

Comparison of PMMA layers doped with methyl red and CdSe quantum dots for application in fibre optic

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Abstract

The paper presents a study of the luminescence properties in the visible spectral range of poly(methyl methacrylate) (PMMA) doped with organic dye-methyl red and CdSe quantum dots. The emission spectra of polymer-doped composite structures were investigated and compared with pure PMMA. Optical characterisation was carried out, focused on the measurement and analysis of excitation and luminescence spectra. Comparison of the spectroscopic characteristics of the developed materials allowed comparing the effect of doping on the luminescence properties of the obtained materials and considering their potential application as luminescent materials in fibre optic sensors.

1. Introduction

The use of fibre optic sensors in a wide range of industries is becoming increasingly prevalent. Compared to traditional electronic sensors, they offer numerous advantages that undeniably make them more appealing for specific applications. Firstly, they provide significantly higher sensitivity, resolution, and dynamic range. The extremely small size of the active part allows to produce compact sensors. The matrix with the active part can be overlaid on the front of the optical fibre. In such cases, the sensor operates through the wave reflection phenomenon (external sensors) or by covering the side surface and utilizing the fading wave (internal sensors).

In recent years, there has been significant development in fibre optic technologies utilizing luminescent materials for light source applications operating in the UV-VIS range. The most well-known and widely used are semiconductor lasers that have a wide bandgap [1]. Ongoing efforts focus on discovering new materials with increasingly superior properties. Particularly noteworthy are polymeric materials with the addition of active dopants. Such materials exhibit excellent optical properties due to

the polymer used and impressive luminescence properties due to the dopants employed. Furthermore, the polymer provides protection to the added compounds from the external environment and other influencing factors. The optical and thermal properties of these structures strongly influence whether polymer optical fibres can be drawn from such preforms. Poly(methyl methacrylate) (PMMA) is a polymer known for its good tensile strength, high hardness, transparency, and low optical loss in the visible range. Research on additives for polymer layers is being conducted using three different groups of compounds: lanthanide(III) ions isolated from the polymer network via nanocrystals [2–5], active organic dyes [6, 7], and quantum dots (QD) [8, 9].

In the case of silica (glass) optical fibres, it is crucial to modify them by applying thin layers with diverse properties and physical-chemical nature. The formation of glass/polymer or polymer/glass-doped coatings is becoming increasingly common. Such coatings can enhance mechanical and chemical resistance, modify spectral characteristics, and impart photocatalytic and hydrophobic properties to the glass surface, preventing fouling and facilitating the cleaning of glass surfaces [10]. It is essential to consider the adverse environmental conditions that optical fibres should be protected against. Due to its hydrophilic surface, glass is susceptible to

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destruction, leading to gradual and irreversible damage. The action of water induces changes in the microstructure of the glass and in the volume phase [11]. Changing the surface to hydrophobic can be achieved by coating it with a polymer layer [12–14]. The oldest technique for applying thin films is the dip-coating method. This method is straightforward, cost-effective, and results in high-quality coatings. The obtained structures are reproducible and can be characterised in a wide variety of ways. This method allows control over parameters such as speed of immersion and emergence of samples, evaporation time, number of immersions, and angle of immersion and emergence.

Research on admixtures for PMMA films has been conducted for over a decade [15, 16]. The addition of the appropriate amount and concentration of dopants affects the physicochemical properties of polymers. By adjusting these quantities, it is possible to obtain compounds adapted to specific applications [17]. Various organic dyes have been investigated, but methyl blue and methyl red deserve special attention due to their electronic, optical, and UV absorption properties [18–20]. Additionally, attempts have been made for many years to combine QD with polymers to improve stability, thermal, and mechanical properties [21, 22]. Methyl red has well-defined absorption and emission peaks that are useful in many optical applications. The absorption maximum of methyl red lies in the range of about 520–560 nm, and the emission in the range of about 580–650 nm. CdSe QD have unique size-dependent emission properties which allows fine-tuning of the emission wavelength. This allows them to be tailored to specific conditions and enables easy comparison with other compounds, including just methyl red. Methyl red and CdSe QD, thanks to their synthesis using a high-boiling solvent, are compatible with many polymers used in optical fibres, including PMMA, allowing them to be easily incorporated into a polymer matrix without degrading the mechanical and optical properties of the polymer. Both compounds are chemically stable (but organic dyes can be sensitive to photodegradation and environmental operating conditions), and both additives allow optimization of fibre optic properties depending on application requirements. In this paper, both methyl red dye and CdSe QD synthesized in a high-boiling solvent are characterised by absorption spectra in the 520–550 nm range, enabling a comparison of these compounds as dopants for polymer optical fibres [23].

In this work, thin films of PMMA and PMMA-doped PMMA formed on glass plates were investigated. In addition, volumetric samples were made as fibre preforms in which PMMA was also doped with methyl red and CdSe QD. The smallest QD can be obtained by precipitating semiconductor crystals from a solution in a liquid. Typically, compounds of elements from groups II and IV, and groups III and V are used to obtain QD. Manipulating the shape and size allows for the influence of their properties, including the phenomenon of luminescence tailored for specific applications. QD are characterised by high quantum efficiency and extremely narrow photoluminescence emission bands. In comparison to standard organic dyes, they exhibit long fluorescence lifetimes, high stability, and resistance to photobleaching [24, 25]. The

luminescence properties of the obtained layers were also analysed. In a laboratory environment, water (steam) is a controllable parameter. However, when utilizing fibre optic sensors with external active layers in an outdoor environment, attention should be given to this parameter.

2. Materials and methods

Methyl methacrylate (MMA, 99%, SIGMA-ALDRICH), Dichloromethane (CH_2Cl_2 , $\geq 99\%$, SIGMA-ALDRICH), methyl red (POL-AURA), 1-octadecene (ODE for synthesis, SIGMA-ALDRICH), Cadmium oxide (CdO , $\geq 99.99\%$ trace metals basis, SIGMA-ALDRICH), trioctylphosphine (TOP, 97%, SIGMA-ALDRICH), selenium powder (Se, -100 mesh, 99.99% trace metals basis, SIGMA-ALDRICH), oleic acid ($\geq 99\%$, ROTH), Chloroform (CHCl_3 , $\geq 99.9\%$, SIGMA-ALDRICH), PMMA granules (Plexiglas, Darmstadt, Germany), thioglycolic acid TGA (98%, Aldrich), benzoyl peroxide (for synthesis, SIGMA-ALDRICH) were used.

QD were synthesized using a colloidal method like the procedure outlined in Refs. 26 and 27, but with the incorporation of an electric stirrer to ensure thorough mixing of the substrates. The solution containing the selenium ion precursor was prepared in a flat-bottomed flask by adding 0.03 g of powdered selenium, 0.4 cm^3 of trioctylphosphine, and 5 cm^3 of 1-octadecene. The entire mixture was thoroughly mixed, resulting in a colourless TOPSe solution. In a three-necked round-bottom flask, 0.013 g of cadmium oxide, 0.6 cm^3 of oleic acid, and 5 cm^3 of 1-octadecene were added. The mixture was placed in a heating bowl and heated until the cadmium oxide was completely dissolved. The synthesis system also included a thermocouple for continuous temperature control and a magnetic stirrer. After this step, 1 ml of the previously prepared solution containing selenium ions was added. A gradual colour change occurred, starting from colourless and progressing to yellow, orange and red, until maroon. Samples were taken at different time intervals: 60, 120, 300, 600, 1800, and 3600 s. A sample taken after 300 s was chosen for further study due to its favourable optical properties.

2.1. PMMA thin films

Thin films were produced using the dip-coating method with KSV NIMA's dip coater. The coatings were applied to 76×26 mm microscope slides, each 1 mm thick, obtained from ChemLand. Chloroform solutions of PMMA with concentrations ranging from 1% to 6% were prepared. Table 1 presents the masses of individual PMMA granules, the mass of chloroform CHCl_3 with a density of 1.49 g/cm^3 , and the corresponding concentrations. The selection of the solvent is a crucial consideration. In this method, moderate volatility is essential, with a boiling point ranging from 50 to 120 $^\circ\text{C}$ (chloroform has a boiling point of 61.2 $^\circ\text{C}$). This ensures the formation of a liquid film on the surface, facilitating rapid solvent evaporation and resulting in a uniform polymer film. Polymethyl methacrylate, as the solute, must exhibit good solubility in the chosen solvent and have a low tendency to precipitate or crystallize during the process.

Table 1.

Description of the composition of the obtained PMMA solutions with different concentrations.

PMMA granules mass [g]	0.497	0.994	1.487	1.994	2.494	3.001
CHCl ₃ mass [g]	49.17	47.68	47.68	47.68	47.68	46.94
Percentage concentration [m/m %]	1	2.04	3.02	4.01	4.97	6

Glass plates were immersed in vessels containing PMMA solutions of various concentrations. Afterward, plates with the applied layers were allowed to undergo solvent evaporation. Similarly, layers incorporating dopants were created, resulting in PMMA/QD+CdSe and PMMA/methyl red thin films (Fig. 1). To achieve this, 1 ml of a previously synthesized solution of CdSe QD with a concentration of $7.6 \cdot 10^{-5}$ M was added to a solution of PMMA granules in chloroform. The entire mixture was blended, and layers were subsequently applied to glass plates, followed by solvent evaporation. For the PMMA/methyl red films, an indicator dye was introduced directly into the polymerization mixture in an amount of 0.02 g. The mixture was then placed in an ultrasonic bath and deposited onto a slide, allowing the solvent to evaporate. The quantity of dye added was calculated stoichiometrically to ensure a meaningful comparison with the amount of QD.

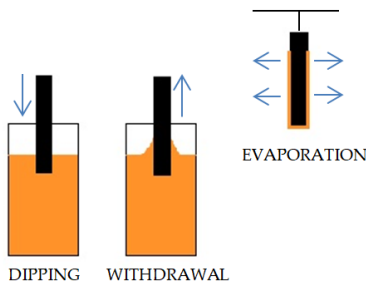


Fig. 1. Schematic of the dip-coating method.

2.2. PMMA fibre optic preforms

Thermal free radical polymerization was employed to preform fabrication both pure PMMA and PMMA with an admixture. A polymerization mixture comprising 50 g of methyl methacrylate was prepared. The initiator used was benzoyl peroxide (0.2 g), and the chain transfer agent was thioglycolic acid (TGA, 0.3 g). This mixture was divided into three parts. The first part received 1 ml of previously prepared CdSe QD. The second part received 0.1 g of methyl red, while the third part served as a comparison sample containing only PMMA. These samples were then placed in an oven at 120 °C for 2 h to allow the polymerization process to take place. Subsequently, the samples were left in the oven to cool to room temperature, removed, and subjected to further testing. The resulting doped PMMA structures are illustrated in Fig. 2.

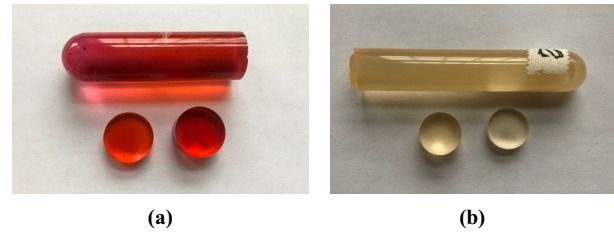


Fig. 2. PMMA sample with the addition of (a) methyl red, (b) CdSe QD.

3. Results

The thickness of layers applied using the dip-coating method was measured. Plates containing layers of PMMA, PMMA with dye, and PMMA with QD were compared. The thickness increases proportionally with the concentration of PMMA in chloroform for each of the three samples. The highest thickness was observed for the sample with PMMA alone at all concentrations produced (Fig. 3). To determine the mass of polymer applied to the glass surface, the plates were weighed before and after the application of PMMA. After calculating the microscope plate area, the mass of polymer per cm² was determined. Considering the density of PMMA (1.18 g/cm³) allowed for the calculation of the thickness of the applied film at each concentration.

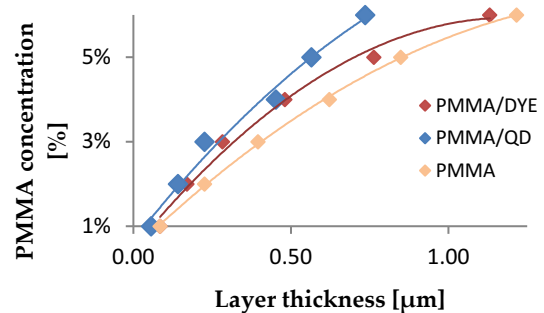


Fig. 3. Comparison of the thickness of the layers applied to the wafers.

The investigation of optical absorption, particularly absorption edges, proves to be a valuable method for studying optically induced transitions, offering insights into band structures and energy gaps in both crystalline and amorphous materials. The absorption of QD is size-dependent. Figure 4 displays the absorption spectra of solutions containing CdSe QD and methyl red dye.

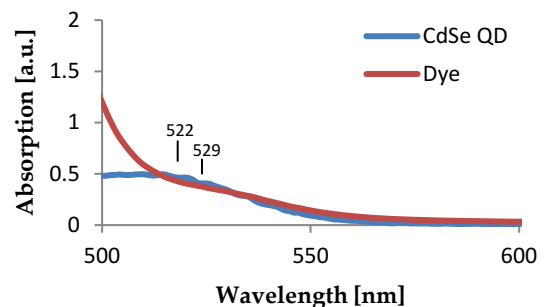


Fig. 4. Absorption plots of CdSe (blue line) and methyl red (red line) QD solutions.

Emission spectra were recorded when all samples were excited with the light of the same wavelength. The spectrum indicates that the addition of dopants increases the intensity of the emission peak maximum. The highest intensity was achieved when doped with CdSe QD (Fig. 5).

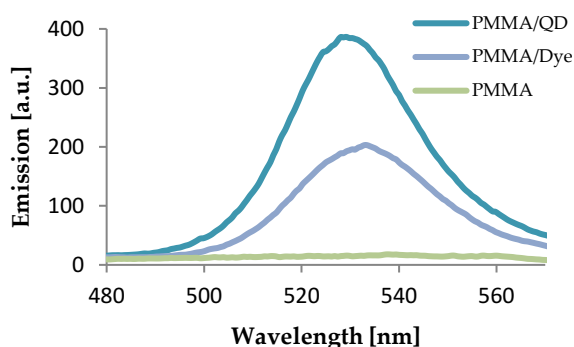


Fig. 5. Emission graphs of the obtained PMMA, PMMA/QD CdSe, and PMMA/dye (methyl red) structures at the same excitation length.

Thermogravimetric (TG) analysis of dopant-containing preforms was carried out using a NETZSCH STA 449 F1 Jupiter at a heating rate of 10 °C/min in the temperature range of 0–200 °C in an O₂/N₂ mixture flow. The sample mass was about 10 mg and a TG-DCS type S sensor thermocouple was used. An empty Al₂O₃ crucible served as a reference. A detailed study of PMMA is available in the article [4]. Figure 6 illustrates the weight change of the sample up to 200 °C. Given that the processing of polymer optical fibres does not exceed 200 °C, measurements up to this temperature are crucial. Both samples show significant thermal resistance. The sample containing CdSe QD made with 1-octadecene (number 2-red line) shows higher stability than the sample containing methyl red (number 3-blue line), which can be attributed to the thermal properties of the QD. It is noteworthy that in the case of CdSe QD additive, the decrease is about 1% from the initial mass, while in the case of methyl red additive, it is more than 3%. In addition, the graph also includes the spectrum of pure PMMA as a reference (number 1-green line).

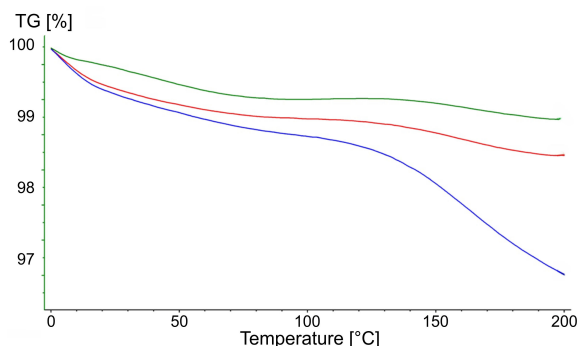


Fig. 6. TG plot of pure PMMA preforms (green line) PMMA/QD (red line) and PMMA/dye (blue line).

4. Discussion and conclusions

PMMA, as a polymer, has found many applications in various industrial fields. With numerous advantages, including biocompatibility, non-toxicity, and processability, it is widely used in polymer optical fibres for fibre optic

sensors. Coatings applied to materials, including optical fibres, should be characterised by hydrophobicity, reducing capillary rise, high resistance to external agents, no significant changes in aesthetic appearance, and ease of application. Modification of PMMA properties with QD and methyl red allowed obtaining better optical properties of the polymer, as evidenced by the emission spectra of the doped layers. According to the literature, the absorption of CdSe QD and methyl red solutions was located at about 525 nm, which makes it possible to compare these dopants as an active additive. The emission spectrum of the PMMA-doped structures showed that both structures have high luminescence. Thermal stability is also an important aspect. The TG plot shows that the addition of the dopant slightly affects the thermal properties of the polymer. Obtaining and processing polymer optical fibres does not exceed 200 °C, so measurements up to this temperature are important. The decrease in mass at 200 °C by less than 1% is a promising result. The addition of dopants does not significantly affect thermal decomposition, which is a promising result for obtaining polymer active optical fibres. The resulting structures provide a good material for further research toward fibre optic engineering.

Authors' statement

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. Conceptualization, A.K. and P.M.; methodology, A.K. and P.M.; validation, A.K. and P.M.; formal analysis, A.K. and P.M.; investigation, A.K.; resources, A.K.; data curation, A.K. and P.M.; writing – original draft preparation, A.K.; writing – review & editing, A.K. and P.M.

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