS-40) into PC, the conductivity value shows a slight decrease to 8.46 S/m. For a material to be suitable for EMI shielding, its volume electrical conductivity...
conductivity should be at least 1 S/m.\textsuperscript{40,41} Here, the CB network attains this marginal value.

### Dielectric and Magnetic Properties.

The permittivity and permeability of materials determine their response in the EM field. The absorbance of the EM wave by a material is directly related to its complex permittivity $\varepsilon_r = \varepsilon' - j\varepsilon''$ and complex permeability $\mu_r = \mu' - j\mu''$. The real part of permittivity ($\varepsilon'$) and permeability ($\mu'$) accounts to the energy confining potential of the material, whereas the imaginary part of these two quantities ($\varepsilon''$ and $\mu''$) gives the energy dissipation.

The frequency dispersion curve of permittivity and permeability within the frequency range from 10 MHz to 1 GHz at room temperature is shown in Figure 7a,b. The $\varepsilon'$ of the PC composite is about 10² times higher than that of PVDF. This sudden rise in permittivity may be attributed to the increased conductivity of the PC composite compared to PVDF. The variation in the permittivity with SYCO addition is in accordance with two reasons, one is due to the crystallized polar phases of PVDF induced by CB and SYCO and other is due to MWS polarization. The higher value of dielectric loss is due to the high conductivity and the variations observed are due to the polarization loss arising from the increased interfaces and the polar phase content in PVDF.

For the hot-pressed PVDF/MWCNTs/BaTiO$_3$ (3.0/37.1 vol %) system fabricated by the miscible−immiscible coagulation method has a real permittivity and dielectric loss of 71.7 and of 0.045, respectively, at 1000 Hz frequency\textsuperscript{45} and for PVDF/functionalized graphene−BaTiO$_3$ (1.25/30 vol %) composites fabricated by two-step solution mixing followed by hot-pressing, real permittivity is 65, and loss is 0.35 at 1 MHz frequency.\textsuperscript{46} Here, we could attain a real permittivity of 617.1 and a dielectric loss of 6.09 for 30 wt % of the CB-added composite and for PCS-30, these values are 454.0 and 27.6, respectively, at 10 MHz.

Figure 7d,e shows the complex permeability spectra of PCS-30 and PCS-40 composites. The $\mu''$ and $\tan \delta_\mu$ plots corresponding to P and PC are avoided here due to the absence of the magnetic component SYCO in them. The contributions to complex permeability arise mainly from the
domain wall motion occurring at low frequencies and spin rotation preponderant at high frequencies. Here, beyond 100 MHz, the real and imaginary permeability increases with frequency. The dielectric and magnetic losses are expressed as loss tangents \( \tan \delta_e = \varepsilon''/\varepsilon' \) and \( \tan \delta_\mu = \mu''/\mu' \), respectively, and Figure 7c,f shows the variation of these quantities with frequency. The higher values of \( \tan \delta_e \) compared to \( \tan \delta_\mu \) indicate that the composite possesses high dielectric loss than magnetic loss. For microwave absorption, it is very important to have a compatibility of these two losses. In this case, the microwave absorption is mainly contributed by dielectric loss rather than magnetic loss.

**EMI Shielding Properties and Mechanism.** The EMI shielding effectiveness (EMI SE) of a material describes its ability to attenuate the energy of EM radiation. The shielding mechanism mainly include reflection, absorption, and multiple internal reflection. For materials having dominated absorption or having thickness greater than skin depth, the energy of multiple reflected signals will be absorbed by the material. In such cases, the EMI SE due to multiple internal reflection is ignored. The energy absorbed from EM radiation is generally converted as heat energy. The EMI SE values due to absorption (\( SE_A \)) as well as reflections (\( SE_R \)) can be calculated from the reflection and transmission scattering parameters \( (S_{11}, S_{22} \text{ and } S_{12}, S_{21}) \) using the relations:

\[
SE_A (\text{dB}) = -10 \log\left( \frac{S_{11}^2}{1 - S_{11}^2} \right) \\
SE_R (\text{dB}) = -10 \log(1 - S_{11}^2) \\
SE_T (\text{dB}) = SE_A (\text{dB}) + SE_R (\text{dB})
\]

Here, \( SE_T \) is the total SE.

Above 20 dB of \( SE_T \) value is required for commercial applications and it means that the material can attenuate 99% of the incident EM wave. The SEs dependence on frequency of the X and Ku band regions for the PCS composites having thickness 2.5 mm is displayed in Figure 8a.

The neat PVDF has an average \( SE_T \) value of 1.3 dB and 30 wt % CB-added PVDF composite crosses the marginal value of 20 dB to an average \( SE_T \) value of 29.0 dB, which corresponds to 99.9% blockage of the incident EM wave. This abrupt change in the shielding value mainly stems from the conductivity of CB. A steady value of SE is observed in the entire frequency range, even for the composite having higher loading of SYCO. This specifies the fact that, in spite of the SYCO content, an excellent homogeneity and regularity is maintained in the composites, which is supported by the conductivity studies as shown in Figure 6.

The EMI shielding performance of PVDF/SYCO composites having thickness 1.8 mm and the frequency dispersion curve of EMI SE in the two regions are given in the Figure S6a. The shielding performance of PVDF/SYCO composites is less than 5 dB and in which the main contribution to total shielding is from the reflection of EM waves at the shielding material and the absorption value almost remains constant (Figure S6b). The reflection mechanism in these composites is related to the mismatching of input impedance of the composite materials with the free space impedance.

In the case of PCS composites, the main contribution to shielding is due to absorption rather than reflection, which almost remains as constant for all the composites. The PC composite itself has an EMI SE value of 29.0 dB, in which 20.0 dB is due to absorption and 9.0 dB is due to reflection and for the PCS-40 composite, out of the total SE value of 50.2 dB, absorption contributes 41.2 dB and reflection contributes 9.0 dB. The dominating absorption mechanism in PCS composites indicates that the input impedance values of the composite materials are close to the free space impedance, so that maximum EM signal can enter into the material. The reversal of dominated shielding mechanism from reflection to absorption from PVDF/SYCO composites to PCS composites suggests that the synergy among the dielectric and magnetic loss is essential to attain the maximum input impedance match with the free space impedance. As soon as the signal enters into the material, the energy of the signal gets absorbed due to different mechanisms arising from the individual filler materials and from their synergistic effect. This results in much enhanced EMI SEs of the PCS composite with the increased content of SYCO (Figure 8a).

In PCS composites, the dielectric, magnetic losses, and their synergy contributes to the EM energy attenuation. The permittivity and permeability studies indicate that the composite materials have dictating dielectric loss than magnetic loss. According to the Debye theory, the imaginary part of the permittivity \( (\varepsilon''/\varepsilon') \) represents both polarization loss and conducting loss. Here, the high conductivity of the PCS composites indicates that the main contribution to the energy attenuation is due to the presence of nomadic electrons in conducting CB and this still exists in all the composites with different wt % of SYCO, hence the incorporation of SYCO will not form any discontinuities in the conducting percolation network formed by CB as it is evident from the dc conductivity studies (Figure 6).

The second contribution to microwave absorption in the composites is due to the polarization losses which consists of
both interfacial polarization losses and dipolar relaxation losses. As the content of SYCO increases, the interfacial polarization becomes more prominent. Then, MWS polarization can happen at the interfaces due to the migrating as well as hopping electrons. Moreover, the WAXS and FTIR studies indicate that the incorporation of SYCO and CB in PVDF facilitates the polar $\beta$ and semipolar $\gamma$ phase nucleation in the polymer and this polar phase content in the composite can also act as charge trapping centers and can enhance the interfacial polarization losses. Also, there are interactions of polar fluorine atoms in PVDF with the surfaces of SYCO and CB grains. This specific interaction causes a damping effect when these dipoles interact with EM radiation and cause dipolar relaxation losses, and hence, the polar phases in PVDF are beneficial for the EM energy absorption.

In addition to the dielectric loss, magnetic properties are favorable for EM energy attenuation. Here, the progressing shielding performance with SYCO loading stems from the natural resonance losses in SYCO due to the time lag of magnetization, produced by the orientation of magnetic moments as well as domain wall motion behind the magnetic field. The magnetic loss could also be arisen from the eddy current loss. Since the presence of conducting network formed by CB can reduce the EM energy by eddy current loss. In addition to these individual contributions to EM energy absorption, synergy between SYCO and CB also improves the microwave absorption performance in PCS composites. Their combined effect can be explained like this: the SYCO particles inside the composites cause multiple reflections of radiations inside, which allows more time for CB to absorb the EM energy. It is clear in the fracture surface SEM images of the composites that the radiation reflected from the SYCO particles is radiated into the conducting regions of CB. The possible mechanisms contributing the shielding performance are schematically shown in Figure 9. These different mechanisms result a maximum $SE$ of 50.2 dB for the PCS-40 composite with a thickness of 2.5 mm, which can shield about 99.9991% of the incident EM radiation within the 8.2–18 GHz frequency range. The EMI SE of some polymer composites containing carbon materials like CNTs and graphene and iron oxides with the comparable filler content is listed in Table 1. Here, low-cost conducting CB and ferromagnetic SYCO reinforced PVDF composites show high-performance EMI shielding compared to other composites.

The absorption property mainly depends on the thickness of the shield ($d$) and skin depth ($t$), the relation is as follows:

$$SE_A = 20 \log \left( \frac{d}{t} \right) \log e$$

(Skin depth is defined as the distance from the surface of the shield at which the EM energy decreased to $1/e$ times of the incident energy. The skin depth variation with frequency for PCS composites is shown in Figure 10. From the $SE_A$ values,

### Table 1. EMI SEs of Some Carbon-Based and Magnetic Filler-Incorporated Polymer Composites

| material                  | filler content (wt %) | thickness (mm) | EMI SE (dB) | refs |
|---------------------------|-----------------------|----------------|-------------|------|
| WPU/CNT                   | 76.2                  | 2.3            | 35          | 62   |
| cellulose/CNT             | 33                    | 0.64           | 30          | 63   |
| PS/graphene foam          | 30                    | 2.5            | 29.3        | 68   |
| PMMA/CNT                  | 20                    | 4.5            | 30          | 64   |
| PVDF/CB                   | 30                    | 2.5            | 29          | this work |
| PVDF/CB/SYCO              | 50                    | 2.5            | 45.4        | this work |
| PVDF/CB/SYCO              | 60                    | 2.5            | 48.3        | this work |
| PVDF/CB/SYCO              | 70                    | 2.5            | 50.2        | this work |
| PANI/rGO/$\delta$-Fe$_2$O$_4$ | 40                   | 0.36           | 20.3        | 65   |
| PANI/rGO/Fe$_2$O$_4$      | 66                    | 2.5            | 30          | 66   |
| PANI/rGO/$\gamma$-Fe$_2$O$_3$ | 75            | 2.5            | 51          | 67   |
| PVDF/CB/PMMA/CNT          | 76.2                  | 2.3            | 35          | 62   |
| WPU/CNT                   | 20                    | 4.5            | 30          | 64   |
| PS/graphene foam          | 20                    | 2.5            | 29.3        | 68   |
| PMMA/CNT                  | 20                    | 4.5            | 30          | 64   |
| PVDF/CB                   | 30                    | 2.5            | 29          | 67   |
| PVDF/CB/SYCO              | 50                    | 2.5            | 45.4        | this work |
| PVDF/CB/SYCO              | 60                    | 2.5            | 48.3        | this work |
| PVDF/CB/SYCO              | 70                    | 2.5            | 50.2        | this work |

The average value of skin depth obtained for the PCS-40 composite is 0.53 mm. The shielding due to absorption depends on its thickness and should be greater than the skin depth. Another factor has to be taken into consideration is the density of the material. The specific $SE$ (SSE) is a normalized value that account for the thickness and density of the material, which can be obtained as follows:

$$SSE = \frac{EMI SE}{density \times d} = dB \ cm^{-2} \ g^{-1}$$

The high SSE is the signature of a material to provide better shielding with minimum thickness having lower density. For PC and PCS-40, the SSE values are 82 and 113 dB cm$^{-2}$ g$^{-1}$, respectively. Here, the attained SSE values are higher than the values reported for graphene/polystyrene composites having 30 wt % of functionalized graphene with 2.5 mm thickness. The average values of shielding, shielding efficiency, and SSE of PCS composites are listed in Table S1.

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**Figure 9.** Mechanism of EM energy attenuation by PCS composites.

**Figure 10.** Frequency response of the skin depth of PCS composites.
Here, the PCS composite is a magnetic–dielectric composite material, having a competitive synergy to enhance EM energy attenuation. Because the dielectric loss is due to the conducting and relaxation losses, the EM energy conversion power is contributed by charge transport and relaxation. Likewise, the magnetic energy loss includes power conversion from hysteresis loss, eddy current loss, and residual loss. This competing synergy has a significant role in energy harvest and conversion. A systematic investigation on temperature-dependent EMI shielding properties is required to understand wave attenuation and energy conversion in PCS composites.

**CONCLUSIONS**

In conclusion, we fabricated PVDF composites reinforced with CB and room temperature ferromagnetic Sr$_3$YCo$_4$O$_{10+x}$ (SYCO) by a simple solution mixing and coagulation method. It is a very effective method for fabricating homogeneous composites of materials having large particle size and higher tendency to form aggregates. The polar $\beta$ and semipolar $\gamma$ phases of PVDF formed during its nucleation process in the presence of CB and SYCO have an effect on the dielectric properties of the composites. Furthermore, the electrical conductivities of the PCS composites remain nearly constant even with the highest loading of SYCO. The dictating dielectric loss over magnetic loss, the conducting losses of composites as well as other mechanisms derived from the synergy among the fillers and matrix result in an impressive EM SEs of 50.2 dB; out of it, 41.2 dB is from the absorption of EM energy by the material. This study can also be extended to other matrix materials to achieve different physical properties like flexibility, compressibility, and so forth. Hence, this composite can be used as efficient microwave absorbers in radar absorbing materials and also for military applications.

**EXPERIMENTAL SECTION**

**Materials.** PVDF (average $M_n = 534,000$ by GPC) was purchased from Sigma-Aldrich Co. USA. The organic solvent N,N-dimethylformamide (DMF) ($\geq 99.8\%$) was purchased from Merck Life Science Private Limited, Mumbai. Carbon black (carbon black, acetylene, 50% compressed, purity 99.9+ % and S.A. 75 m$^2$/g) and cobalt(II,III) oxide (99.7%) were purchased from Sigma-Aldrich Co. USA. Strontium carbonate (99.9%) and yttrium(III) oxide (99.99%) were purchased from Sigma-Aldrich, USA. All the chemicals were used as received without any further treatment.

**Sample Preparation.** Oxygen-deficient double perovskite Sr$_3$YCo$_4$O$_{10+x}$ (SYCO) was synthesized by a solid-state ceramic route and a calcination temperature of 1050 °C for 15 h is used. The synthesis procedure is given in the Supporting Information. CB and SYCO-reinforced PVDF composites were fabricated by solution mixing and rapid coagulation procedure schematically shown in Figure 11. PVDF powder was dissolved in DMF and required weight percentages of filler materials were uniformly dispersed in DMF. Then, these solutions were mixed well by magnetic stirring for 12 h and then coagulated using distilled water as the antisolvent. The coagulated product was washed several times with distilled water and then dried at 75 °C in a hot air oven. The dried composites were then hot pressed at 250 °C temperature into rectangular pellets having dimensions 22.86 × 10.16 mm (for X-band measurement) and 15.79 × 7.89 mm (for Ku-band measurement) under a pressure of 1 MPa applied for 1 h. Cylindrical pellets of diameter 15 mm and thickness 2.5 mm were prepared by hot pressing at the same temperature and pressure conditions for permittivity measurements and toroid-shaped pellets of inner diameter 6.7 mm, outer diameter 15 mm, and thickness 2.5 mm are used for permeability measurement. The sample codes assigned are P (for PVDF), PC (for 30 wt % CB in PVDF matrix), and PCS-$m$ ($m = 10$–$40$, m wt % of SYCO in PC matrix).

**Characterizations.** XRD studies of SYCO and PCS composites were carried out by a Bruker D8 ADVANCE diffractometer (40 kV, 40 mA) using Cu Ka radiation ($\lambda = 1.5406$ Å) having a nickel filter and Lynxeye position detector with the $\theta$–$2\theta$ scan mode. The various oxidation states of Co ions in SYCO were identified using a Thermo Scientific ESCALAB X-ray Photoelectron Spectrometer with Al Ka radiation (1486.6 eV) as the excitation source and a twin-crystal: micro-focused monochromator. The temperature dependence of magnetization in SYCO and isothermal magnetic field response at 300 K of SYCO and PCS-30 was measured using Quantum Design Versa Lab PPMS VSM. Morphological characterizations were done with a FEI-Nova nanoSEM 450 field-emission scanning electron microscope with a beam potential of 10 kV. PVDF phase identification in composites was carried out using FTIR spectra taken by a PerkinElmer frontier FT-IR/far-infrared spectrometer with a resolution of 2 cm$^{-1}$ and 44 scans in the mid IR region and WAXS patterns. WAXS measurements made in the transmission mode were carried out on a XEUSS SAXS/WAXS system using a GenIX microsource from Xenocs operated at 50 kV and 0.6 mA. In which, the Cu Ka radiation ($\lambda = 1.54$ Å) was collimated with the FOX2D mirror and two pairs of scatterless slits from Xenocs and 2D-patterns were recorded on a Mar345 image plate and processed using the Fit2D software. The sample to detector distance was calibrated with the silver behenate standard. Tensile tests were carried out for the hot-pressed samples using a universal testing machine (Instron model; 1195-S500R) at a strain rate of 1 mm/min at room temperature. The experiments were repeated four times for each composite and average values are reported. The room-temperature dc conductivity of the composites was measured by the two-probe method using the Keithley 2400 Source. The permittivity and permeability of the composites within the frequency range from 10 MHz to 1 GHz was analysed using a Keysight E4991B impedance analyser. The permittivity measurements were carried out using 16453A test fixture after reducing the residual impedance and calibrating the fixture by performing open/short calibration and load compensation, respectively. The permeability measurements

![Figure 11. Illustration of the solution mixing and coagulation procedure for the fabrication of composites.](image-url)
were done using 16454A test fixture after open/short and load compensation. The EMI SEs values in the X (8.2–12.4 GHz) and Ku (12.4–18 GHz) band regions were calculated from the reflection \((S_{11})\) and transmission \((S_{21})\) and scattering parameters measured using a Vector Network Analyzer (Agilent E5071C) using the waveguide method.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00454.

Synthesis procedure of \(\text{Sr}_2\text{YCo}_5\text{O}_{12}\) (SYCO) and its SEM image, XPS spectra of SYCO and its analysis, VSM studies of SYCO and PCS-30, permittivity dispersion curves of PVDF/CB and PVDF/SYCO composites, and the EMI SE of PVDF/SYCO composites in the X and Ku band regions (PDF)

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