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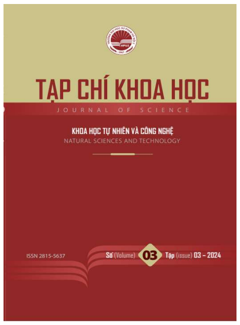

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The one-pot fabrication of green-emitting composites based on PMMA

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Abstract

Photoluminescent composites consisting of a photoluminescent material dispersed in a suitable matrix have been applied in many applications, such as light-emitting diodes, solar concentrators, and anti-counterfeiting inks. The traditional method for the fabrication of composites by blending an as-synthesized photoluminescent material and a matrix is very challenging as it is difficult to obtain homogeneous composites. In this study, we have demonstrated a one-step method to prepare homogeneous composites by inducing the formation of *in-situ* photoluminescent centers in a stable matrix. Poly(methyl methacrylate) (PMMA) coated with o-phenylenediamine (oPD) was thermally annealed at 165°C for a duration of 5 minutes in an extruder to obtain green-emitting composites. The composites exhibited a broad absorption peak at 425 nm and an absorption shoulder at 495 nm. The emission spectrum of the composite was broad, ranging from 400 nm to 700 nm, and reached the maximum at 525 nm. The photoluminescent maximum position was independent of the excitation wavelength. The photoluminescent excitation spectrum of the composite resembled the absorption near 425 nm. Time-dependent density functional theory (TD-DFT) calculations suggested that 2,3-diaminophenazine and 3-amino-2-hydroxyphenazine are the main molecular fluorophores accounting for the optical properties of the composites. The synthetic method demonstrated in this study is transferable for preparing numerous photoluminescent thermoplastics.

Keywords: PMMA, composite, photoluminescent, fluorophore, one-pot

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1. Introduction

Photoluminescent materials have been used in many important applications. For example, in light-emitting diodes (LEDs), composites of phosphors and an encapsulant are used to convert a portion of the light emitted from the chip to light of different colors [1]. The light conversion ability of photoluminescent materials is also utilized in solar concentrators that absorb the incoming light and transmit the emitting light toward solar cells at the edge of the concentrator [2]. In sensing applications, changes in the emission efficiency of photoluminescent materials induced [3], [4]. In several applications, such as LEDs, light conversion films, anti-counterfeiting inks, and light concentrators the photoluminescent materials are employed together with a matrix in the form of composites. The matrix is used to disperse the luminous material to minimize the photoluminescent quenching induced by aggregation, re-absorption, or photo-bleaching effects [5]. An ideal photoluminescent composite is a true solution of a photoluminescent material dispersed homogeneously in a matrix.

The conventional strategy for preparing homogeneous composites involves blending a photoluminescent material with a matrix that has similar solubility parameters [6], [7]. This method is very challenging due to the difficulty in selecting the active material and the matrix [8], [9]. Alternatively, bonding the active material to the matrix has been used to prepare homogeneous composites by preventing the active material from segregation [10]–[13]. This bonding method exhibits several disadvantages(,) including the requirement of a chemical bonding step and unwanted photoluminescent quenching [5], [10].

To overcome the aforementioned issues, a novel strategy has been developed to create individual luminous centers in the dispersive matrix. Suitable molecular precursors that were pre-dispersed in the matrix are converted into individual luminous centers. For example, Y. Tang and co-authors blended a mixture of polycaprolactone, lead (II) iodide, and methylammonium bromide (MABr) to create a homogeneous composite [14]. PbI_2 reacted with MABr to form $MAPbBr_3$ perovskite quantum dots that were homogeneously dispersed in the matrix. Mai *et al*. annealed a solution of citric acid (CA) and ethylenediamine (EDA) in poly(vinylalcohol) (PVA) to produce homogeneous and highly photoluminescent composites [15]. The authors attributed the formation of homogeneous composites to the creation of luminous centers by the intermolecular condensation between CA and EDA. The same author has applied this synthetic strategy to prepare photoluminescent composites using poly(methyl methacrylate) (PMMA) [16] and polycarbonate (PC) [17]. Notably, PMMA and PC are typical thermoplastics used in the process. The applicability of this novel strategy to thermoplastics adds the advantages of plastics to photoluminescent composites for many outdoor applications.

Recent insights into the formation mechanism of carbon nanomaterials from molecular precursors reveal that some photoluminescent molecules could be formed by simple thermal annealing of suitable organic precursors [18]. For instance, heating a mixture of CA and EDA in PVA [15] or PMMA [16] matrix creates composites with intense blue emission. The photoluminescent properties of those composites originate from 5-oxo-1,2,3,5-tetrahydroimidazo-[1,2-α]-pyridine-7-carboxylic acid (IPCA) that is formed by the condensation between CA and EDA. By using o-phenylenediamine (oPD) to prepare carbon nanomaterials, it has been found that oPD can form various molecular fluorophores [19], [20]. Depending on the synthetic environment the resultant fluorophores give different emission colors across the visible range. Those findings may benefit the development of homogeneous photoluminescent composites. In this work, we have examined the fabrication of a photoluminescent composite using oPD as a luminous precursor and PMMA matrix. Thermal annealing was conducted on an extruder, which is one of the most common machines used in thermoplastic molding. The composite exhibits excitation-independent green emission. By comparing the optical properties of the composite with a reference sample and density-functional theory (DFT) calculations we propose that 2,3-diaminophenazine and 3-amino-2-hydroxyphenazine possibly accounts for the optical properties of the composite.

2. Experimental section

2.1. Materials

PMMA commercially known as ACRYREX®PMMA Resin Optical was purchased from Chimei. O-phenylenediamine (oPD, 98%) and ethanol (98%) were received from Aladdin Chemicals. A SJ15 extruder (YunlinLi, China) was used for the thermal extrusion of PMMA and composites. A JSR JSVO-30T vacuum drying cabinet was used to fabricate composite membranes.

2.2. The synthesis of composite wires

Dissolve 0.16 g of oPD in 40 ml of ethanol. The ethanol solution was sprayed onto 20 g of PMMA species. The PMMA coated oPD was fed into the extruder which was operated at 165 ^{o}C and with rotation speed of 6 rounds per minute to fabricate composite wires.

2.3. The preparation of composite membranes

The composite wires were cut into small species and placed in a mold whose width, length, and height were 2 cm, 2 cm, and 0.2 cm, respectively. The mold was then placed in a vacuum drying cabinet at 140^{o}C for 2 hours to create composite membranes.

2.4. The synthesis of a reference sample

A solution containing 0.3 g of oPD and 30 ml of ethanol was stored in a Teflon-lined autoclave, which was then heated at 180^{o}C for 8 hours. The solution was cooled naturally to room temperature and filtered through a 0.21 µm syringe filter to remove large aggregates.

2.5. Theoretical calculations

All calculations were performed using a Gaussian 09 package. Molecules were first optimized using the B3LYP hybrid function with a 6-31 G basis set. The optimized structures were further used for time-dependent density functional theory calculations which were performed using the same basis set for 16 states. Molecular orbital, ultraviolet–visible (UV-Vis) absorption profile, and vibrational spectrum were resolved on a GaussView 5.08 program.

2.6. Characterizations

The UV-Vis absorption spectra of membranes were conducted on a UV-2540 (Shimadzu) spectrometer while the photoluminescent (PL) and photoluminescent excitation (PLE) spectra were measured on FLS1000 (Edinburgh Instrument) fluorescent spectrometer. Fourier-transform infrared spectroscopy (FT-IR) spectra were recorded using a Jasco FT/IR6300 spectrometer.

3. Results and Discussion

Figure 1 presents the conversion of PMMA coated oPD into green-emitting composites by a thermal extrusion method. After spray coating, oPD coated on PMMA species constituted approximately 3% by weight. Based on the rotation speed of the extruder, the retention time was estimated to be 5 minutes. As seen in Figure 1c, upon thermal annealing the PMMA coated oPD turned brown while PMMA remained transparent. Additionally, under UV light, the composite in either wire or membrane forms exhibit(s) green emission while the PMMA counterparts emit negligibly, Figure 1.d-e.

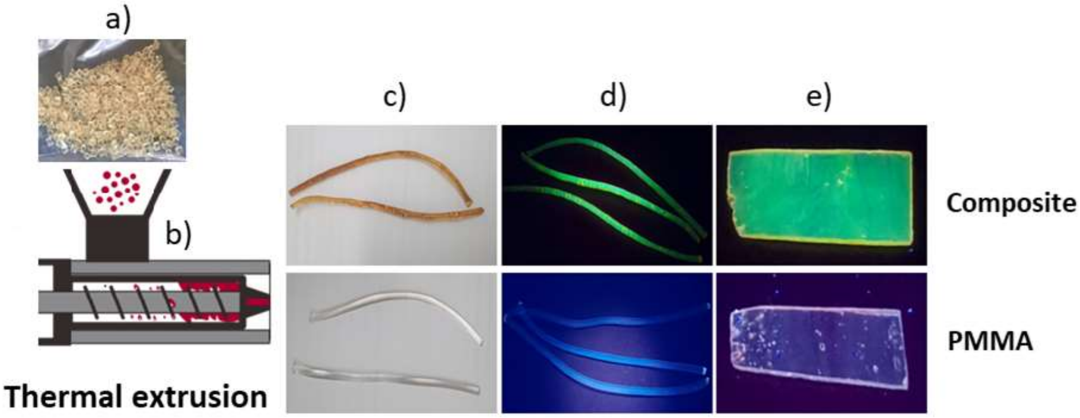

Figure 1. The preparation of composite by a thermal extrusion method. **a)** PMMA species coated with o-phenylenediamine (oPD); **b)** a thermal extruder. The comparison between composite wires or membranes with PMMA blank samples under daylight **(c)** or under UV light at 365 nm **(d-e)**.

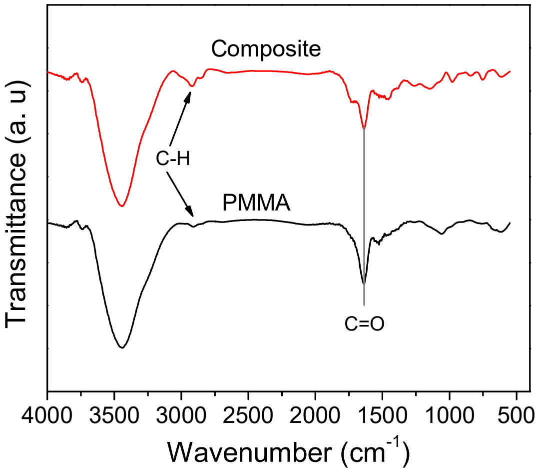

Figure 2. The FT-IR spectra of composite and PMMA matrix

FT-IR spectra of the composite and PMMA shown in Figure 2 were nearly identical, indicating that the structure of PMMA remains unchanged in the composite. UV-vis spectra of a composite membrane are shown in Figure 3a in comparison with that of a PMMA membrane. While the thermally annealed PMMA membrane has a negligible absorption above 400 nm the composite exhibits an absorption peak at about 425 nm and an absorption shoulder at about 495 nm. The photoluminescent (PL) spectrum of the composite shown in Figure 3c was broad, ranging from 450 nm to about 700 nm, and peaked at about 525 nm. Additionally, the position of PL maximum was independent of the excitation wavelength in the range from 350 to 450 nm. The photoluminescent excitation (PLE) recorded at 525 nm and the absorption spectra of the composite, shown in Figure 3d, have a common broad band in the 400-450 nm range. This similarity indicates that the absorption at the peak around 425 nm mentioned in Figure 3a results in emission. Additionally, the excitation-independence of the PL spectrum suggests the origin of emission to be molecular fluorophores [18], [21].

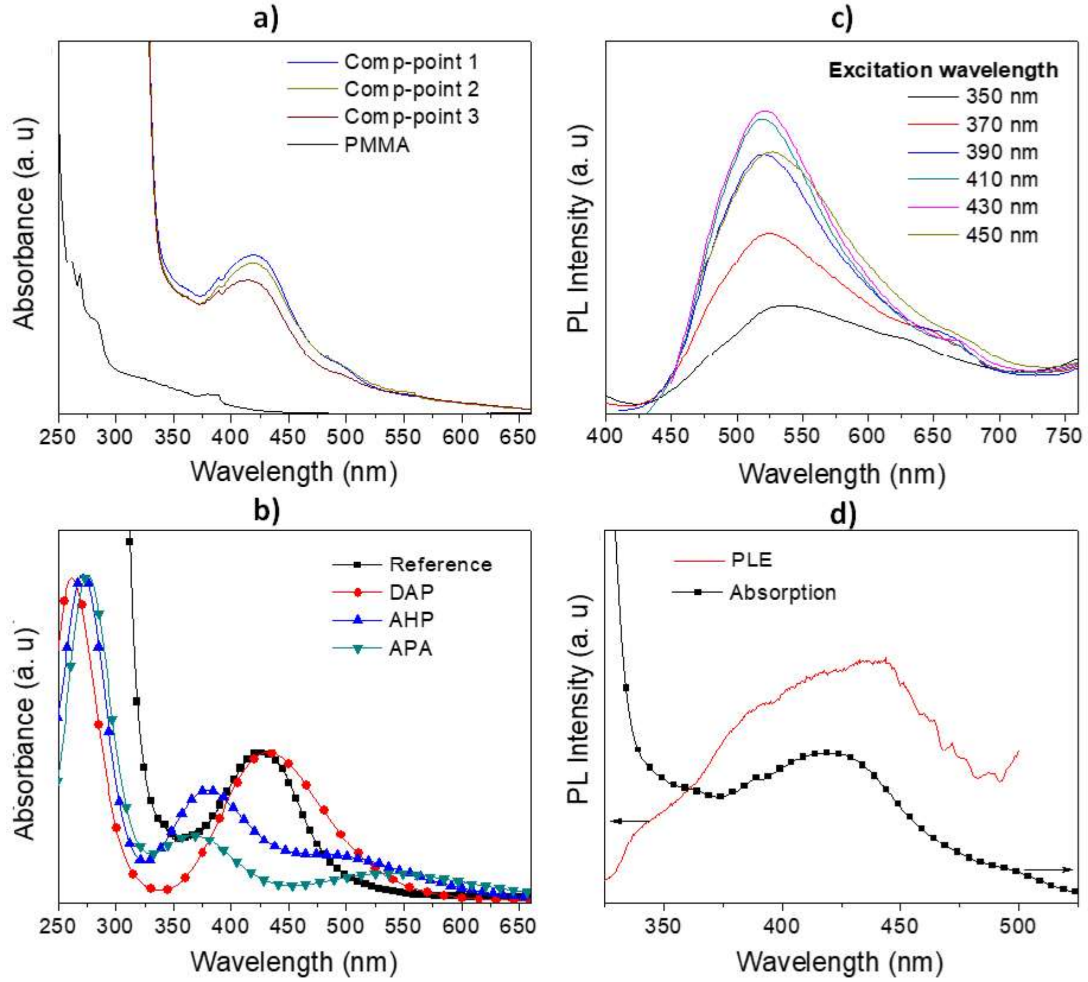

Figure 3. a) UV-Vis absorption spectra of a composite membrane measured at different points; **b)** UV-Vis absorption spectra of a reference sample and calculated absorption profile of 2,3-diaminophenazine (DAP), 3-amino-2-hydroxyphenazine (AHP), and N-(3-aminophenazin-2-yl)acetamide (APA); **c)** photoluminescent (PL) spectra of the composite membrane obtained at different excitation wavelengths; **d)** comparison between the photoluminescent excitation (PLE) and the absorption spectra of the composite membrane.

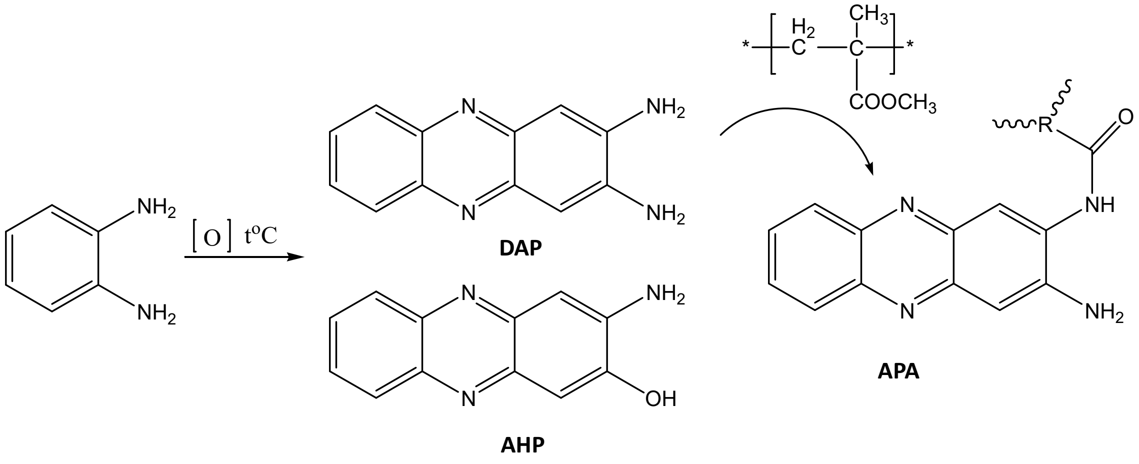

Figure 4. The formation of possible molecular fluorophores by thermal annealing o-phenylenediamine.

Table 1. The calculated electronic transition for interested molecules.

Excitation	**Criteria**	**Molecules**		
		DAP	**AHP**	**APA**
The first excitation	Position (nm)	486.3	496.1	536.8
	Oscillator strength (a.u)	0.0283	0.1824	0.1498
	Transition	H→L	H→L	H→L
The second excitation	Position (nm)	431.4	397.0	416.2
	Oscillator strength (a.u)	0.7303	0.0043	0.0038
	Transition	H-1→L* H→L+1	H-2→L	H-2→L
The third excitation	Position (nm)	395.7	379.5	370.5
	Oscillator strength (a.u)	0.0043	0.4657	0.3328
	Transition	H-2→L	H-1→L* H→L+1	H-1→L* H→L+1

H: the highest molecular orbital (HOMO); L: the lowest unoccupied molecular orbital (LUMO);
* *the transition with a higher possibility*

To study the molecular origin of the emission of the composite, we tried to extract molecular species from the composite but they were unable to be separated. Alternatively, we compared the optical properties of the composite with a reference sample and with DFT calculations. The reference sample was prepared by solvothermal treatment of oPD in ethanol. Recent studies [19], [21], [22] have revealed that 2,3-diaminophenazine (DAP) and 3-amino-2-hydroxyphenazine (AHP) are formed mainly by such solvothermal treatment. Therefore, it is reasonable that DAP and AHP could also be formed via thermal annealing oPD in the PMMA matrix. Additionally, the –NH$_2$ groups of DAP can react with the –COOCH$_3$ of the PMMA matrix to form amide derivatives. The molecular structures and the conversion of oPD into DAP, AHP, and APA are shown in Figure 4 while the UV-Vis absorption spectra of those relevant molecules are shown in Figure 3b. As seen in Figure 3b, the reference sample and DAP exhibited a common absorption peak at about 427-431 nm. This similarity indicates that the reference sample consisted of DAP as reported previously [21]. Based on the theoretical calculation summarized in Table 1, the absorption peak at 427-431 nm was attributed to the electronic transition from HOMO-1 to LUMO with an oscillator strength of 0.7303. The absorption peak is very close to the absorption peak at 425 nm of the composite seen in Figure 3a. Therefore, it is fair to attribute the absorption peak at 425 nm observed in the composite to DAP. The absorption shoulder at 395 nm observed in Figure 3a is likely due to the first excitation of AHP whose oscillator strength (0.1824) is comparable to that of the absorption peak at 427-431 (0.7303) mentioned above. Finally, APA, which is an example of possible products formed by amniolysis of PMMA, exhibits the first excitation at 536.8 nm. As seen in Figure 3a, the composite exhibited featureless absorption above 500 nm. Possibly, chemical interactions between DAP and the PMMA matrix could form various products, such as APA, that absorb light in the region above 500 nm. In summary, by comparing the absorption properties of the composite with the reference sample and theoretical calculations, it has been demonstrated that DAP and AHP are likely molecular fluorophores in the composite.

4. Conclusions

Green-emitting composites based on PMMA thermoplastic have been fabricated by thermally annealing a mixture of o-phenylenediamine and PMMA. The annealing was conducted by a thermal extrusion method, which is one of the most common technologies used in thermoplastic molding. After the thermal annealing, the chemical structure of the PMMA matrix remained unchanged in the composites. The composites exhibit green emission that maximizes at about 525 nm, and is independent of the excitation wavelength. The absorption spectrum and the photoluminescent spectrum of the composites shared a broad range around 425 nm. Theoretical calculations suggested that 2,3-diaminophenazine and 3-amino-2-hydroxyphenazine are molecular fluorophores accounting for the optical properties of the composites. The preparation of composites by the thermal extrusion demonstrated in this study paves a rapid method to fabricate photoluminescent thermoplastics for diverse applications.

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