Impregnation of Microwave treated exfoliated MoS2 nanosheets into PMMA matrix by solution casting for reinforcing applications

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Abstract. In the present work, poly methyl methacrylate (PMMA)-MoS2 nanocomposite films were prepared by impregnation of exfoliated MoS2 nanosheets into PMMA matrix by solution casting method. Synthesis of exfoliated MoS2 nanosheets through microwave irradiation techniques was found to be simple, less time consuming, eco-friendly and cost effective. We have identified the optimization conditions by varying the parameters like microwave heating time, power and concentration of bulk MoS2. The structural and optical properties of the exfoliated MoS2 nanosheets were investigated. These optimized exfoliated MoS2 nanosheets were introduced into the polymer matrix which was then subjected to different characterization techniques. The effect of exfoliated MoS2 nanosheets on the mechanical properties of the polymer-MoS2 composite was evaluated in detail.

Keywords: Exfoliation, MoS2 nanosheet, Microwave heating, nanocomposite.

1. Introduction

Nowadays, polymer nanocomposite has been getting much attention in the areas of scientific and industrial fields. Polymer nanocomposite is a class of composite materials which contains a polymer matrix and an inorganic material that has at least one dimension in the nanorange [1]. The addition of inorganic nanomaterials into polymer matrix enhances their mechanical, thermal, barrier and fire-retardant properties [2]. This property enhancement is due to the reinforcement mechanism of the inorganic nanomaterials in polymer nanocomposite and strongly depends on the properties of the polymer matrix, nature and type of nanomaterials, concentration of polymer and nanomaterials, particle aspect ratio, particle size, particle orientation and particle distribution [2]. Polymer nanocomposite with layered reinforcing agents exhibit high storage modulus, increased tensile properties, heat distortion temperature and reduction in gas permeability. They also exhibit substantially improved self-extinguishing behavior, tunable biodegradability and enhanced optical and electrical properties when compared with pure polymer and conventional micro and macro composites [3, 4].

Compared to other polymers, poly methyl methacrylate (PMMA) is a one of the most widely used industrial plastics which is also known as acrylic glass [5]. PMMA is a transparent polymer which is easily...
soluble in different solvents like acetophenone, chloroform, toluene and dimethylformamide [6]. Due to its advantages such as high transparency, light weight, and shatter resistance, this polymer is predominantly used in optical and biomedical applications [5].

In recent years, exfoliated two dimensional nanomaterials such as graphene and transition Metal dichalcogenides (TMDCs) have been more focused due to their extraordinary optical and electrical properties [7]. In order to overcome the disadvantages of graphene due to its zero-bandgap, layered TMDC’s which are analogues to graphene in several respects have gained considerable attention in recent time [8]. Among TMDCs family, MoS2 is the most studied material because of its robustness [9]. The crystal structure of single layer MoS2 consists of one layer of Molybdenum atoms sandwiched between two layers of Sulphur atoms. In contrast to graphene, bulk MoS2 and monolayer MoS2 have indirect bandgap of 1.2eV and direct bandgap of 1.9eV respectively [10]. There are two different strategies like ‘top-down’ and ‘bottom-up’ for synthesizing MoS2 nanosheets. Top-down approach includes liquid phase exfoliation [11-12] micro-mechanical exfoliation [13-14], Taylor-Couette flow [15] etc. whereas bottom-up approaches are Physical Vapor Deposition [16], Solution Chemical Processes [17-18], Chemical Vapor Deposition [19], ALD [20] etc. Exfoliated MoS2 material promise a wide variety of applications like sensing [21], photo catalyst [22], Li-ion battery etc. [23]. Their antibacterial activity [25] and bio marking [24] property make them suitable for several important biological applications.

The improvements in electrical, optical, thermal, mechanical, tribological, and flame-retardant properties of MoS2-polymer nanocomposite strongly depend on the synergistic combination of MoS2 and PMMA [26]. There are various methods such as physical blending and in-situ polymerization methods which have been widely used to fabricate PMMA–MoS2 nanocomposite [26]. The obtained MoS2-PMMA nanocomposite has been explored for different applications from optical limiters [27], data storage [28] gas sensor [29] and photo detectors [30].

In this work, we synthesized the exfoliated MoS2 nanosheets from bulk MoS2 by Microwave irradiation techniques. It is simple, eco-friendly and less time-consuming method. A few papers have reported the exfoliation of MoS2 nanosheets via microwave irradiation techniques. But none of them have reported on the structural and optical properties of exfoliated MoS2 nanosheets. In our method, we used water as the solvent. Usually most of the papers related to microwave assisted synthesis methods, reports the use of ethylene glycol, DMF (Dimethylformamide) or other organic solvents as the solvent material due to their high susceptibility to microwave. But use of these organic solvents reduces the eco-friendly nature of this method. Hence, we chose water in our method for its ease of use and suitability in biomedical applications. For getting the optimized condition, bulk MoS2 is subjected to different microwave power and heating time at constant quantity of raw materials. Structural and optical properties of the optimized MoS2 nanosheets are characterized. In addition, mechanical properties of PMMA-MoS2 nanocomposite are also carried out.

2. Material and Methods

2.1 Materials

Molybdenum disulfide (MoS2 powder, size<2 μm, molecular weight: 160.07 and 99% purity), PMMA (poly methyl methacrylate-C5O2H8) and chloroform (CHCl3) were purchased from Sigma Aldrich. In order to prepare aqueous solution of the sample, double distilled water was used.

2.2 Methods

2.2.1 Preparation of exfoliated MoS2 Nanosheet

Domestic Microwave oven (model: Electrolux Solo, frequency 2450 MHz, output power 700W) was used for the synthesis of nanosheets.2.5μg bulk MoS2 dispersed in 20ml distilled water(DW) was subjected to microwave irradiation for different power and time duration. The final product was washed
with distilled water and centrifuged for 2 minutes at 5000 rpm and dried at 80°C in an oven. The powder sample was used for further characterizations.

2.2.2 Preparation of PMMA and PMMA+ exfoliated MoS2 nanocomposite thin film

0.05g PMMA crystal was dissolved in 5ml chloroform and 0.013mg of exfoliated MoS2 was added into the stirring PMMA solution. This was followed by drop casting onto glass substrate and was then kept in room temperature for 1hour for evaporation of the solvent.

Crystal structure of the PMMA-exfoliated MoS2 nanocomposite was characterized using Powder X-ray diffraction (Bruker AXS D8 Advance) with CuKα radiation in the 2θ range of 3-80°, and scan speed of 3°/min. Surface Morphology of the samples was analyzed using Scanning electron microscopy (JEOL JSM 6390 LA, SEM) and transmission electron microscopy (JEOL JEM 2100, TEM). Raman Spectroscopy was used to characterize the vibrational modes of the samples (Horiba JY LabRAM HR 800 Micro Raman Spectrometer). Scanning probe microscopy was used to carried out the Nano mechanical properties of these samples (NanoGuru, N50). Elemental composition of the samples was identified using Energy dispersive analyzer (OXFORD XMX N, EDAX), UV-VIS spectrophotometer (Varian, Cary 5000) and photoluminescence spectroscopy (HORIBA FLUOROLOG FLUOROSCENCE SPECTROMETER) were used to investigate the optical properties of the samples.

3. Results and discussion

3.1 Optimization of exfoliated MoS2 nanosheets

The control parameters viz microwave irradiation time and power was used to optimize the preparation conditions of exfoliated MoS2 nanosheets. These parameters were optimized by the following method. A fixed concentration of 2.5mg bulk MoS2 in 20ml distilled water was used for further experiments. The microwave power and irradiation time were used as the optimizing parameters of exfoliation process, keeping the volume of the raw materials constant. In order to study the exfoliation details of the nanosheets, microwave treated six samples were marked as L2(low power-119W for 2minutes), M2(medium power-462W for 2 minutes), H2(high power-700W for 2 minutes), H4(high power -700W for 4 minutes), H6(high power-700W for 6 minutes) and H8(high power -700W for 8 minutes) respectively. The details of trials and parameters are tabulated in table1.

| Volume of raw materials (0.0025g/20 ml DW) | Microwave power (W) | Time (minutes) | Raman spectra (cm⁻¹) | Electron Microscopy |
|----------------------------------------|---------------------|----------------|---------------------|------------------|
| 20 ml                                  | L2 (119W)           | 2              | 26.6                | Agglomerated     |
| 20 ml                                  | M2 (462W)           | 2              | 26.2                | Agglomerated     |
| 20 ml                                  | H2 (700W)           | 2              | 25.9                | Sheets are seen; but agglomerated |
| 20 ml                                  | H4 (700W)           | 4              | 25.3                | Agglomerated   |
| 20 ml                                  | H6 (700W)           | 6              | 24.8                | Sheets are seen; but agglomerated |
| 20 ml                                  | H8 (700W)           | 8              | 24.2                | Sheets separated |

The experiment was conducted by varying the power and time. Initially the samples were subjected to microwave irradiation at (low, medium, high) powers for 2 minutes. The results from above trials showed
that compared to low and medium power, the sample irradiated at high power for 2 minutes resulted in more exfoliation of the sheets. Hence optimum power level was identified as 700W. Further trials were conducted for optimizing the time of irradiation. It was found that after 8 minutes of microwave irradiation at higher power (700W), separate sheets were formed without agglomeration, and the solvent evaporated completely. Therefore, the optimized condition for the preparation of few layer MoS$_2$ nanosheets was selected to be H8 (high power-700W for 8 minutes). Electron microscopy (SEM and TEM) and Raman spectroscopy were characterization tools used for this optimization process. Henceforth, the optimized sample H8 is marked as MoS$_2$E.

**Electron microscopy (SEM) Studies**

![SEM images](image)

Figure 1. SEM images of (a) Bulk (b) L2 (c) M2 (d) H2 (e) H4 (f) H6 and (g) H8.
Figure 1 shows the SEM images of MoS$_2$ samples of different trials. It is evident that, as explained in the optimization section, exfoliation is maximum at H8 condition. As we move from low power to high power, bulk MoS$_2$ is gradually exfoliated to nanosheets and the process is complete at H8 conditions.

**Electron microscopy (TEM) Studies**

![TEM images](image)

Figure 2. TEM images of (a) Bulk (b) L2 (c) M2 (d) H2 (e) H4 (f) H6 and (g) H8 (MoS$_2$E).

The SEM observations are confirmed by TEM images of Figure 2. As the microwave power and time of irradiation increase to condition H2 (ie. 700W, 2 minutes) the exfoliation starts. The process improves when the time of irradiation is further increased and neat separated sheets are obtained at eight minutes exposure time.

3.2 **Raman studies**

Raman spectrum of the layered MoS$_2$, which helps us to study the vibrational modes of MoS$_2$, exhibits thickness dependent behavior. Figure 3 shows Raman spectrum of the optimization trials (bulk to
H8) of the preparation of exfoliated MoS2 nanosheets. In bulk MoS2, the dominant vibrational modes are located at 377.34 cm⁻¹ (A₁g) and 403.66 cm⁻¹ (E'₁₂g). As thickness of the MoS2 decreases from bulk to exfoliated layers, the dominant vibrational modes of in-plane vibration and out-of-plane vibration modes are slightly shifted. The frequency difference between these two vibrational modes is found to be 24.01 cm⁻¹ (bulk to MoS2-E) when compared with bulk (26.32 cm⁻¹). This value is close to the trilayer MoS2 in reported literature [31].

![Raman spectra of Bulk, L2, M2, H2, H4, H6, and H8(MoS2E) samples.](image)

Figure 3. Raman spectra of Bulk, L2, M2, H2, H4, H6, and H8(MoS2E) samples.

3.3 Structural properties

Figure 4 shows XRD patterns of both bulk and exfoliated MoS2. The only difference between these two spectra is in Intensity of peaks. It is found that the reduction in XRD intensity of the (002) plane is due to the formation of exfoliated MoS2 in the sample [32]. In addition to this, there is no other extra peak present in the samples.

![XRD spectrum of bulk MoS2 and MoS2E.](image)

Figure 4. Shows XRD spectrum of bulk MoS2 and MoS2E.
Atomic Force Microscopy (AFM) technique was also used to further examine the morphology and thickness of the synthesized MoS$_2$ nanosheets. AFM topography images were captured with contact mode in air using cantilever tip and the images are shown in Figure 5. The theoretical thickness of MoS$_2$ monolayer is around 0.9-1.3nm [33]. From the AFM height profile of the areas marked in Figure 5(b), the thickness of the MoS$_2$ nanosheets is found to be below 5nm. This indicates existence of a few layers in the samples. During drying process, some particles show agglomeration.

![Figure 5. (a,b) AFM images of bulk MoS$_2$ and MoS$_2$ nanosheets. (c) AFM height profile measured along the area 1 in (b).](image)

![Figure 6. EDAX spectrum of MoS$_2$E.](image)

It is confirmed from EDAX, that the sample MoS$_2$E (Microwave power 700W and irradiation time 8 minutes) has Mo to S stoichiometry of 1: 2.04 and is shown in figure 6.

### 3.4 Optical properties

Figure 7 shows the optical absorbance of the dispersed solution of bulk and exfoliated MoS$_2$ and Tauc’s plot of exfoliated MoS$_2$. From the spectra, it is found that the exfoliated MoS$_2$ nanosheets exhibit higher absorbance than bulk. This is due to the fact that, being lighter the nanosheets have lower sedimentation rate than bulk MoS$_2$ and hence more surface area will be exposed to the UV-Vis radiation,
which in turn increase the absorption in MoS$_2$E sample [34]. The absorption peaks at 631 nm and 691 nm correspond to the exciton A and exciton B arising due to the direct band transitions [35]. The peak at 460 nm can be attributed to the optical transitions between the density of states peaks in the valance and conduction bands [36, 37].

According to Beer’s law, the absorbance ($A$) = $\varepsilon cl$. Where $A$ is the absorbance of the material taken from UV-Vis spectra, $\varepsilon$ is the molar extinction coefficient, $l$ is the path length and $c$ is the concentration of the solution [38].

$$\varepsilon = A / lc$$ (1).

Using Tauc’s plot, bandgap energy of the exfoliated MoS$_2$ was calculated [39].

$$(\alpha hv) = B(hv - E_g)$$ (2)

Where $\alpha$ is the absorption coefficient, which is a function of frequency $v$. $B$ is a constant that depends on the transition probability. The exponent $\gamma = 1/2$ or $3/2$ for direct transitions whereas, $\gamma = 2$ or 3 for indirect transitions. $E_g$ is bandgap energy. Here, molar extinction coefficient ($\varepsilon$) is molar absorption coefficient $\alpha$.

![Figure 7](image)

**Figure.7** (a). UV-Vis spectrum of bulk MoS$_2$ and MoS$_2$E. Fig.7 (b) Tauc plot curve of MoS$_2$E.

In bulk MoS$_2$, the bandgap energy is 1.2 eV. For direct transition, the calculated optical bandgap energy of the exfoliated MoS$_2$ is 1.81 eV which is close to the reported value [36]. Compared to bulk, the exfoliated MoS$_2$ sample has higher bandgap value due to quantum confinement [36].
Figure 8. PL emission spectrum of bulk MoS$_2$, exfoliated MoS$_2$ and distilled water, with excitation wavelengths (a) 280nm (b) 480nm.

The photoluminescence properties of dispersed solution of bulk MoS$_2$, and exfoliated MoS$_2$ nanosheets in distilled water were characterized and is shown in Figure 8. The samples were excited with two excitation wavelengths of 280nm and 480 nm and corresponding emission spectrum were recorded. At both wavelengths, the emission peaks of exfoliated MoS$_2$ nanosheets are observed to be at 465nm, 595nm, 652nm, 720nm, 786nm and 913nm. The peaks observed at 595nm and 652nm are attributed to exciton A and exciton B respectively [40]. The peaks at 780nm (1.59eV) and beyond are ascribed to indirect bandgap transitions [41]. It is also observed from the PL spectra that the exfoliated MoS$_2$ samples show enhanced photoluminescence compared to bulk MoS$_2$. This enhancement is due to the lower relaxation rate of interband transition and it reflects significant changes in the electronic structure of the exfoliated MoS$_2$[42].

3.5 Mechanical properties

In order to investigate the effect of concentration of exfoliated MoS$_2$ in the PMMA matrix, the composite was analyzed using Nano indentation. In this technique, Berkovich diamond probe is used to indent and scan the surface of the samples. The topographical images of the samples are shown in Figure 9.
In this test, load-displacement of the indenter probe is measured continuously throughout the analysis. The data is used to extract hardness and elastic modulus of the materials. Hardness and Elastic modulus of the samples are calculated using the following equations.

Hardness (H) = \frac{Load maximum (\mu N)}{contact area (nm^2)} \quad (3)

The probe area function of the ideal Berkovich indenter is given by

\[ A_c = 24.6 h_c^2 \]

Where \( h_c \) is the contact depth and \( A_c \) is the projected contact area at maximum load [43].

Elastic modulus (Er) = \sqrt{\pi/2} \, \beta \, S / \sqrt{A_c} \quad (4)

Where \( \beta \) is the Berkovich indenter geometry constant, is equal to 1.034 and \( S \) is the contact stiffness [43].

The measured hardness of PMMA and nanocomposite samples is 0.2507GPa and 0.2755GPa respectively. Similarly, elastic modulus of PMMA and nanocomposite samples is found to be 6.7815GPa and 8.5547GPa respectively. Thus, it is clear that incorporation of exfoliated MoS\(_2\) into PMMA matrix has caused significant improvement in the mechanical properties of the polymer. This improvement is due to the strong interaction between the polymer molecules and nanosheets. It is important to note here that no cracks and pores were visible in the film. This is confirmed by scanning electron microscopy images and
given in Figure 10 shows SEM images of PMMA film and PMMA-MoS\textsubscript{2}E film. Hence it is safe to conclude that efficient load transfer takes place between MoS\textsubscript{2} nanosheets and the PMMA matrix. This paves the way for using this nanocomposite material for load bearing applications [44] while retaining most of its transparency.

4. Conclusions

Exfoliated MoS\textsubscript{2} nanosheets are synthesized successfully by microwave irradiation method, which is a simple, eco-friendly, fast and cost-effective technique. The structural and optical properties of the exfoliated MoS\textsubscript{2} nanosheets are characterized. The optimization of the exfoliation process of MoS\textsubscript{2} nanosheets is carried out with the help of Electron microscopy and Raman spectroscopy. Raman spectroscopy studies reveal that there is a small shift in the vibrational frequencies of E\textsubscript{12g} and A\textsubscript{1g} peaks of exfoliated samples. Using electron microscopy, few layer nanosheets are visualized. The stoichiometric ratio of exfoliated MoS\textsubscript{2} nanosheets (1:2) is confirmed using Energy Dispersive X-ray analyzer. Optical properties of MoS\textsubscript{2} nanosheets are investigated using UV-VIS Spectrophotometer and Photoluminescence Spectroscopy. PMMA-MoS\textsubscript{2} nanocomposite is prepared by incorporation of optimized MoS\textsubscript{2} nanosheets into the polymer matrix by solution casting. Compared to PMMA, the mechanical properties like hardness and elastic modulus of the nanocomposite are enhanced. From these observed results, one can safely conclude that this PMMA- MoS\textsubscript{2}E nanocomposite is a suitable material for potential reinforcing applications.

Acknowledgement

The authors acknowledge ‘Sophisticated Test and Instrumentation Centre (STIC)’ and ‘Sophisticated Analytical Instrumentation Facility (SAIF), Cochin’, for providing analytical facilities and for valuable discussions. We are thankful to Dr. Chintan Bhat, Mr. Kiran Raphael for giving SPM facility (NanoGuru, N50) and also grateful to Dr. E.I. Anila and Miss Ebitha (UC College, Aluva) and Prof. M. K. Jayaraj and Miss. Anju (Department of Physics, CUSAT) for providing PL facility and Raman spectroscopy for this work.

Conflicts of Interest

All authors declare that they have no conflict of interest.

Financial funding

This research received no external financial funding and support.

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