



## HPU2 Journal of Sciences: Natural Sciences and Technology

journal homepage: <https://sj.hpu2.edu.vn>



Article type: *Research article*

### The one-pot synthesis of photoluminescent polycarbonate based on the pyrolysis of citrate

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#### Abstract

Photoluminescent composites that are air-stable and water-resistant are important for outdoor applications such as road marking paints, light-converting membranes, fluorescent paints, and security inks. Photoluminescent thermoplastics fulfill all conditions but their preparation methods which are vastly based on mixing pre-synthesized fluorescent dyes and plastic could lead to emission quenching due to dye aggregation or thermal degradation. Herein, we demonstrated a simple method to prepare photoluminescent polycarbonate by thermal extrusion polycarbonate with citric acid and urea. UV-vis absorption and photoluminescent studies indicate that fluorescent carbon materials were formed via pyrolysis of the citrate. The composites exhibit light blue emission and a broad excitation band. The results demonstrated herein offer a cost-effective method to prepare diverse photoluminescent composites for outdoor applications.

**Keywords:** Thermoplastics, extrusion, luminescent, photoluminescent, composite

#### 1. Introduction

Polymeric composites that have photoluminescent properties have been applied in various fields such as solar concentrators, light-converting materials, security ink, and sensors [1]–[5]. Conventionally, photoluminescent composites are prepared by mixing an as-prepared photoluminescent material with a suitable polymer. This method allows one to adjust the concentration as well as the type of photoluminescent materials. However, it is very challenging to select

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<https://doi.org/10.56764/hpu2.jos.2024.3.1.57-63>

Received date: 19-10-2023 ; Revised date: 01-02-2024 ; Accepted date: 12-3-2024

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photoluminescent material and polymer so that they have similar solubility parameters to perform homogeneous composites [6]. Bonding the photoluminescent materials to the polymer matrix [1], [4], [7] or decorating the polymer with *in-situ* formed photoluminescent centers [8] have been debated to prepare homogeneous composites. To this end, we have demonstrated a one-pot method to prepare homogeneous and highly photoluminescent composites of poly(vinyl alcohol) PVA relying on the thermal-induced formation of 5-oxo-1,2,3,5-tetrahydroimidazo-[1,2- $\alpha$ ]-pyridine-7-carboxylic acid (IPCA) from a mixture of citric acid and ethylenediamine [8], [9]. Although PVA composites are environmentally friendly and biodegradable they are easy to deformation when exposed to moisture. To enhance the stability of composites toward outdoor applications we used poly(methyl methacrylate) (PMMA) instead of PVA and demonstrated that the optical properties of PMMA composites also rely on IPCA [9].

IPCA is a fluorophore formed by the intermolecular condensation of a polymeric amide that is pre-formed by acid–base reactions between citric acid and ethylenediamine [8], [10], [11]. The intermolecular condensation takes place at about 160°C [8], [9] when heating as-made blends of citric acid and ethylenediamine in PVA or PMMA matrix. The formation of IPCA in PMMA paves a method to adopt current thermal processing technologies such as extrusion, injection molding, thermoforming, and calendaring which are widely used in the industry to fabricate finishing products of thermoplastics in the preparation of photoluminescent composites. Additionally, the one-pot thermal annealing method is potentially applicable to other citrate-derived fluorophores [12]–[15].

In this article, we used polycarbonate (PC) as a thermally stable polymeric matrix and mixtures of citric acid (CA) and urea (URA) as solid precursors and demonstrated the preparation of photoluminescent composite using an extrusion method. The composite exhibited blue-green emission under excitation at a wavelength ranging from 360 nm to 480 nm. The results demonstrated herein suggest a universal strategy to prepare photoluminescent thermoplastics by adopting current available procession technologies.

## 2. Experimental section

### 2.1. Chemicals and facilities

Citric acid monohydrate (CA, 99.8%) and urea (URA, 99.5%) were purchased from Aladdin Chemicals. Ethanol (HPLC grade) was supplied by Daejung Chemical. Polycarbonate (technical grade) was purchased from Lotte Chemicals. All chemicals and solvents were used directly without any purifications. An extruder (model SJ15, Jennyprinter) was used to fabricate wires of composites.

### 2.2. The synthesis of photoluminescent composites

CA and URA were dissolved in ethanol to perform a solution with a concentration of CA and URA of 1.5M and 1.0 M, respectively. The solution was used to spray coating over PC particles so that the final weight of CA and URA was about 1–3 percent by dried mass. The mass content of the precursor was calculated from the mass difference between PC before and after the coating step to perform photoluminescent PC in the wire form. The PC particles were put into an extruder which then operated at 240°C and a feeding speed of 100 g/h. The preparation of composites was illustrated in Figure 1. To fabricate membranes of composite for optical characterizations, the as-prepared composite wires were placed in a homemade flat presser with a space of 2 mm and heated at 180°C for about 1 hour in a vacuum oven.

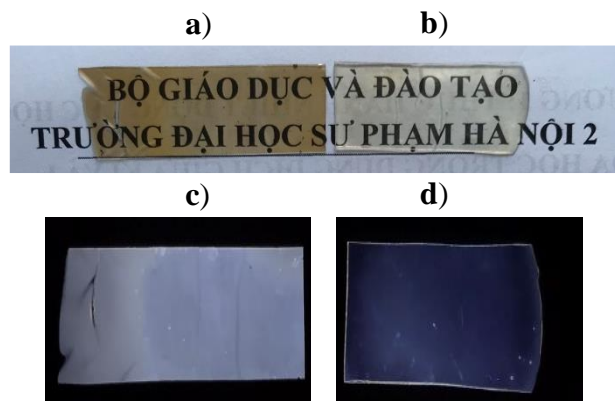
### 2.3. Characterizations

The absorption spectra of composites were conducted on a UV-2450 (Shimadzu) spectrometer using membrane forms of the composite. The photoluminescent (PL) and photoluminescent excitation spectra (PLE) of composite membranes were carried out on FLS1000 (Edinburgh Instrument).

## 2. Results and discussion



**Figure 1.** A thermal extrusion method to prepare photoluminescent polycarbonate composites.

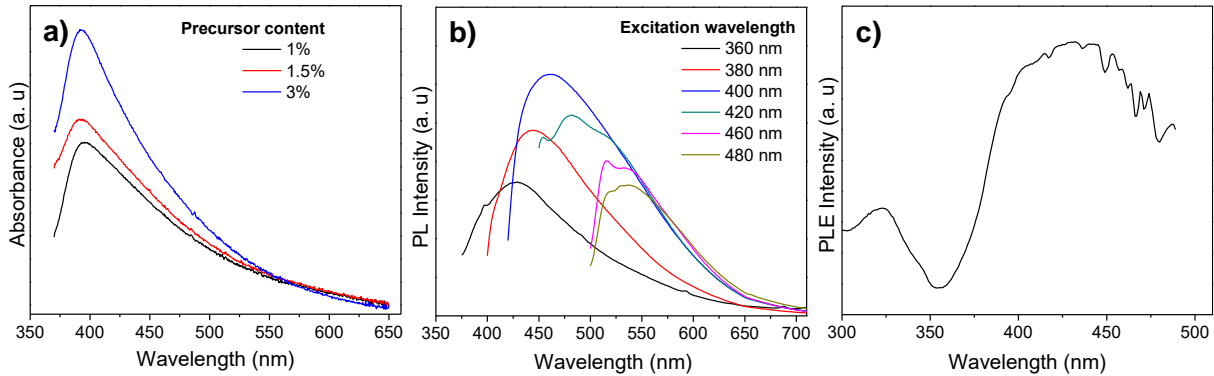


**Figure 2.** Pictures of a) composite and b) PC only membranes under daylight; c) composite and d) PC only membranes under UV light (at 365 nm).

After thermal extrusion, wires of composites were obtained with a lot of air voids. The voids were not observed when only PC was used to prepare reference samples. Therefore, the voids were likely formed due to the evaporation of small molecules such as water and ammonia which are the products of various condensation and carbonization processes between CA and URA at high temperatures [14], [16], [17]. Under UV light (365 nm), the composite emits intensively in the visible region, as seen in Figure 1, Figure 2c and 2d, indicating that photoluminescent composites were successfully formed.

One of advantages of thermoplastics is that they can be reshaped in diverse forms using thermal processes [18]. To test the thermal processability of the photoluminescent composites we used a plate pressing method to prepare membranes of either composites or pristine PC. As shown in Figure 2a and 2b, both membranes were transparent as indicated by the fact that the underneath sentences "BỘ GIÁO DỤC VÀ ĐÀO TẠO TRƯỜNG ĐẠI HỌC SƯ PHẠM HÀ NỘI 2" could be seen clearly. It implies that the composites retain the thermal processability as PC [19], [20].

The optical properties of the photoluminescent composites are summarized in Figure 3. The absorption spectra of composite membranes with different precursor content after subtracting the absorption profile of a pristine PC membrane are shown in Figure 3a. All membranes exhibited featureless absorption profile above 400 nm, the absorbance decreased gradually as the wavelength increased and only vanished in the near IR region accounting for the black color of composite (Figure 1). The absorption in the UV region (<400 nm) is meaningless because PC is a typical UV-blocking polymer [21].

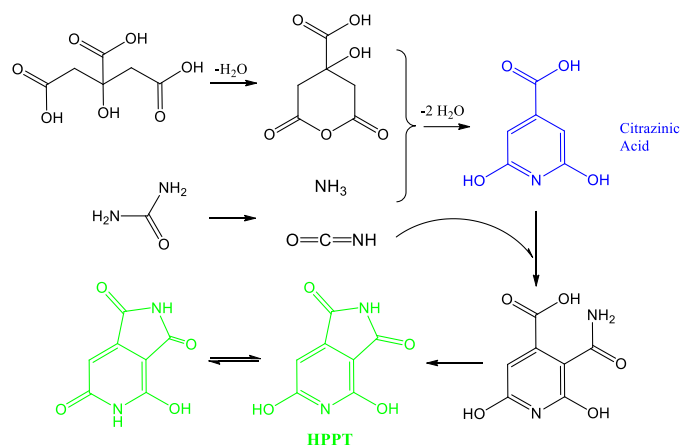


**Figure 3.** The optical properties of photoluminescent polycarbonate. a) The absorption, b) photoluminescent excitation observed at 525 nm, and c) photoluminescent spectra of composites.

Therefore, the absorption peak observed at 393 nm was likely a combination between the UV-blocking property of PC and the black absorption of carbon materials. Nevertheless, as the precursor content increased from 1 to 3% the absorbance above 400 nm increased linearly indicating that the absorbance above 400 nm originated from carbon materials and that when CA and URA increased the amount of carbon materials increased. Upon excitation at different wavelengths (indicated as legends in Figure 3b), the PL spectra of composites were broad, ranging from about 400 nm to 650 nm. This result explains why the composite wires and membranes appear almost white under UV light at 365 nm as shown in Figure 1 and Figure 2. The PL maxima shifted from about 425 nm to 540 nm as lengthening the excitation wavelength, from 360 nm to 480 nm. To reveal the excitation range of composites, we measured the variation in PL intensity at 525 nm with the excitation wavelength, and the results are shown in Figure 3c. The photoluminescent excitation spectrum exhibits two excitation bands in 300–340 nm and 380–480 nm ranges. It means that the composite could be excited with various wavelengths. For example, if the composite is excited by a blue LED chip at 450 nm the composite will give green emission (Figure 3b). It is clearly from Figure 3a and 3c that the absorption and PLE spectra were different. Those differences mean that excited carriers (electrons and holes) formed upon absorption did not always recombine radiatively. This phenomenon has been widely reported for composites [5] or solid films of carbon nanomaterials [21] and explained to be due to charge transfer among carbon dots in aggregated assemblies or non-radiative recombination of excited carriers.

To explain the optical properties of the photoluminescent polycarbonate mentioned above we adopted recent understandings of the formation mechanism of carbon nanodots [15]. Briefly, citric acid reacts with different amino ( $-NH_2$ ) containing molecules forming polymeric amides. At high temperatures (160-300°C), the amides undergo condensation processes resulting in different products among which there are some highly photoluminescent molecules called as fluorophores [15]. The

fluorophores could be digested or be included in carbonization forming carbon nanodots [10]. The fluorophore molecules retained in final carbon nanodots play key roles in governing the optical properties of the dots [15], [22]. V. Strauss [17] and W. Kasprzyk [22] conducted pyrolysis mixtures of CA and URA in different environmental conditions and demonstrated two molecular fluorophores including citrazinic acid and 4-hydroxy-1H-pyrrolo[3,4-c]pyridine-1,3,6(2H,5H)-trione (HPPT) which give emission in blue and green regions, respectively. W. Kasprzyk and co-workers showed that citrazinic acid is likely formed in a closed reactor while HPPT is more likely formed in the presence of air [22]. In our case, mixtures of CA and URA underwent thermal extrusion in the presence of PC thermoplastic. It is reasonable that PC partially prevented CA-URA from air to support the formation of citrazinic acid while surficial CA-URA that was exposed to air likely converted to HPPT, Figure 4. The coexistence of citrazinic acid and HPPT in the resultant composite explains why their emission spectra involve both blue and green emitting centers as shown in Figure 3b. The existence of citrazinic acid and HPPT should be confirmed by suitable spectroscopies such as mass, nuclear resonance spectroscopies, infrared spectroscopy, and so on followed by careful separations. We could perform such analysis on polyvinyl alcohol composites [8] where IPCE fluorophores could be separated by the simple dialysis. In current study, we could make solutions of the photoluminescent composites but we were unable to observed separated fluorophores by paper chromatography techniques. Probably, citrazinic acid and HPPT were tightly bounded to PC matrix, even in solution states.



**Figure 4.** The formation of blue (citrazinic acid) and green (HPPT) emitting fluorophores upon pyrolysis of citric acid and urea.

#### 4. Conclusions

The conversion of citrate into fluorescent dyes under pyrolysis conditions has been adopted to prepare photoluminescent thermoplastics using a thermal extrusion method. It has been demonstrated that CA-URA-coated polycarbonate particles were successfully converted into photoluminescent composites. The emission spectrum of photoluminescent polycarbonate is broad, ranging from 400 nm to 640 nm depending on the excitation wavelength. Citranizic acid and HPPT were likely the molecular origin of the photoluminescent properties of the composites. The results demonstrated here could pave the way to prepare diverse photoluminescent thermoplastics using currently available thermal processing technologies.

## Acknowledgments

This research was supported by Hanoi Pedagogical University 2 under a grant number SV.2023.HPU2.05.

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