Structural and optical properties of synthesized poly(methyl methacrylate) (PMMA) and lanthanide β -diketonate complexes incorporated electrospun PMMA nanofibres for optical devices

PRINCY PHILIP¹, PAULOSE THOMAS², E TOMLAL JOSE^{1,*} , K C PHILIP¹ and P C THOMAS¹

¹Research and postgraduate, Department of Chemistry, St. Berchmans College, Changanacherry, Kottayam 686 101, India

²Department of Physics, Marthoma College for Women, Perumbavoor 683542, India

*Author for correspondence (tomlalj27@gmail.com)

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Abstract. Fabrication of electrospun nanofibres is the glittering area of research because of their flexible characteristics and numerous applications in almost all walks of life and technology. Poly(methyl methacrylate) (PMMA) is one of the significant and interested synthetic polymers in the recent research because of their characteristic properties like higher environmental stability, resistance to attack by moulds and enzymes, commercial availability, easiness to handle, etc. In the present study, pristine PMMA nanofibres with diameters of 60–150 nm with 109 nm as the most distributed one are prepared by an electrospinning method using a binary solvent mixture. An enhancement in the intensity of visible photoluminescence emission is observed in PMMA nanofibres embedded with samarium and neodymium β -diketonate complexes. The morphological incorporation of samarium and neodymium β -diketonate complexes in PMMA nanofibres and material composition of the samples are examined by high resolution electron microscopy analyses. The amorphous nature and molecular bonding of pure PMMA nanofibres and incorporated fibre complexes are elucidated through structural and molecular analyses. The supreme optical absorptions and reemissions of samarium and neodymium β -diketonate complexes embedded in the pure PMMA fibre sample in the visible region indicate not only their application in lighting or display devices, but also as active materials in organic light emitting diodes for new era curved/rolled display devices.

Keywords. Electrospinning; lanthanide β -diketonate PMMA nanofibre complexes; photoluminescence; PMMA nanofibre.

1. Introduction

Today, nanomaterials form a major part of research and analysis. Nanostructures like nanoparticles, nanowires, nanotubes, nanofibres, etc. are the topics of interest to the modern researchers since their applications are numerous. Among the various nanostructures, nanofibres have several characteristic properties like high surface area to volume ratio, flexibility in surface functionalities and superior mechanical properties like stiffness and tensile strength compared to other forms of the materials [1]. Polymer nanofibres act as good host matrices for nanoparticles, drugs, metals, etc. They have a wide variety of applications such as tissue engineering scaffolds, filtration membranes, dressings for wound healings, etc. [2] which enhanced the preparation of nanofibres through various methods like drawing, template synthesis, phase separation, self-assembly, electrospinning, etc. [1]. Among these methods, electrospinning is the most important and favourable one. It is the technique capable of producing polymer fibres in the nanometre diameter range from an electrostatically driven jet of polymer solution (or polymer melt). The different dimensions, shapes and porosity of polymer nanofibres can

be obtained by varying the spinning parameters and polymer characteristics [3].

Herein, the present study progresses through three different stages. First is the preparation of electrospun poly(methyl methacrylate) (PMMA) nanofibres. PMMA is preferred since it is a commercially available synthetic polymer with exceptional characteristics like transparency, good tensile strength and processability as compared with other commercially available polymers. It is an economical alternative to other polymers such as polyacrylonitrile (PAN), polyvinylidene difluoride (PVDF), etc. [4]. The production of PMMA nanofibres with diameter <100 nm is very much rare in the electrospinning field. The second stage of the study is the preparation of lanthanide β -diketonate complexes. Lanthanides like samarium and neodymium show excellent luminescence properties. β -Diketone ligands are preferred to prepare complexes because of their chemical stability, highly molar extinction coefficient and high energy transfer efficiency from the ligand to the Ln(III) ions [5]. Lanthanide β -diketonate complexes are well-known molecular luminescent materials and they have characteristic emission bands [6]. Therefore, the incorporation of the luminescent material into

the transparent matrix offers great advantages and hence the analyses on their optical properties are highly significant. The third stage of the study is the incorporation of these prepared lanthanide complexes into the prepared electrospun PMMA nanofibres and different analyses are carried out with special focus on the photoluminescence (PL) properties of pristine PMMA and PMMA nanofibres incorporated into the prepared samarium and neodymium complexes.

Today, numerous studies are being conducted for the preparation and characterization of electrospun polymer nanofibres and lanthanide complexes. For example, Lenaerts *et al* [6] prepared the lanthanide diketonate complexes with the theonyl-trifluoroacetone (TTA) ligand by a precipitation method and immobilized these complexes into 1,10-phenanthroline functionalized merrifield resin and the luminescence characters were studied. Basak *et al* [7] worked on the PL properties of PMMA dispersed with silver nanoparticles and they observed a red shift when the polymer is dispersed with nanoparticles. Chahar *et al* [8] worked on PMMA nanofibres with neodymium oxide nanoparticles for lasers. They observed a shift in the PL spectrum with an increase in the concentration of lanthanide oxides. Most of the studies on PMMA electrospun polymer nanofibres are carried out either with silver nanoparticles or lanthanide oxides. Some of the researchers were found to prepare the lanthanide diketonate complexes but their further studies were quite different from that of us. Usually the particles, oxides or complexes are incorporated into nanofibres or any matrices after some surface treatments or with the assistance of ligands [6]; but here we are neither using any types of surface modification methods nor ligands; instead just using sonication, electrospinning and make advantage of the porous nature of electrospun nanofibres.

Usually the polymer nanofibres are prepared with single solvent like acetone or DMF or chloroform, etc. Herein, the present study, we have prepared PMMA electrospun polymer nanofibres with a binary solvent mixture, lanthanide diketonate complexes through the precipitation method and the PMMA nanofibres embedded with the prepared lanthanide (Sm and Nd) β -diketonate complexes and the various analyses are carried out to reach the goal of our study. In the present study, the comparative studies on the photoluminescent analysis of the PMMA nanofibres and PMMA nanofibres incorporated with the prepared lanthanide complexes show the characteristic properties and evidence for the ability of PMMA nanofibres to act as the best host matrices for lanthanide complexes with much enhancement in intensity. The present study is distinct from the other referred studies in the selection of the mentioned binary solvent mixture for the preparation of PMMA—which leads to the formation of better miscible solution of PMMA than using single solvent—and in the own preparation of lanthanide diketonate complexes and incorporation of the prepared lanthanide complex rather than the commercially available lanthanide complexes in our own prepared PMMA nanofibres and in the PL studies were further carried out. Studies on the incorporation of the as-such prepared complexes into PMMA electrospun nanofibres are

not reported yet to the best of our knowledge. The present analysis proved that PMMA fibres could act as the best host matrix not only for pure lanthanides or lanthanide oxides but also for the lanthanide complexes with supreme optical properties. Accordingly, such type of lanthanide complex-incorporated PMMA electrospun nanofibres can be used in various fields like lasers [8], light emitting diodes (LEDs) [9], chromatography, catalysts, sensors [10], waveguides, amplifiers, etc.

2. Experimental

2.1 Materials

The materials used in the present study are PMMA (molecular weight 15,000, Alfa Aesar), samarium chloride ($\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$; Alfa Aesar; 99.9%), sodium hydroxide (NaOH) (Merck), 2-TTA ($\text{C}_8\text{H}_5\text{F}_3\text{O}_2\text{S}$; Alfa Aesar; 99%) and neodymium nitrate ($\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$; Alfa Aesar; 99.9%).

2.2 Preparation of electrospun PMMA nanofibres

The pristine PMMA nanofibres are synthesized through an electrospinning route. PMMA solution was prepared by dissolving $\sim 1\%$ PMMA in a novel binary solvent mixture of chloroform and acetone in an equal ratio followed by mechanical stirring until a clear transparent solution of PMMA is obtained. It is then subjected to electrospinning and the parameters applied for the production of electrospun PMMA nanofibres are shown in table 1. The electrospinning machine that we used for the production of PMMA nanofibres and the collected PMMA nanofibres are shown in figure 1a and b.

2.3 Synthesis of lanthanide(III) complexes

The lanthanide β -diketonate complexes are prepared by precipitation method as described in the literature [6,11]. The solution is then subjected to centrifugation and washing with water. The precipitate obtained is then dried in a vacuum oven at 115°C for 6 h. The samarium and neodymium β -diketonate complex powders prepared are shown in figure 2a and b.

2.3a Principle for the preparation of lanthanide complexes: β -Diketones exhibit keto–enol tautomerism. A total of 81% of the acetyl acetone molecules are present in the enol form at room temperature [9,12]. Keto–enol tautomerism in ligands like TTA is represented as L (keto) $\leftrightarrow$ L (enol) or HL, where HL represents the enol form of the β -diketonate ligand. This

Table 1. Parameters of electrospinning.

Voltage	Distance	Flow rate
20 kV	20 cm	0.5 ml h ⁻¹

Figure 1. (a) Electrospinning machine and (b) electrospun PMMA nanofibres.

Figure 2. (a) Samarium β-diketonate complex and (b) neodymium β-diketonate complex.

Scheme 1. Keto-enol tautomerism in diketonate ligands.

HL form of the β-diketonate ligand is believed to chelate with the metal ion as shown in scheme 1.

Here 'y' represents the number of hydrated water molecules. The reaction of the enolic TTA to form the chelate with the metal ion is accompanied by the deprotonation of the ligand [11]. The common bases that are used for the deprotonation of β-diketones are ammonia, sodium hydroxide, piperidine or pyridine. When β-diketone is deprotonated, the

proton is removed from the alcoholic group since β-diketone is in the enol form. The addition of ethanol enhances the complexation due to an increase in dissolution and tautomerization of TTA to the 'enol' form from the 'keto' form [9]. The formed chelate includes water molecules, i.e., the chelate will be in the form of Sm(TTA)₃ · (H₂O)₂ and Nd(TTA)₃ · (H₂O)₃. This means that the samarium complex formed by chelation with TTA is found to be dihydrate and the neodymium complex is found to be trihydrate [6].

2.4 PMMA electrospun nanofibres embedded with the samarium (+3) and neodymium (+3) β-diketonate complex

The prepared Sm(III) and Nd(III) β-diketonate complex is dispersed in 1% PMMA solution and subjected to sonication [9]. It is then electrospun with an applied voltage of 20 kV at a flow rate of 0.5 ml h⁻¹ with a collector distance of 20 cm and the fibres are collected in

Figure 3. FTIR spectra: (a) pure PMMA nanofibres, (b) Sm complex, (c) Nd complex and (d) (i) PMMA nanofibres incorporated with the Sm complex and (ii) PMMA nanofibres incorporated with the Nd complex.

an aluminium foil. The obtained pure PMMA nanofibres, Sm(III) β -diketonate complex, Nd(III) β -diketonate complex, PMMA electrospun nanofibres embedded with the Sm(III) β -diketonate complex and Nd(III) β -diketonate complex were subjected to various analytical techniques like scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), Fourier transformed infrared (FTIR), ultraviolet (UV), PL, etc.

2.5 Measurements

FTIR analyses of the samples were carried out using an instrument PerkinElmer spectrum two, XRD analyses of the samples were carried out using a Rigaku MiniFlex 600 X-ray diffractometer, UV-visible absorption analyses are carried out with a T90+ spectrometer from PG instruments, SEM analyses of the samples are carried out with a JEOL Model-JSM 6390LV, field emission scanning electron microscopy (FESEM) analysis of the PMMA nanofibres is carried out using a Nova NanoSEM 450 UoK, transmission electron microscopy (TEM) and EDX analyses of the samples were performed with a high-resolution transmission electron microscope facility, JEM 2100 and PL studies were conducted using PerkinElmer LS45.

3. Results and discussion

3.1 FTIR analysis

The FTIR spectra of the pure PMMA, samarium β -diketonate complex, neodymium β -diketonate complex, electrospun PMMA nanofibres embedded with the samarium and neodymium β -diketonate complexes and the assignment of peaks in each case are shown in figure 3a–d and table 2, respectively.

The characteristic peaks of PMMA are obtained at 2951 cm^{-1} which is assigned to the C–H stretching band of PMMA and at 1734 cm^{-1} which is due to the vibration of the C=O group in PMMA [13–16]. The obtained FTIR spectra in the case of the samarium and neodymium β -diketonate complex clearly give evidence for the successful production of these complexes with the TTA ligand. The broad band appeared in the range of $3734\text{--}3078\text{ cm}^{-1}$ is highly notable as it clearly proves the presence of the OH group in the sample. The absence of the peak at 3109 cm^{-1} , which is characteristic of the CH_2 stretching of TTA spectra of the complex, also proves the presence of the complex in the enol form [17].

Most of the previous literature studies specify two strong bands in the range of $1500\text{--}1650\text{ cm}^{-1}$ in which the bands with higher frequency is associated with the chelated

Table 2. FTIR assignments.

Sl. no.	Sample	Wavenumber (cm^{-1})	Assignments
1	Pure PMMA	2951	PMMA C–H stretching band
		1734	PMMA C=O band
		1440	H–C–H bend in PMMA
		1144	C–O–C of the methoxy group of PMMA
		985	C–C stretching PMMA
		803	C=O in plane bending
		746	C=O out of plane bending
2	Samarium complex	3734–3078	OH group present in the sample
		1614	Chelated C=O group
		1539	C=C in the complex
		1400	Double bonds in thiophene ring
		1300	C–F stretching vibration of TTA
		1109	C–S stretching vibration of TTA
		528	Stretching vibration of Sm_2O_3 molecules
3	Neodymium complex	3734–3078	OH group present in the sample
		1614	Chelated C=O group
		1539	C=C in the complex
		1400	Double bonds in the thiophene ring
		1300	C–F stretching vibration of TTA
		1109	C–S stretching vibration of TTA
		548–560	Stretching vibration of Nd_2O_3 molecules
4	PMMA nanofibres incorporated with samarium complex	2954	PMMA C–H stretching band
		1738	PMMA C=O band
		1442	H–C–H bend in PMMA
		1400	Double bonds in thiophene ring
5	PMMA nanofibres incorporated with neodymium complex	1226–1300	C–F stretching vibration of TTA
		2954–2935	PMMA C–H stretching band
		1740	PMMA C=O band
		1428–1489	Double bonds in thiophene ring
		1300	C–F stretching vibration of TTA

carbonyl group, while the other with lower frequency is associated with the carbon–carbon double bond present in the complex. However, some literature studies narrate only one band which assigns to the carbon–carbon double bond in the complex [18]. Two peaks are obtained at 1614 and 1539 cm^{-1} which are characteristic of the chelated C=O group and C=C group, respectively. The spectrum also shows the existence of the thiophene ring in the complex with a peak at 1400 cm^{-1} which is a strong evidence for the successful production of the complexes with the TTA ligand.

The peak at 528 cm^{-1} shows the presence of Sm_2O_3 molecules present in the sample [19] and the peak at 548–560 cm^{-1} shows the presence of Nd_2O_3 molecules present in the sample [20,21]. The observed peak at 2954 cm^{-1} in PMMA nanofibres embedded with the samarium β -diketonate complex and that at 2954–2935 cm^{-1} in PMMA nanofibres embedded with the neodymium β -diketonate complex correspond to the stretching band of PMMA. The peak obtained at 1738 cm^{-1} in PMMA nanofibres embedded with the samarium β -diketonate complex and that at 1740 cm^{-1} in PMMA nanofibres embedded with the neodymium β -diketonate complex also highlights the presence of PMMA

with the vibration of the C=O group. Both these peaks show a blue shift of 3–4 cm^{-1} from their corresponding peaks in pure PMMA which indicates the replacement of coordinated water molecules with carbonyl groups from PMMA. This also indicates that the interaction between C=O groups of PMMA and lanthanide ions are formed by doping besides the Van der Waals contacts and electrostatic forces [22].

The broad peak obtained in the range 3734–3408 cm^{-1} totally disappears in the spectra of PMMA embedded with lanthanide complexes which is a clear evidence of the absence of the OH group due to the complete evaporation of ethanol and water molecules in the complex during the process and it also agrees to a strong interaction between the complex and the PMMA fibres in electrospinning. The sharp peaks obtained at 1400 and 1300 cm^{-1} correspond to the vibrations of double bonds in the thiophene ring and the C–F stretching of TTA in the complexes, respectively. These peaks become broadened when the complex is incorporated into the host PMMA matrix which supports the notable interaction between PMMA and the complex on electrospinning. The spectra of electrospun PMMA nanofibres embedded with samarium and neodymium β -diketonate complexes contain

Figure 4. XRD spectra: (a) pure PMMA nanofibres, (b) Sm complex, (c) Nd complex and (d) (i) PMMA nanofibres incorporated with the Sm complex and (ii) PMMA nanofibres incorporated with the Nd complex.

the characteristic peaks of both pure PMMA electrospun nanofibres and samarium and neodymium β -diketonate complexes. It is also observed that the peaks are shifted to higher wavenumbers on incorporating the complexes into PMMA.

3.2 XRD analysis

The XRD pattern of the pure PMMA, samarium β -diketonate complex, neodymium β -diketonate complex and electrospun PMMA nanofibres embedded with the samarium and neodymium β -diketonate complexes are shown in figure 4a–d.

The peaks at 24.2, 43.3 and 63.1° observed in figure 4a correspond to PMMA and they match well with the data available in the literature [7]. The XRD patterns of the prepared complexes shown in figure 4b and c are compared with the standard results available in MATCH! 2 software and found that the obtained XRD patterns are in good agreement with samarium oxide and neodymium oxide. The broadened peaks observed at 20 and 39° in the complex samples indicate their amorphous nature [23,24]. The XRD pattern obtained for the sample containing the samarium and neodymium complexes incorporated into PMMA nanofibre (figure 4d) is the same as that observed for pure PMMA. It does not show separate peaks of PMMA but the complexes show that the particles are well incorporated into the PMMA nanofibres. It is also observed that on incorporating the complexes into PMMA

nanofibres the values show a slight shift to lower angles than in pure PMMA. This is due to the interaction between the fibres and complexes.

3.3 UV–visible absorption analysis

The UV–visible spectra of the pure PMMA, samarium β -diketonate complex and neodymium β -diketonate complex, PMMA nanofibres embedded with the samarium and neodymium β -diketonate complexes are shown in figure 5a–d.

It is evident from figure 5a that PMMA has absorption in the visible region. The UV–visible spectra of samarium and neodymium β -diketonate complexes shown in figure 5b are in close agreement with the previous reports [25]. The prepared samarium and neodymium complexes show strong absorption in the UV–visible region. Two main absorption peaks observed at 266 and 340 nm denote the π – π^* transitions of the thiophene ring and the carbonyl group present in the TTA ligand [18]. This indicates the formation of the complexes. The UV–visible spectra of PMMA electrospun nanofibres embedded with the samarium and neodymium β -diketonate complexes shown in figure 5c and d exhibit a significant difference from those of samarium and neodymium complexes.

When the complex is inserted into the host PMMA polymer matrix the absorption observed at 266 nm of the complex

Figure 5. UV-visible absorption spectra: (a) pure PMMA nanofibres, (b) (i) Sm complex and (ii) Nd complex, (c) PMMA nanofibres incorporated with the Sm complex and (d) PMMA nanofibres incorporated with the Nd complex.

is shifted to 278 nm in the case of PMMA incorporated with samarium and to 281 nm in the case of PMMA nanofibres incorporated with neodymium and the band obtained at 340 nm is broadened to 390 nm in both cases. This is because of the interactions between the complex and the polymer fibre and this again confirms the successful incorporation of the complex into the polymer matrix.

3.4 SEM analysis

The SEM analysis results of the pure PMMA, samarium β -diketonate complex, neodymium β -diketonate complex, PMMA nanofibres embedded with the samarium and the neodymium β -diketonate complex are shown in figure 6a–e.

The SEM image of pure PMMA electrospun nanofibres shows the uniform production of nanofibres without any beads or deformations. The diameters of the fibres are determined using WCIF image J software and it is found to be in the range of 60–150 nm with 109 nm as the most distributed fibre. The pristine PMMA nanofibres with a diameter below 100 nm by using only 1% PMMA solution are a new milestone in the polymer field.

The SEM analysis of samarium and neodymium β -diketonate complexes shows that the obtained morphologies are not uniform and it does not show any predicted surface morphology. It is observable from figure 6b and c that the complexes have a variety of shapes like square, rectangular,

pentagonal, hexagonal, etc. The luminous nature of the complexes is also visible in the SEM images of these complexes. The agglomerated nature of the complex elucidated the formation of a precipitate when the solution is cooled from 60°C to room temperature. The SEM images of lanthanide complexes incorporated PMMA do not contain any beads which indicates the appropriate combination and the intended interaction between the complexes and the host PMMA polymer matrix. The luminous nature of PMMA nanofibres, as observable from figure 6d and e, indicates the successful incorporation of a luminescent complex with the transparent PMMA polymer matrix. Figure 7b and c shows that the diameter of PMMA nanofibres is increased to a certain extent after incorporating the complexes into them which again shows the successful incorporation of the complexes into PMMA nanofibres.

Some broken structures which look like flakes are observed in the electrospun PMMA nanofibres incorporated with samarium and neodymium complexes as shown in figure 6d and e. These flake structures are originated by the micro-explosions on the nanofibres due to the high electric field used in electrospinning. Some of the regions of the nanofibres are unstable and hence it has a possibility to break these regions by high pressure during the incorporation of lanthanide complexes into fibres. The flake-like regions are part of fibres and not separated from fibres. Thus, it is confirmed that the broken regions are not originated by any chemical reaction between the fibres and complexes.

Figure 6. SEM images: (a) pure PMMA nanofibres, (b) Sm complex, (c) Nd complex, (d) PMMA nanofibres incorporated with the Sm complex and (e) PMMA nanofibres incorporated with the Nd complex.

The incorporation of particles into the nanofibre is also well established by TEM images. The complex particles can be incorporated into nanofibres as the fibre surface is porous due to the evaporation of solvents besides the physical interaction between PMMA and complexes. The particles can spread everywhere in a non-uniform pattern since particles are non-uniform in size and shape; but it is clear from SEM images that the number of flakes is much less than the number of fibres which show that the properties of fibres incorporated with particles will be influenced by particles alone than flakes. These flakes still exist as parts of fibres only. We cannot say that the particles are inside or on the surface of the fibre since the fibre is too thin to measure on the inside and the outer surface and also since it is not in the coaxial hollow form. The particles can be trapped into the hollow space inside the fibre if the fibre is in the coaxial hollow form only. But here it is not like that.

The fibre diameter distribution of pure PMMA and PMMA nanofibres embedded with samarium and neodymium β -diketonate complexes is shown in figure 7a–c and the surface plot image of pure PMMA and PMMA nanofibres embedded with the samarium and neodymium β -diketonate complexes are shown in figure 7d–f.

The surface plot images, a tool available in WCIF Image J software, shown in figure 7d–f also proves the fibre diameter distribution. Here X and Y axes represent the length and breadth of the selected area of the image under consideration and the Z axis represents the diameters of the fibres in the selected area as height. We can see from figure 7d that the diameter of the produced PMMA fibres are in the range of 60–150 nm with 109 nm as the most distributed one. It also shows the presence of ultrafine PMMA nanofibres with a diameter below 100 nm. Figure 7e and f shows that there is an increase in the fibre diameter after incorporation of

Figure 7. (a) Histogram of PMMA nanofibres, (b) histogram of PMMA nanofibres incorporated with the Sm complex, (c) histogram of PMMA nanofibres incorporated with the Nd complex, (d) surface plot of PMMA nanofibres, (e) surface plot of PMMA nanofibres incorporated with the Sm complex and (f) surface plot of PMMA nanofibres incorporated with the Nd complex.

the complexes into PMMA. There is a little variation among the individual fibre diameters in the case of PMMA nanofibres embedded with the samarium β -diketonate complex but these types of variations are not oftentimes present in the case of PMMA nanofibres embedded with the neodymium β -diketonate complex. Histograms of these samples also prove this point. All these factors give clear cut evidence for the successful incorporation of the lanthanide complexes in the PMMA nanofibre.

3.5 FESEM analysis

FESEM analysis of the PMMA nanofibres is carried out to understand the surface properties and characteristics of the prepared nanofibres in very high resolution and is shown in figure 8. The result shows the production of smooth electrospun PMMA nanofibres without any beads or deformations. The inset of figure 8 shows the close up view of the porous surface of electrospun PMMA nanofibres. All the

electrospun fibres are porous to an extent due to the evaporation of solvents during the electrospinning process itself. The porous nature of electrospun PMMA fibres helps to hold thoroughly the complex incorporated into it which supports the results of XRD. The porous surface can hold those complex particles which are suitable to its size and shape. The enhanced intensity observed in PL spectra of these samples also shows that sufficient number of particles is present in the fibre. The porous surface also proves the heterogeneous nature of the fibre surface which is helpful for further investigations that are progressing very well.

3.6 TEM analysis

TEM analysis of the PMMA electrospun nanofibres embedded with samarium and neodymium β -diketonate complexes are shown in figure 9a and b, respectively. The TEM images of the PMMA electrospun nanofibres embedded with samarium and neodymium β -diketonate complexes show the successful

Figure 8. FESEM image of pure PMMA nanofibres; inset shows the close up view of the porous single PMMA nanofibre.

incorporation of the complex particles into the host matrix. The result shows the non-uniform nature of the particles in its size and shape. As the fibre is ultra-fine in both diameter and thickness, some fibres are damaged in the preparatory steps for taking TEM which can be seen in the images.

The selected area electron diffraction (SAED) patterns of the PMMA electrospun nanofibres embedded with samarium and neodymium β -diketonate complexes are shown in figure 10a and b, respectively. This shows diffused rings formed by bright spots which indicated the polycrystalline nature of the complexes. Thus TEM analysis is evidence for the formation of complexes into the PMMA nanofibres.

3.7 EDX analysis

The EDX of PMMA electrospun nanofibres embedded with samarium and neodymium β -diketonate complexes are shown in figure 11a and b. The corresponding information about the abundance of each element is shown in table 3a and b.

The results obtained from EDX analysis show the successful incorporation of the complexes into the polymer matrix as the polymer contains 2.12 and 1.21% of the samarium and neodymium, respectively which again supports the results of SEM and TEM.

3.8 PL studies

The PL spectra of the pure PMMA, samarium and neodymium β -diketonate complexes and PMMA nanofibres embedded with samarium and neodymium β -diketonate complexes excited at their respective highest occupied molecular orbital–lowest unoccupied molecular orbital gap energy are shown in figure 12a–d. The excitation wavelength for each sample is determined based on the maximum absorption wavelength obtained in UV–visible absorption analysis.

PMMA is subjected to different excitation wavelengths of 250, 300, 350 and 400 nm and it was observed that a broad peak is obtained in the range of 370–450 nm in the visible region as shown in figure 12a. The PMMA nanofibres show the maximum intensity with 300 cps at an excitation wavelength of 250 nm. The samarium β -diketonate complex is subjected to photoluminescent studies at different excitation wavelengths of 320, 400 and 420 nm and the result is shown in figure 12b. The peak observed at 480 nm in the visible region indicates the band edge emission which is clear from the UV–visible absorption spectra of the present samples. The two peaks at 595 and 645 nm correspond to the characteristic

Figure 9. TEM images: (a) PMMA electrospun nanofibres embedded with the samarium β -diketonate complex and (b) PMMA electrospun nanofibres embedded with the neodymium β -diketonate complex.

Figure 10. SAED images: (a) PMMA electrospun nanofibres embedded with the samarium β -diketonate complex and (b) PMMA electrospun nanofibres embedded with the neodymium β -diketonate complex.

Figure 11. EDX spectra: (a) PMMA electrospun nanofibres embedded with the samarium β -diketonate complex and (b) PMMA electrospun nanofibres embedded with the neodymium β -diketonate complex.

Table 3. Percentage abundances of various elements obtained from EDX.

Element	Weight (%)	Atomic (%)
(a) In the PMMA electrospun nanofibres embedded with samarium β -diketonate complexes		
C K	90.90	94.50
O K	6.59	5.14
Na K	0.19	0.10
S K	0.21	0.08
Sm L	2.12	0.18
(b) In the PMMA electrospun nanofibres embedded with neodymium β -diketonate complexes		
C K	78.51	87.03
O K	13.50	11.24
Na K	0.54	0.31
Cu K	6.24	1.31
Nd L	1.21	0.11

emissions from $^4G_{5/2}$ to $^6H_{7/2}$ and to $^6H_{9/2}$ of interstitial Sm^{3+} ions present in the complex respectively [26].

The PL spectra of the pure neodymium β -diketonate complex at excitation wavelengths of 300, 400, 500 and 520 nm are shown in figure 12c. The peak observed at 430 nm is

assigned as band edge emission. The broad peak observed in the range of 440–470 nm corresponds to the main transitions from $^4F_{3/2}$ to $^5I_{9/2}$ of interstitial Nd^{3+} ions present in the complex [27,28]. The blue shift occurring in the PL emission of the Nd complex from the near-infrared region to visible region is attributed to the presence of diketonate ligands in the prepared complex. Other peaks present in the photoluminescent spectrum of Sm and Nd complexes are due to emission from intermediate energy levels, donor–acceptor pair transitions, oxygen vacancies and interstitial ions present in the prepared complexes. No significant shift is observed in the photoluminescent results of the samples when subjected to different excitation wavelengths as shown in this figure. When the samarium and neodymium complexes are incorporated into the PMMA nanofibres, a broad PL emission is observed in the visible region as shown in figure 12d. The emission is similar to the emission of PMMA which proves the successful incorporation of the complexes into the PMMA fibre. Complexes incorporated PMMA fibres show much enhancement in intensity as evidenced from figure 12.

In the present work, a comparative PL study is employed between the pristine PMMA and PMMA nanofibres incorporated with lanthanide complexes for determining the

Figure 12. PL spectra: (a) pure PMMA, (b) Sm complex, (c) Nd complex and (d) (i) PMMA incorporated with the Sm complex and (ii) PMMA incorporated with the Nd complex.

ability of the PL emission properties of the prepared samples. The PL emission intensity of the pure PMMA, pure samarium β -diketonate complex and complex-incorporated PMMA is 300, 800 and 3800 cps, respectively as shown in figure 12a, b and d. The intensity of PMMA nanofibres incorporated with the samarium diketonate complex is about thirteen times higher than that of pristine PMMA nanofibres. Figure 12a, c and d shows that PL emission intensity of pure PMMA is 300 cps, the pure neodymium β -diketonate complex shows the maximum intensity at 1000 cps whereas PMMA incorporated with the neodymium diketonate complex shows the maximum intensity at 4800 cps which is sixteen times higher than the intensities of pure PMMA nanofibres. Hence, it could be indicated that the intensity of nanofibres incorporated with the lanthanide β -diketonate complex shows much higher intensity than that of pure PMMA nanofibres. The enhanced intensity behaviour can be attributed to the combined characteristics of transparent PMMA, luminescent lanthanides and fluorinated ligands present in the samarium and neodymium β -diketonate complexes incorporated PMMA nanofibre sample. Therefore, PMMA nanofibres incorporated with samarium and neodymium diketonate complexes are considered as suitable materials for modern display device applications such as lighting, organic LEDs and curved displays.

4. Conclusion

In summary, the PMMA nanofibres with diameter between 60–150 nm with 109 nm as the most distributed one are prepared through electrospinning. Sm and Nd β -diketonate complexes are prepared using TTA ligand by precipitation method. The lanthanide complexes are found to be amorphous in nature and have a non-uniform and unpredicted morphology. The structural and molecular analysis shows the presence of some lanthanide oxides in the complex samples. The ‘enol’ form of the prepared lanthanide complex is proved using FTIR analysis. The successful incorporation of complexes into the PMMA nanofibre is well established by SEM, FESEM, TEM and FTIR analyses. The visible light absorption and reemission of the prepared samples are carried out by UV–visible absorption and PL analyses. The PL emission intensity of the lanthanide complexes incorporated PMMA nanofibre sample is much higher than that of the pure PMMA nanofibre due to the combined characteristics of luminescent lanthanide complexes and transparent PMMA. The present analysis proved that PMMA could act as the best host matrix not only to pure lanthanides or lanthanide oxides but also to lanthanide complexes with supreme optical properties. Hence, the PMMA polymer supported lanthanides have varieties of applications such as display devices, lighting devices and organic LEDs for curved display devices.

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