Visible Light-Induced Fabrication of a Clickable Cu(I) Benzophenone Dicarboxylate Polymer - Polyacrylamide Hydrogel Composite

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Abstract: Hydrogels are a class of hydrophilic polymers that have been widely applied in numerous fields, most of which are related to bioengineering such as tissue scaffolds, biosensing, and antibacterial activity. Especially, polyacrylamide (PAAm) hydrogels, due to their superior stability, non-toxicity, and viscoelasticity, have been extensively studied over the last two decades in different bio-related applications. Coordination polymers (CPs) including metal-organic frameworks (MOFs), due to tunability of the organic linkers and metal ions, and their robustness, have been incorporated with hydrogels in order to improve the physical/chemical properties of the final composite. Herein, we report, for the first time, the utilization of a photoactive Cu(I) coordination polymer as a Norrish type II photoinitiator for the in situ fabrication of a clickable and highly-crosslinked Cu(I)CP-PAAm hydrogel composite under visible light-induced conditions, employing water as the solvent. Due to the high stability of the Cu(I)CP in water, that was demonstrated by powder X-ray studies, the release of copper ions was observed to occur after more than two days. Another advantage of the developed synthetic method is the facile post-modification of the hydrogel composite by utilizing an azide-functionalized polymer through an internal copper-catalyzed azide-alkyne click reaction.

Keywords: Hydrogels, polyacrylamide, coordination polymers, light-induced polymerization, Type II photoinitiator.

Görünür Işık Altında Klik Tepkimesine Girebilecek Cu(I) Benzofenon Dikarboksilat Polimeri-Poliakrilamid Hidrojel Kompozitinin Eldesi

Özet: Hidrojeller doku mühendisliğinden, biyosensörlere ve antibakteriyel araştırmalara kadar geniş bir biyomühendislik uygulama alanına sahip hidrofilik polimerlerdir. Özellikle poliakrilamid (PAAm) hidrojeller, sahip oldukları düşük toksisite, yüksek stabilite ve viskoelastisite nedeniyle son 20 yılda birçok biyo-ilişkili alanda yoğun bir şekilde denenmişlerdir. Öte yandan, koordinasyon polimerleri (CPs) ve onların alt sınıfı olan metal-organik çerçeveler (MOFs), sahip oldukları sağlamlık ve organik ligand/metal iyonlarının rahatça değiştirilebilmesinden dolayı hidrojellerle karıştırılmış ve ortaya üstün fiziksel ve kimyasal özelliklere sahip kompozit malzemeler çıkmıştır. Bu çalışmada, Cu(I) bir koordinasyon polimeri, ilk defa bir tip II fotobaşlatıcı olarak kullanılarak, görünür ışık *altında in situ* olarak yüksek çapraz bağlanma oranına sahip bir Cu(I)CP-PAAm hidrojel kompozitinin sentezi, çözücü su olmak üzere gerçekleştirilmiştir. Sentezlenen Cu(I)CP'nin sudaki yüksek stabilitesi X-ışını toz difraksiyonu yöntemiyle kanıtlanmış ve bu sayede bakır iyonlarının yavaş salınımı gözlemlenmişitr. Ortaya atılan bu yeni sentetik yöntemin bir başka avantajıysa Cu(I)CP'nin kendi içinde bulundurduğu bakırın katalizör olarak kullanılabilmesi sayesinde kompozitin herhangi azid uçlu başka bir polimer ile azid-alkin klik tepkimesi üzerinden post-modifiye edilebilme potansiyeline sahip olmasıdır.

Anahtar Kelimeler: Hidrojeller, poliakrilamid, koordinasyon polimerleri, ışık-başlatmalı polimerleşme, Tip II fotobaşlatıcı.

RESEARCH PAPER

1.Introduction

Hydrogels are chemically and/or physically cross-linked 3D hydrophilic macromolecules that are capable to absorb large quantities of water without dissolving (Ahmed, 2015; Cao et al., 2021). Their hydrophilicity is attributed to the functional groups they contain, such as –OH, -NH₂, -COOH, -SO₃, and –CONH₂. Besides their ability to hold large water content, hydrogels are considered as biocompatible and have no or very little organism invasion (Yu et al., 2018). All these features have recently rendered hydrogels, a distinct class of materials that found great use in many bio-related applications including drug carriers (Vigata et al., 2020),

biomolecular supports (Heo & Crooks, 2005), nano-reactors (Soto-Quintero et al., 2017) and tissue scaffolds (Zhang et al., 2018).

Gelatin, chitosan, agarose, and alginate are the mostly known naturally occurring hydrogels that have been well studied (Taghipour et al., 2020). Among synthetic hydrogels, particularly polyacrylamide (PAAm) hydrogels, due to their stability, swelling capacity, non-toxicity, non-immunogenicity and viscoelasticity, have been extensively investigated by many research groups (Orakdogen & Okay, 2006) (Ceylan et al., 2006) (Norioka et al., 2021). In the last two decades, PAAm hydrogels have found wide application as soft tissue fillers (Wang et al., 2022) and antibacterial

scaffolds (Dsouza et al., 2022). PAAm is a colorless hydrogel that can be combined with other molecules in order to tailor many of its properties like physical toughness, anti-bacterial activity, thus, finally obtain the desired features for the aimed application(s). One of the main drawbacks of PAAm hydrogels is their relatively low elastic modulus, thus low mechanical strength, limiting their standalone use in several applications which require robustness (Dsouza et al., 2022). In order to solve this problem, PAAm hydrogels have been combined with a variety of materials possessing better mechanical performances (Abdurrahmanoglu et al., 2011).

Coordination polymers (CPs) and their subclass of metal-organic frameworks (MOFs) are classes of materials formed by the connection of metal ions to organic linkers (binders). CPs have been immensely researched for potential applications like gas sensing, drug delivery, water purification, catalysis, and batteries (Engel & Scott, 2020). In addition, they have been also incorporated with hydrogels, including PAAm, to enhance the physical properties of the composite (Samav et al., 2023) (Al-Mahamad et al., 2017). Moreover, synthetic flexibility of the organic linkers and metal ions of CPs, brings a great versatility to the both physical and chemical features of the CP-hydrogel composite. Metal ions present inside CPs are generally in nano-size and non-biodegradable. While many transition metals are known to be highly toxic (lead, chromium, arsenic, cadmium), copper is one of the essential trace elements found in the human body and has been demonstrated to promote the proliferation of various cells and angiogenesis (Zhou et al., 2020). Furthermore, copper ions which are known to be bioactive, play critical roles in many anti-inflammatory actions due to their anti-bacterial properties (Tao et al., 2019). Latest studies have revealed excellent performance of copper-based MOF-hydrogel composites in skin wound healing (You et al., 2022). However, due to the considerable cytotoxicity of copper ions, achievement of their slow release is an important criterion for the bio-related applications of Cu-based CP-hydrogel composites (Xiao et al., 2017). Another drawback associated with CPs, is their instability in aqueous media, resulting in their gradual decomposition (Terzyk et al., 2019).

Regarding the synthetic methods for the transition metal CP-hydrogel composites, CPs are most of the time introduced into hydrogels either by *in situ* growth or by direct mixing methods (Lim et al., 2023). While *in situ* growth technique implies the growth of CP in the pores of a pre-prepared hydrogel network, the direct mixing method forms CP-hydrogel composites via physical encapsulation of CPs during the cross-linking or gelation process of the hydrogel matrix (Hou et al., 2023). Lately, new strategies have also been developed for the successful synthesis of CP-hydrogel composites (Sun et al., 2023).

One of the most promising strategies to obtain CP-hydrogel composite is to use light as the energy source. Especially after the environmental concerns related to pollution caused by high demand of energy, light-induced polymerization reactions have become sustainable tools to obtain industrially important materials (Sanchez-Rexach et al., 2020) (Kaya, 2023) (Tabak et al.) (Kocaarslan et al., 2022). Among the advantages brought to hydrogels by photochemical reactions stand rapid curing/gelation and excellent spatiotemporal control occurring at room temperature (Nguyen & West, 2002). Particularly, the use of visible light is crucial to acquire efficient curing due to higher penetration ability of visible light compared to UV light (Kalayci et al., 2020). Several hydrogels have been recently synthesized by our group under UV or visible light, by employing both Norrish type I and type II photoinitiators (Bilgic et al., 2022) (Murtezi et al., 2014) (Yilmaz et al., 2011) (Uygun et al., 2009).

In this work, for the first time, a benzophenone containing, visible light active Cu(I) coordination polymer has been used as type II photoinitiator for the *in situ* synthesis/fabrication of a post-modifiable/clickable CP-PAAm hydrogel composite. The advanced approach possesses several advantages over the conventional methods such as the straightforwardness, avoiding the use of additional photoinitiator, high cross-linking, possibility of post-modification through internal (self-containing) copper-catalyzed azide-alkyne click chemistry, relatively stable nature of the Cu(I) CP and slow release of copper ions that was observed by the slow change in the color of the hydrogel-composite over time.

2. Materials and Methods

2.1 Materials

Propargyl acrylate (PA) (98%, Sigma) and triethylene glycol dimethacrylate (TEGDMA) (Sigma) were passed through a short column filled with neutral activated aluminium oxide (0.063−0.200 mm) prior to use in order to remove the inhibitors. Acrylamide (AAm, Sigma-Aldrich) and trimethylamine (TEA) (99%, Sigma), copper sulfate pentahydrate ($CuSO_4.5H_2O$) (Merck, 98%), benzophenone-4,4'-dicarboxylic acid (Sigma, 95%) and glacial acetic acid (Merck,100%), were all used as purchased. Distilled water was obtained by a reverse-osmosis system equipped with a VONTRON ULP2012-100 membrane.

2.2. Methods

2.2.1 Instrumentations

IR Measurements. Fourier-transform infrared (FTIR) spectra were recorded on Perkin–Elmer Spectrum One spectrometer with an ATR Accessory (ZnSe, PikeMiracle Accessory) and mercury cadmium telluride (MCT) detector. 16 scans were averaged.

PXRD Measurements. Crystallographic identifications were accomplished by powder X-ray diffraction (PXRD) method on a benchtop Rigaku Miniflex diffractometer with a Cu-Kα radiation source operated at 30 kV and 10 mA. The acquisition angle ranged from 5º to 90º with 10º·min⁻¹ scan speed.

UV–vis Measurements. UV-vis diffuse reflectance spectroscopy was measured with a UV 2600 spectrophotometer from Shimadzu with the respective accessory (ISR-2600 integrating sphere) in the range of 250 to 800 nm against $BaSO_4$ as the background. The Shimadzu LabSolutions UV–Vis Software package was used for measurement control and data analysis.

DSC measurements were performed on a Perkin Elmer Diamond DSC 4000 with a heating rate of 10 K·min⁻¹ under nitrogen flow of 20 mL·min⁻¹.

TGA measurements were carried out with a PerkinElmer Diamond TA/TGA instrument at a heating rate of 10 °C/min from 25 to 900 °C under a nitrogen atmosphere with a flow rate of 40 mL·min⁻¹.

2.2.2 Synthesis of Cu(I)CP

Cu(I)CP was synthesized according to a previously reported method where excess of $Cu(SO_4).5H_2O$ was mixed with benzophenone-4,4'-dicarboxylic acid in formic acid - *N,N*-dimethylformamide (DMF) mixture prior to heating inside a conventional oven at 85º C for 24 h (Bilgic et al., 2022).

2.2.3 Fabrication of Cu(I)CP-PAAm Hydrogel Composite

For the synthesis of the Cu(I)CP-PAAm hydrogel composite, 10

mg of Cu(I)CP, 142 mg of AAm (2.0 mmol), 10 μL of PA (0.1 mmol), 25 μL of TEGDMA (0.1 mmol) and drops of TEA were dissolved in 1 mL of distilled water inside a test tube. In order to obtain a homogeneous mixture, the tube was ultrasonicated for 10 minutes and then transferred into a 1000 μL syringe. The syringe was irradiated horizontally, inside a photoreactor equipped with 6 lamps (Philips TL-D 18W Blue) emitting a nominal light at 450 nm with an intensity of 30 mW/cm^2 on the reaction medium. After the irradiation, the hydrogel composite formed inside the syringe was gently pushed by using low pressure to the plunger.

3. Results and Discussion

Our previous studies have demonstrated that, classical Norrish type I photoinitiators like Irgacure-2959, bis(acyl)phosphane oxide (BAPO), 2,2-dimethoxy-2-phenylacetophenone (DMPA), as well as type II initiators like camphorquinone could initiate the light-induced polymerization of AAm-PA mixture (Bilgic et al., 2022; Murtezi et al., 2014). For the case of type II photoinitiators, a co-catalyst possessing hydrogen donor ability such as tertiary amines or compounds containing ethyleneoxide moieties are necessary. Benzophenone and its derivatives are also well-established type II photoinitiators and all these initiators possess lower excited triplet state energy compared to their cleaved state, thus, they do not decompose but form radicals in the carbonyl moiety upon excitation in the wavelength they absorb (Liu et al., 2021).

In the present work, we used AAm and PA as monofunctional monomer and bifunctional monomer possessing both double and triple bonds, respectively, in conjunction with very small amounts of TEGDMA and TEA as cross-linking agent and co-catalyst, respectively. The different reaction rates of the photochemically generated radicals with double and triple bonds were demonstrated by laser flash photolysis studies (Ciftci et al., 2012). Inspired from our previous photopolymerization studies concerning hydrogel formation, we envisioned the use of Cu(I)CP as a type II photoinitiator, due to its benzophenone moiety, for the polymerization of AAm-PA mixture in conjunction with TEA as the co-catalyst. Figure 1 depicts the summary of the synthesis of Cu(I)CP together with the photopolymerization reaction leading to hydrogel composite.
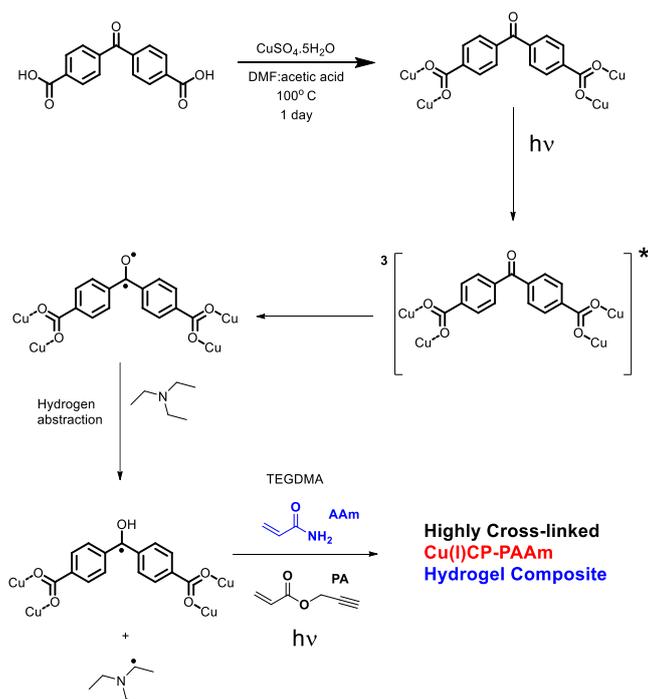
Figure 1. Light-induced fabrication of Cu(I)CP-PAAm hydrogel composite.

Although benzophenone itself absorbs light in the UV-A region, UV-Vis diffuse reflectance measurements of Cu(I)-CP powder exhibited a strong absorbance in the visible region (Figure 2). As mentioned in the introduction part, due to its higher penetrating ability (compared to UV), visible light is crucial for the rapid gelation during the photopolymerization reactions.
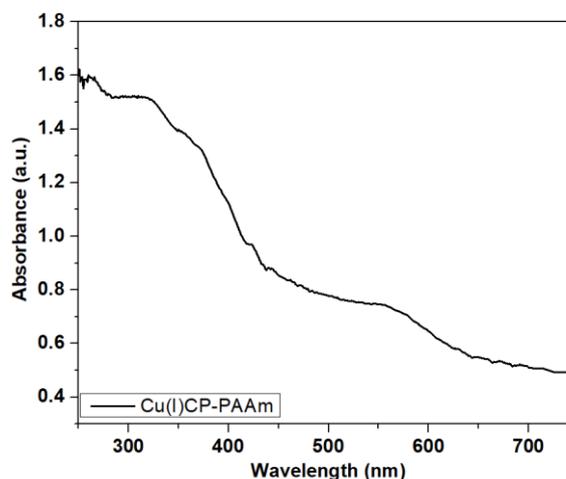
Figure 2. Diffuse reflectance UV-Vis spectrum of Cu(I)CP.

For the purification of the obtained hydrogel-composite, the composite was immersed in distilled water for five days, and then dried at room temperature. Photographs of the hydrogel composite (a) before and (b) after immersion to water for five days, are depicted in Figure 3.
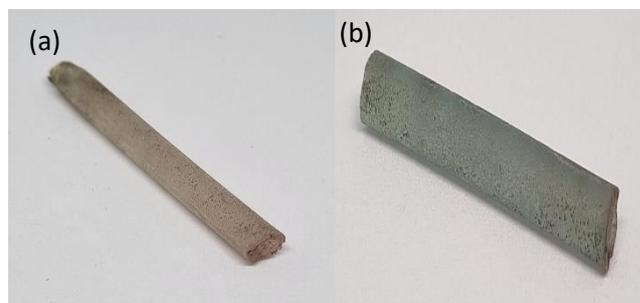
Figure 3. Photograph of the hydrogel composite (a) before (b) after immersion into water for five days.

Swelling degree of the hydrogel composite was calculated as 6.15% according to Equation 1.

Eq. 1 = Swelling (%) = $(W_s (1.414 \text{ g}) - W_d (1.332 \text{ g}))/W_d (1.332 \text{ g}) \times 100 = 6.15$

Where W_d = Weight of polymer and W_s = weight of swollen polymer.

Low degree of swelling of the photochemically synthesized hydrogel composite indicates a high cross-linking degree (Zhan et al., 2021), which was also encountered in the following results. The relatively stable nature of Cu(I)CP was demonstrated by powder X-ray analysis (PXRD) (Figure 4). In addition, it is possible to observe a clear coloring to blue in the hydrogel composite, after five days of immersion to water. This is attributed to the slow release of the Cu(II) ions in the form of Cu(OH)$_2$ giving a greenish blue color (Zhu et al., 2021). Cu(I) ions can easily be oxidized to Cu(II) ions in aqueous medium.
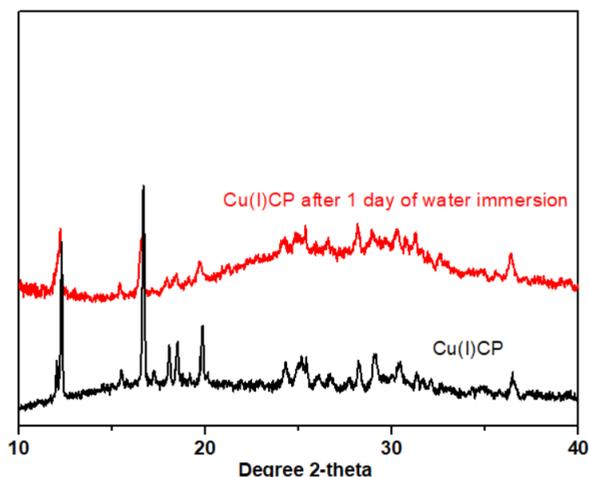
Figure 4. PXRD diffractograms of (black line) Cu(I)CP and (red line) Cu(I)CP after 1 day of immersion in water.

Following the swelling experiment, infrared (FTIR) investigation was employed in order to determine the functional groups present in the hydrogel composite (Figure 5). The composite IR spectrum displayed two different peaks in the carbonyl region; one at around 1650 cm^{-1} corresponding to the carbonyl of the benzophenone moiety of Cu(I)CP and a peak at *ca.* 1720 cm^{-1} corresponding to the carbonyls of PAAm, poly (propargylacrylate) and PEGDMA units. There is also a peak, although very weak, at around 2150 cm^{-1} belonging to the triple bond of the alkyne unit of PA. The weakness of the peak is attributed to several factors including the reaction between the triple bonds and the radicals formed by excitation, the relatively lower amount of PA used in the photoreaction mixture and low sensitivity of ZnSe crystal of ATR equipment on that region (2000-2300 cm^{-1}) (Aakeröy et al., 2013). Lastly in the IR spectrum, there is a very broad peak centered at 3400 cm^{-1} corresponding to the water absorbed by the hydrogel composite.
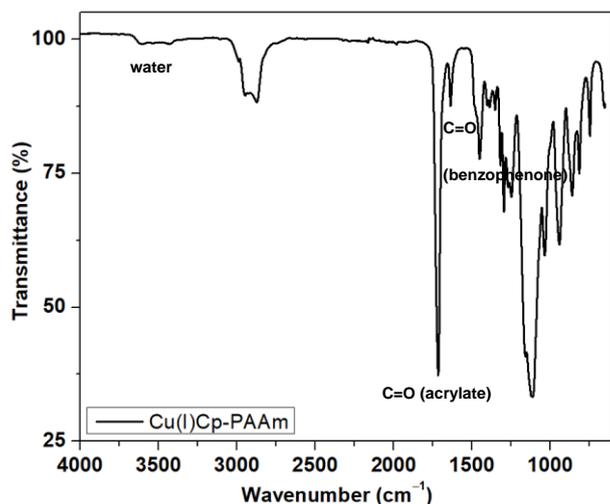
Figure 5. FTIR spectrum of the photochemically obtained hydrogel composite.

Differential scanning calorimetry (DSC) was performed on Cu(I)CP-PAAm hydrogel in order to investigate the thermal transitions (Figure 6). A large endotherm starting from around 70 °C going until 110 °C is due to the evaporation of large amount of water absorbed inside the hydrogel composite. In the DSC thermogram, besides this large endotherm, a weak endotherm at 202 °C can be observed. This peak is attributed to the glass transition temperature (Tg) of PAAm and is due to the amorphous structure of PAAm. Tg of the previously synthesized PAAm hydrogels were observed around 190 °C (Qin et al., 2016). The increase of the glass transition

temperature indicates a higher cross-linking degree and is also possibly related to the chemical incorporation of the Cu(I)CP into the PAAm hydrogel. After 275 °C, a large endotherm which corresponds to the initiation of the thermal degradation of the hydrogel composite, can be observed. This observation is in accordance with the thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) data which will be discussed below (Figure 7).
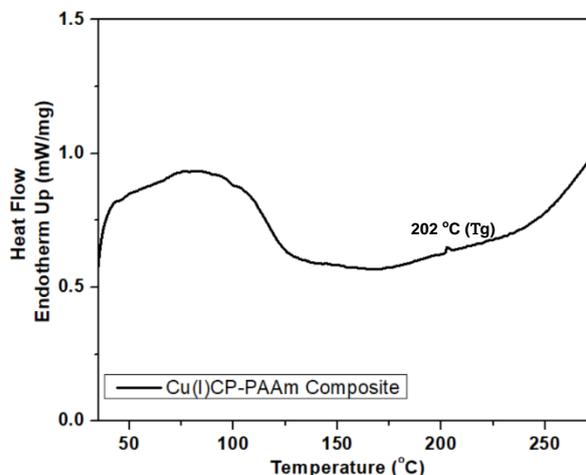
Figure 6. DSC thermogram of Cu(I)CP-PAAm hydrogel composite.

The thermal decomposition of Cu(I)CP, Cu(I)CP-PAAm hydrogel composite and PAAm hydrogel (synthesized using benzophenone instead of the coordination polymer), was carried out from 25 °C to 800 °C under nitrogen atmosphere with a heating rate of 20 °C min^{-1}. The corresponding TG curves can all be observed in Figure 7. The weight loss of the hydrogel composite can be roughly divided into three stages. Up until 110 °C, 5% weight loss can be observed. This is due to the evaporation of water absorbed by the hydrogel composite. After 110 °C, up until 250 °C, a second weight loss (5%) can be observed. This might be due to the evaporation of other reactants trapped inside the hydrogel network. After 250 °C, 60% weight loss (90% to 30%) occurs and this phenomenon is due to the gradual degradation of the hydrogel composite, which was also encountered in the DSC thermogram. From 450 °C until 900 °C, there is only 0.5% weight left. This should belong to the copper present inside the hydrogel composite. Due to the lower crosslinking degree in PAAm synthesized by benzophenone, under UVA irradiation, especially until 300 °C, thermal stability of the composite is higher than pristine PAAm. This is attributed to the higher penetration ability of visible light over UVA light. Overall, thermal stability of the photochemically obtained PAAm hydrogel composite is much higher than pristine PAAm reported in the literature (Aydınoğlu et al., 2014) (Gün Gök & Inal, 2022).
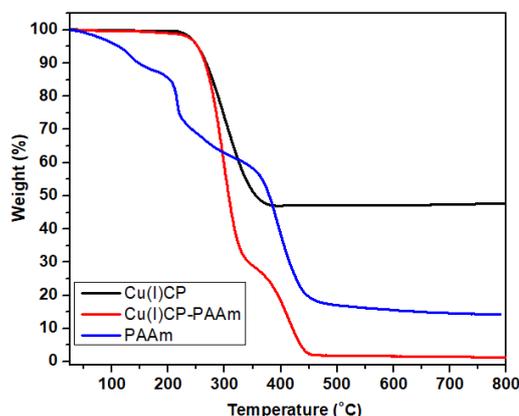
Figure 7. TGA thermograms of (blue) PAAm, (red) hydrogel composite, and (black) Cu(I)CP.

4. Conclusion

We have developed a straightforward and sustainable strategy for the light-induced *in situ* fabrication of a highly cross-linked copper(I) coordination polymer-polyacrylamide based hydrogel composite. The *in situ* generated hydrogel composite was thoroughly investigated by multiple spectroscopic and thermal analyses. DSC and TGA data displayed the improved thermal performance of the hydrogel composite, compared to pristine PAAm hydrogels. The novelty of the work is mainly the employment of a photoactive coordination polymer as a type II photoinitiator. Another advantage of the advanced approach is the possibility to post-modify the *in situ* generated hydrogel composite through the use of copper catalyzed azide-alkyne click chemistry. The presence of copper ions would avoid the necessity of additional copper species for the catalysis. We believe that the results of this work could open a new path for the sustainable fabrication of clickable hydrogels and can guide future research on copper containing hydrogels. The click reactions between the hydrogel composite and several azide species, are undergoing in our lab.

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