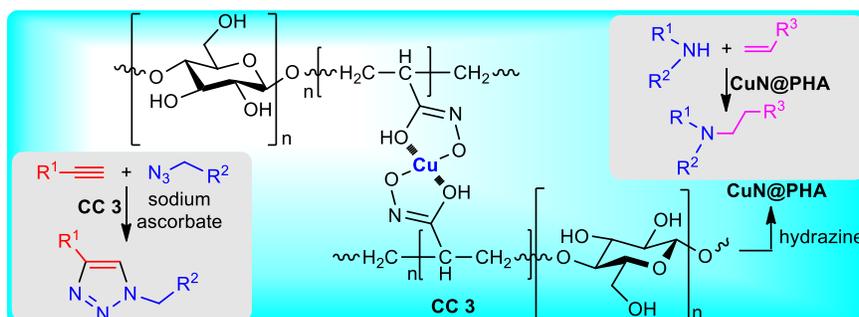


Highly Active and Reusable Kenaf Cellulose Supported Bio-Poly(hydroxamic acid) Functionalized Copper Catalysts for C–N Bond Formation Reactions

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Distinctly active poly(hydroxamic acid) anchored copper (Cu) catalysts were synthesized from chemically modified kenaf cellulose. They were characterized by Fourier transform infrared spectroscopy (FT-IR), field emission scanning microscopy (FESEM), high resolution transmission electron microscopy (HRTEM),



inductively coupled plasma atomic emission spectrometry (ICP-AES), UV-vis spectroscopy (UV), and X-ray photoelectron spectroscopy (XPS). The Cu-catalysts were successfully applied to the Michael addition reaction of amines with α,β -unsaturated carbonyl/cyano compounds and to the Click reactions of organoazides with alkynes under mild reaction conditions. The catalysts enabled excellent yields (88% to 95%) in both of the C–N bond formation reactions and showed easy recycling with outstanding reusability for seven cycles without any distinguished decrease in their catalytic activity.

Keywords: Graft Co-polymerization; Catalyst; Poly(hydroxamic acid); Polymer; Cellulose

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INTRODUCTION

Due to increased environmental consciousness and corresponding efforts to develop green synthetic methods, heterogeneous catalyzed organic transformation reactions have become extremely attractive to the chemical community in recent years (Sheldon and Dakka 1994; Lancaster 2002). Heterogeneous catalysis is particularly interesting because it allows for the easy separation of large quantities of products with the use of a small amount of catalyst. It is also important because catalysts have the potential for reusability and tolerance to drastic reaction conditions (Clark 2001; Guibal 2005).

To achieve an environmentally friendly and sustainable chemical process, the use of renewable materials as solid support could be a good choice. In this respect, biopolymers

are an attractive candidate as a solid support material in preparation of heterogeneous catalysts. Although a variety of supports, *e.g.*, alginate (Wei *et al.* 2004), gelatin (Zhang *et al.* 2001), starch (Huang *et al.* 2002), chitosan (Quignard *et al.* 2000), and cellulose derivatives have been used (Reddy and Kumar 2006; Yu *et al.* 2016), many of which are not economical, widely available, or easy to use. Cellulose is the most common natural biopolymer available all over the globe; approximately 1.5×10^{12} tons of the biomass are produced annually (Reddy *et al.* 2006). Its derivatives are also produced on an industrial scale and used for wastewater treatment, coatings, laminates, and optical films, as well as for property-determining additives in building materials, pharmaceuticals, foodstuffs, and cosmetics (Klemm *et al.* 2005; Kamel *et al.* 2006). Nevertheless, its application as support in catalytic applications is not well studied.

Michael addition and azide-alkyne cycloaddition (referred to in this article as the Click reaction) are two important C–N bond formation methods that are widely used for preparing β -amino carbonyl/nitrile compounds and 1,2,3-triazoles, respectively, due to their atom economy and simplicity (Huisgen 1984; Rostovtsev *et al.* 2002). Moreover, β -amino carbonyl compounds, 1,2,3-triazoles, and their derivatives have received immense interest because of their widespread presence and use in organic synthesis.

Many heterogeneous metal catalysts have been utilized for the Michael addition as well as for the Click reaction. Namely, MOF-99 (metal organic framework) (Nguyen *et al.* 2012), polystyrene supported Cu(I)-imidazole complex (Li *et al.* 2012), silica sulfuric acid (Wang *et al.* 2009), phosphate-impregnated titania (Nath and Chaudhuri 2009), PSSA (polystyrenesulfonic acid) (Polshettiwar and Varma 2007), Amberlyst-15 (Das and Chowdhury 2007), MCM-41 (Mobil composition of matter) immobilized heteropoly acids (Xie *et al.* 2013), HY zeolite (Jeganathan *et al.* 2014), polystyrene-supported DABCO (1,4-diazabicyclo[2.2.2]octane), and TBD (1,5,7-Triazabicyclo[4,4,0]dec-5-ene) (Sodhi *et al.* 2015; Yu and Xu 2015), silica-bonded imidazolium-sulfonic acid chloride (SBISAC) (Moosavi-Zare *et al.* 2015), zeolites (Chassaing *et al.* 2007), polymers (Yamada *et al.* 2012), non-magnetic and magnetic supported Cu(I) (Megia-Fernandez *et al.* 2010), silica (Mnasri *et al.* 2015), and TiO₂-nanotube (Faraji *et al.* 2016) all showed good catalytic activity. However, they do not completely fulfill the economic and sustainable protocols involved in the development of green processes. Thus, the development of green sustainable heterogeneous catalysts for Michael additions and Click reactions remains a big challenge. In this respect, cellulose, which has some extraordinary characteristics including abundance in nature, low-density, bio-renewability, universal availability, low cost, and interesting mechanical properties similar to glass, could be a perfect choice. Furthermore, its backbone can be tailored by proper chemical modification with suitable functional groups for specific purposes (Gurdag *et al.* 1997).

This paper presents the preparation and characterization of effective heterogeneous copper catalysts, poly(hydroxamic acid) Cu(II) complex, and poly(hydroxamic acid) copper nanoparticles supported by kenaf cellulose for C–N bond formation reactions. Poly(hydroxamic acid) copper nanoparticles efficiently promoted the Michael addition reaction of aliphatic amines with α,β -unsaturated carbonyl/cyano compounds and poly(hydroxamic acid) Cu(II) complex forwarded the Click reaction of organoazides with alkynes in the presence of sodium ascorbate under mild reaction conditions. The catalysts showed high catalytic performance with easy recyclability and reusability.

EXPERIMENTAL

Materials

Methyl acrylate monomer purchased from Sigma Aldrich Chemical Industries, Ltd. (Kuala Lumpur, Malaysia) was passed through a column filled with chromatographic grade activated alumina to remove inhibitors. Other chemicals such as ceric ammonium nitrate (CAN) (Sigma-Aldrich, Kuala Lumpur, Malaysia), methanol, ethyl acetate, and MgSO_4 (Merck, Germany), sulphuric acid (Lab Scan, Bangkok, Thailand), metal salts, and other analytical grade reagents were used without purification. Reagents and solvents were obtained from commercial suppliers and used without further purification. Water was deionized with a Millipore system with a Milli-Q grade. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was purchased from Aldrich Chemical Industries, Ltd.

Analytical Methods

^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were measured with a Bruker 500 spectrometer (California, USA). The ^1H NMR chemical shifts were reported relative to tetramethylsilane (TMS, 0.00 ppm). The ^{13}C NMR chemical shifts were reported relative to CDCl_3 (77.0 ppm). Inductively coupled plasma atomic emission spectrometry (ICP-AES) was performed on a Shimadzu ICPS-8100 (Germany). Fourier transform infrared spectroscopy (FT-IR) spectra were measured with a Perkin-Elmer 670 spectrometer (Germany) equipped with an attenuated total reflectance (ATR) device (ZnSe crystal). X-ray photoelectron spectroscopy (XPS) spectra were measured with a Scanning X-ray Microprobe PHI Quantera II, MIMOS (Kuala Lumpur, Malaysia). Field emission scanning electron microscopy (FE-SEM) was measured with JSM-7800F (USA). Transmission electron microscopy (TEM) was measured with a HT-7700 (Hi-Tech Instruments SDN BHD, Puchong, Malaysia). Thin-layer chromatography (TLC) analysis was performed on Merck silica gel 60 F 254. Column chromatography was carried out on silica gel (Wakogel C-200; Osaka, Japan).

Isolation of Kenaf Cellulose

Kenaf fiber was obtained from the local market at Kuantan, Pahang, Malaysia and cut into small pieces (approximately 0.3 cm in length). The raw fiber (200 g) was boiled with 17% NaOH (700 mL) for 5 h and washed with distilled water. The resulting product was boiled with glacial acetic acid (600 mL) for 1 h and washed with distilled water. The dark-colored kenaf cellulose was bleached with hydrogen peroxide (300 mL) and 7% NaOH (500 mL), washed with distilled water (500 mL) several times to obtain a white-colored cellulose that was oven-dried at 50 °C before use.

Graft Copolymerization (PMA 1)

The kenaf cellulose (3 g) was dispersed in 300 mL of distilled water. The copolymerization reaction was carried out on a water bath in 1 L three-neck round bottom flask fixed with a stirrer, condenser, and thermostat. After nitrogen gas was purged into the flask, the mixture was heated at 55 °C with stirring, and 1.1 mL of diluted sulfuric acid (50%) was added to the mixture. After 5 min, 1.1 g of CAN (10 mL aqueous solution) was added, and the reaction mixture was stirred under nitrogen atmosphere. After stirring for another 20 min, 10 mL of methyl acrylate purified monomer was added into the cellulose suspension, and stirring was continued for 4 h under nitrogen atmosphere. The mixture was cooled at room temperature, filtrated on a glass filter, and washed with an aqueous

methanol (methanol to water ratio was 4:1) to give the cellulose supported poly(methyl acrylate) **PMA 1** (Rahman *et al.* 2016a).

Synthesis of the Poly(hydroxamic acid) Ligand 2 (PHA 2)

The hydroxylamine solution was prepared by dissolving 12 g of hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) in 300 mL of aqueous methanol (the methanol to water ratio was 4:1). A cold aqueous solution of NaOH (50%, 16.6 mL) was added to the hydroxylamine solution, and the resulting NaCl precipitates were removed by filtration. The pH of the reaction was adjusted to pH 11 by the controlled addition of aqueous NaOH. The **PMA 1** (5.0 g) was placed into a two-neck round bottom flask fixed with a stirrer, condenser, and thermostat. The prepared hydroxylamine solution was then added into the flask, and the reaction was heated at 70 °C on a water bath for 6 h. The chelating polymeric ligand (**PHA 2**) was separated from hydroxylamine solution by filtration followed by washing with aqueous methanol. The ligand **PHA 2** was treated with 200 mL of 0.1 M HCl (in methanol) for protonation of the ligand, filtered, washed several times with methanol, and dried at 50 °C to get a constant weight (Rahman *et al.* 2016b).

Preparation of the Poly(hydroxamic acid) Copper Complex (CC 3)

An aqueous solution of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ (246 mg, in 20 mL H_2O) was added into a stirred suspension of poly(hydroxamic acid) ligand **PHA 2** (1 g) in 40 mL water at room temperature. The blue CuSO_4 immediately turned into green color hydroxamic acid copper complex ($\text{Ø} = 17.2 \pm 2$ nm), and the mixture was stirred for 2 h at room temperature. The poly(hydroxamic acid) copper complex **CC 3** was filtered and washed several times with the excess amount of ammonium chloride, water, methanol, and dried at 60 °C for 2 h. The ICP-AES analysis showed that 0.51 mmol/g of copper was adsorbed by the poly(hydroxamic acid) ligand (Wen *et al.* 2012).

Preparation of the Poly(hydroxamic acid) Cu-Nanoparticles (CuN@PHA)

Poly(hydroxamic acid) copper complex **CC 3** (300 mg) was dispersed in 40 mL deionized water and 0.7 mL of hydrazine hydrate was added to the reaction mixture. The reaction mixture was stirred at room temperature for 3 h. The resulting **CuN@PHA** ($\text{Ø} = 3.5 \pm 1$ nm) materials were collected by filtration, washed with water, methanol, and dried under vacuum at 100 °C. The **CuN@PHA** was stored under nitrogen atmosphere (Sarkar *et al.* 2016).

General Procedure for Click Reaction

A 5-mL glass vessel was charged with **CC 3** (1 mg, 0.05 mol%), alkyne (1.1 mmol), and aryl azide (1 mmol) in a 5 mol% aqueous solution of sodium ascorbate (3 mL). The reaction mixture was stirred at 70 °C for 3.5 h; during that time, colorless triazoles were precipitated. The reaction mixture was diluted with ethyl acetate (EtOAc), and the insoluble **CC 3** was recovered by filtration. The organic layer was separated, and the aqueous layer was extracted with EtOAc (3×2 mL). The combined organic layers were dried over MgSO_4 and concentrated under reduced pressure to give the corresponding triazoles. The crude product was purified by silica gel short column chromatography (EtOAc/hexane).

General Procedure for Michael Addition Reaction

In a typical experiment, a mixture of amine (10 mmol), α,β -unsaturated Michael acceptor (11 mmol), and kenaf cellulose supported **CuN@PHA** (2 mg, 0.1 mol%) in 10 mL of MeOH was stirred at room temperature for 5.5 h. The reaction progress was monitored by gas chromatography (GC) analysis. After completion of the reaction, **CuN@PHA** was filtered on a filter paper, washed with MeOH (3×5 mL), dried under vacuum, and reused in the next run under the same reaction conditions. The filtrate was concentrated under reduced pressure and purified by column chromatography (hexane/ethyl acetate) to obtain the corresponding Michael addition products.

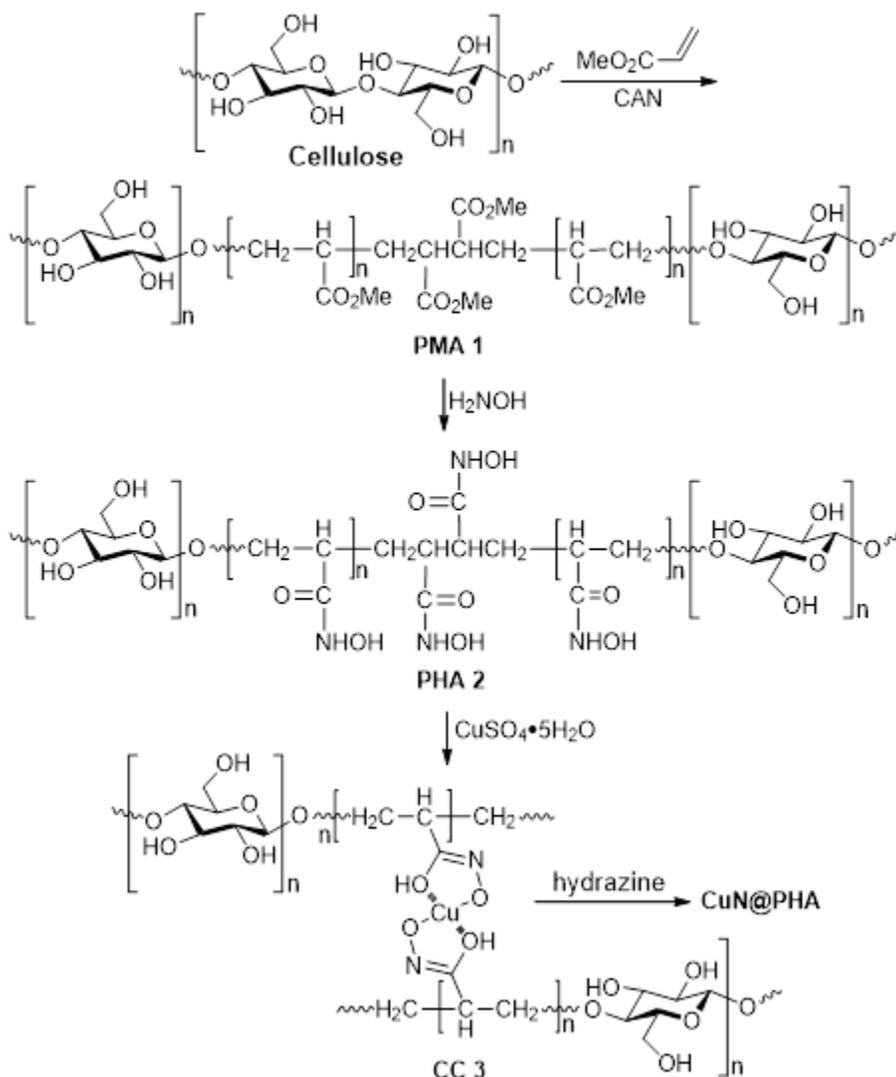


Fig. 1. Preparation of **CC 3** and **CuN@PHA**

RESULTS AND DISCUSSION

Preparation of the catalysts

The catalysts were prepared according to our early report (Fig. 1) (Islam *et al.* 2016; Sarkar *et al.* 2016).

FT-IR Analysis

The IR spectrum of fresh kenaf cellulose showed adsorption bands at 3430 cm^{-1} and 2915 cm^{-1} , which referred to O–H and C–H stretching, respectively (Fig. 2). The band at 1655 cm^{-1} was due to the bending mode of OH, and a smaller peak at 1450 cm^{-1} corresponded to CH_2 symmetric stretching (Liu *et al.* 2006). The absorbance at 1385 cm^{-1} and 1162 cm^{-1} originated from the O–H bending and C–O stretching, respectively. The C–O–C pyranose ring skeletal vibration produced a strong band at 1085 cm^{-1} . A small sharp peak at 908 cm^{-1} corresponded to the glycosidic C–H deformation, with ring vibration contribution and O–H bending indicating β -glycosidic linkages between glucose units in cellulose (Liu *et al.* 2006). The IR spectrum of **PMA 1** showed new absorption bands at 1742 cm^{-1} , 1475 cm^{-1} , and 1402 cm^{-1} due to C=O the scissoring and wagging stretching of methyl group (Haron *et al.* 2009). The peaks at 2980 cm^{-1} and 2870 cm^{-1} represented the stretching of methyl group of C–H (sp^3).

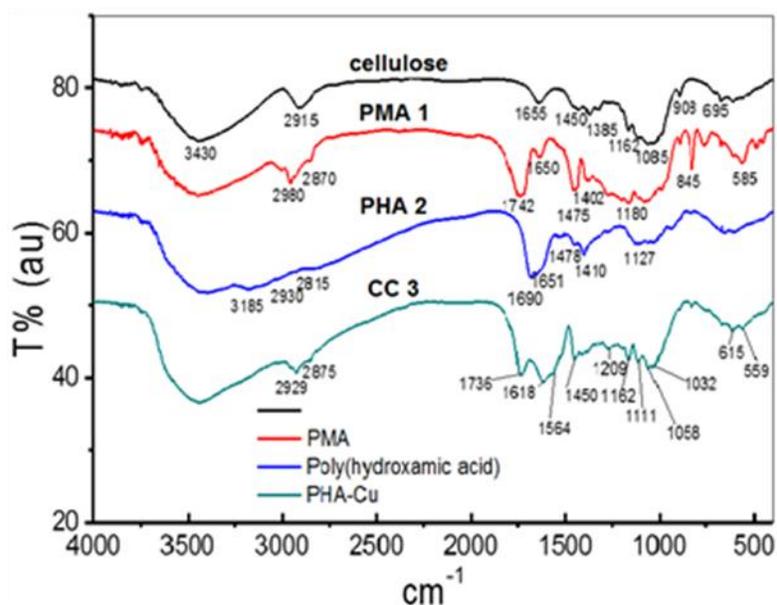


Fig. 2. FT-IR of cellulose and modified cellulose

The poly(hydroxamic acid) ligand **PHA 2** showed new absorption bands at 1690 cm^{-1} and 1651 cm^{-1} , corresponding to the C=O stretching and N–H bending modes. Additionally, a new broad band at 3185 cm^{-1} for N–H stretching and 1410 cm^{-1} for O–H bending were observed. It was found that the C=O band at 1742 cm^{-1} in **PMA 1** shifted to 1690 cm^{-1} , which confirmed the successful production of hydroxamic acid ligand.

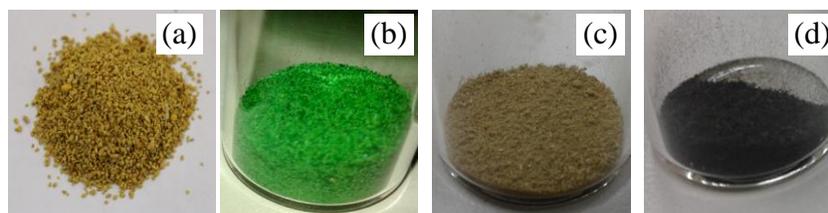


Fig. 3. Photo images of (a) **PHA 2**, (b) **CC 3**, (c) **CC 3** after its reduction using sodium ascorbate [Cu(I)], and (d) **CC 3** after its reduction using hydrazine hydrate (**CuN@PHA**)

After the incorporation of copper salt with poly(hydroxamic acid), the color of **PHA 2** (lite-yellow) changed (Fig. 3a) to green (Fig. 3b) and a new absorption band at 1738 cm^{-1} was observed corresponding to the C=O stretching for hydroxamic acid. New peaks at 1618 cm^{-1} , 1450 cm^{-1} , and 1162 cm^{-1} were assigned for C=N and C–O stretching, respectively. A peak at 615 cm^{-1} was confirmed as the successful incorporation of copper with the **CC 3** (Prenesti and Berto 2002). The green color **CC 3** (Fig. 3b) material was treated with sodium ascorbate (Click reaction) and hydrazine hydrate (Michael addition) to give lite-brown color Cu(I) complex (Fig. 3c) and dark brown color **CuN@PHA** (Fig. 3d), respectively.

FE-SEM, HR-TEM, UV and XPS Analysis

The FE-SEM micrograph of kenaf cellulose showed smooth-like morphology (Fig. 4a), whereas **PMA 1** showed unsmooth surface (Fig. 4b). Poly (hydroxamic acid) ligand **PHA 2** exhibited distinct spherical morphology (Fig. 4c) that indicated the successful hydroximation of **PMA 1**. The SEM image of **CC 3** displayed larger spherical morphology and revealed that **PHA 2** was aggregated due to the cross-linkage between poly (hydroxamic acid) chelating ligands and Cu(II) (Fig. 4d).

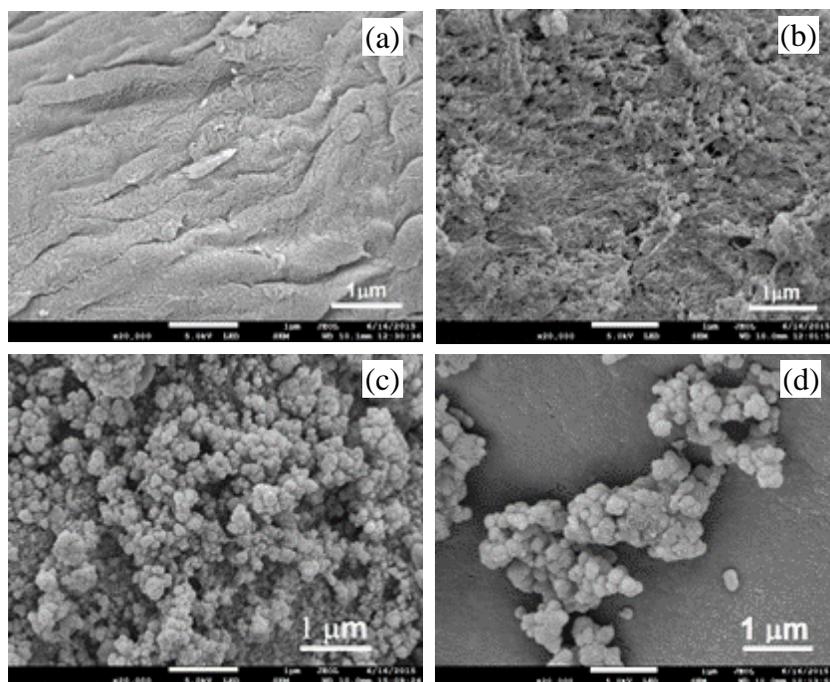


Fig. 4. (a) SEM image of kenaf cellulose, (b) SEM image of **PMA 1**, (c) SEM image of **PHA 2**, (d) SEM image of **CC 3**

TEM analysis of **CC 3** showed the presence of Cu(II) on the cellulose surface (Fig. 5a). The average particle size $\text{Ø} = 17.2 \pm 2\text{ nm}$ was measured. The **CC 3** was then reduced by hydrazine hydrate obtained **CuN@PHA** and the corresponding TEM image revealed good dispersion of smaller copper nanoparticles ($\text{Ø} = 3.5 \pm 1\text{ nm}$) in the cellulose backbone (Fig. 5b). The XPS spectrum of **CuN@PHA** showed a single Cu 2p_{3/2} peak at 931.7 eV (Fig. 6), which corresponded to the binding energy of Cu(0) (Sarkar *et al.* 2016). Additionally, a UV-vis spectrum of **CC 3** (Fig. 7) exhibited a single absorption at 693 nm

that was associated with Cu–N coordination (Yamada *et al.* 2012). The **PMA 1** and **PHA 2** did not absorb UV light in that region.

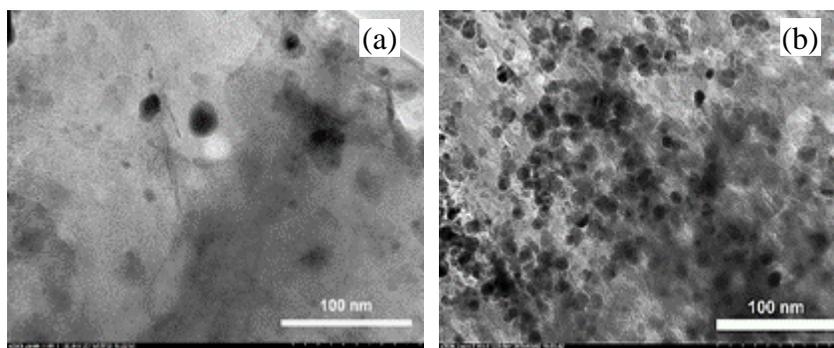


Fig. 5. (a) TEM image of **CC 3**, (b) TEM image of **CuN@PHA**

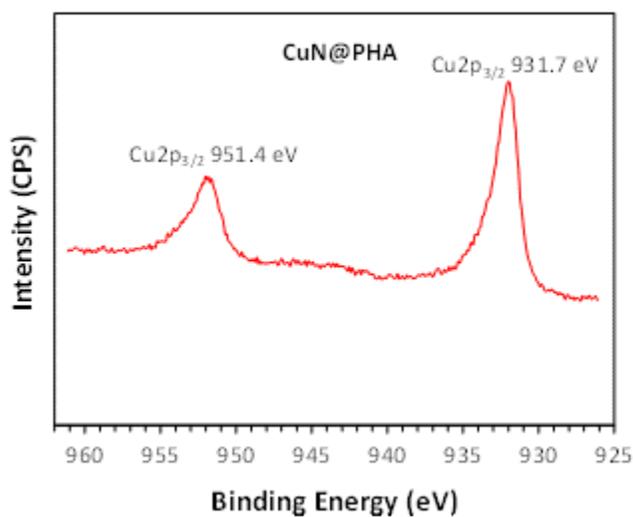


Fig. 6. XPS of **CuN@PHA**

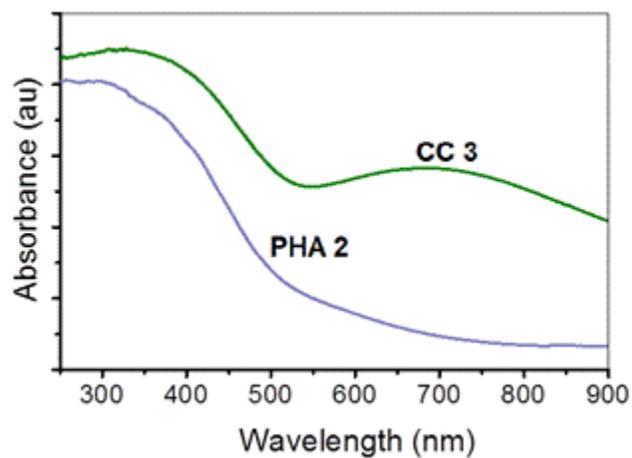


Fig. 7. UV-vis of **CC 3** and **PHA 2**

Click Reaction

The catalytic activities of kenaf cellulose supported **CC 3** in the Click reaction between different alkynes and aryl azides were studied. To set up the optimum reaction conditions, the reaction of phenylacetylene (**i**) and benzyl azide (**ii**) was taken as the model reaction. The initial reaction was carried out using 1 mol% of **CC 3** at 60 °C for 2.5 h in the presence of 5 mol% aqueous solution of sodium ascorbate which smoothly afforded the desired product (**iii**) with 93% yield (Table 1, entry 1). In contrast, 95% and 92% yields were obtained when the same reactions were performed using 0.5 mol% and 0.1 mol% of **CC 3** (entries 2 and 3), and it took 5 h and 7 h to complete the reaction, respectively. The reaction was further carried out by changing the catalyst loading and temperature (entries 4 to 6), and it was eventually found that 0.05 mol% of **CC 3** would be enough to promote this reaction efficiently (entry 4).

Table 1. Optimization of the Click Reaction

Entry	CC 3 (mol%)	Temp (°C)	Time (h)	Yield (%)
1	1	60	2.5	93
2	0.5	60	5	95
3	0.1	60	7	92
4	0.05	70	3.5	97
5	0.01	90	6.5	90
6	0.05	90	3	91

Note: Reactions contained 1.1 mmol of phenylacetylene and 1 mmol of benzyl azide in 5 mol% of sodium ascorbate (3 mL).

When the optimum conditions were established, the broad applicability of **CC 3** in the Click reaction with various alkynes and azides under the optimized reaction conditions were investigated. When the cyclization of phenylacetylene with 4- methylbenzyl azide and 4-methoxybenzyl azide were carried out using 0.05 mol% of **CC 3** in the presence of 5 mol% of sodium ascorbate at 70 °C for 3.5 h, **CC 3** drove the reaction smoothly and yielded triazoles (**iv**) and (**v**) (Fig. 8) with 95% and 93% yields, respectively. The **CC 3** was reduced by sodium ascorbate to give Cu(I); thus, the color of **CC 3** changed from green to light brown during the reaction progress (Fig. 3c). The 4-tolylacetylene reacted with benzyl azide, 1-azido-2-phenylethane, and aliphatic azides efficiently under similar reaction conditions to afford the corresponding triazoles (**vi**)-(viii) with 91% yields, respectively.

An aliphatic alkyne hex-5-yn-1-ol readily reacted with a variety of benzyl and naphthyl azides to give the corresponding triazoles (**ix**)-(xiv) in 87% to 95% yields. **CC 3** also promoted the reaction of alkynes bearing a cyclic tertiary alcoholic group with benzyl azide to give the corresponding product (**xv**) with a 91% yield.

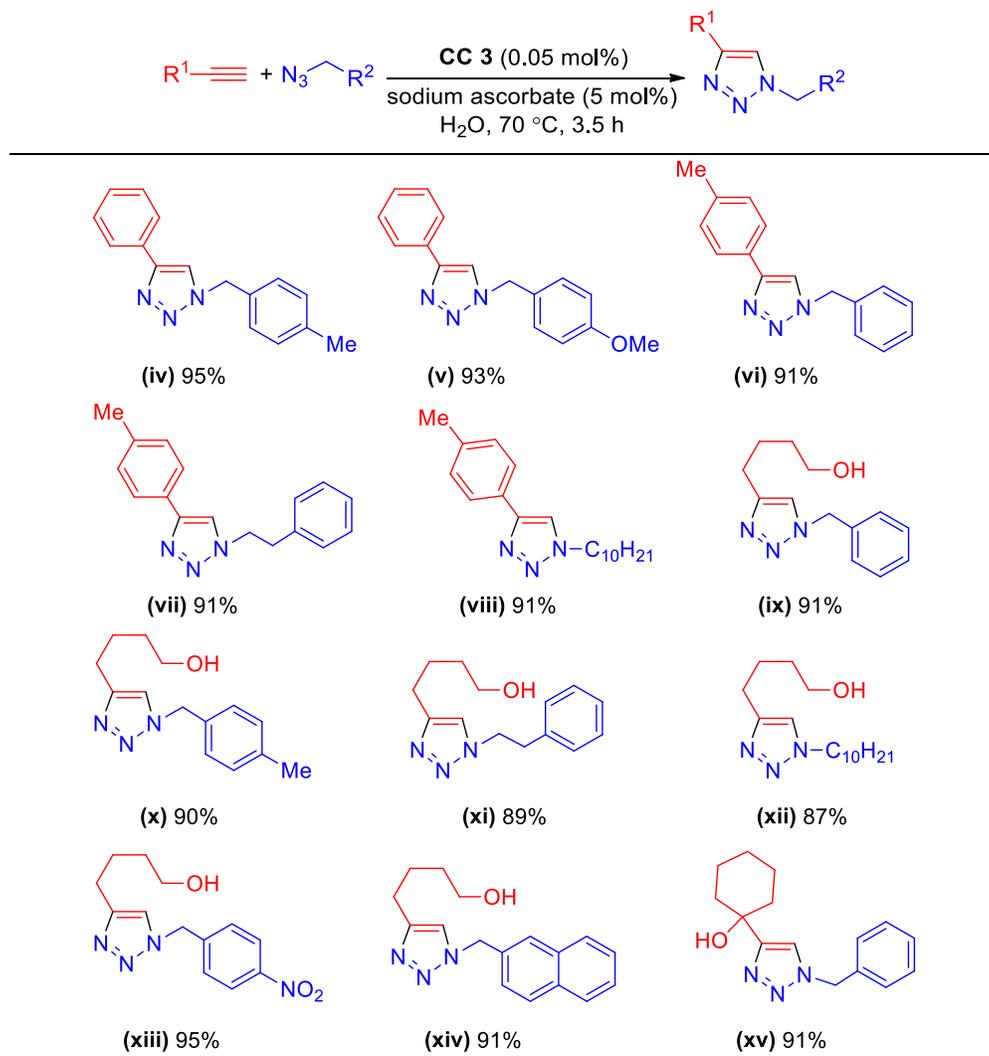


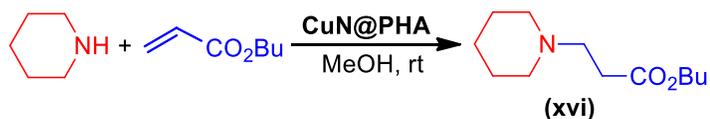
Fig. 8. Click reaction of organic azides and alkynes. The reaction was carried out using 1.1 mmol of alkyne, 1 mmol of organic azide, 0.05 mol% of **CC 3** in 5 mol% of sodium ascorbate (3 mL) at 70 °C for 3.5 h.

Michael Addition Reaction

The Michael addition reaction of amine and α,β -unsaturated compounds was considered to find the catalytic versatility of the prepared kenaf cellulose supported **CuN@PHA**. The addition reaction between piperidine and butyl acrylate at room temperature was chosen to evaluate the optimum conditions for the high catalytic performance of **CuN@PHA**. Table 2 presents the results of the effect of catalyst dosages and reaction time. The initial reaction was carried out using piperidine and butyl acrylate in the presence of 1.6 mol% (32 mg) of **CuN@PHA**, which efficiently promoted the reaction to give the corresponding addition product (**xvi**) with a 92% yield within 1.5 h (Table 2, entry 1). When 0.08 mol% of **CuN@PHA** was used, the reaction time increased as expected to 4 h (entry 2). When the loading of **CuN@PHA** was decreased (0.04 mol% to 0.02 mol%), the reaction took a longer time to complete (entries 3 and 4). The catalyst loading was further decreased to 0.005 mol% (0.1 mg), which also efficiently promoted the addition reaction (entry 5). It is interesting to notice that the Michael addition reactions

that were carried out using **PHA 2** and **CC 3** generated only 15% and 19% yield of the product, respectively (entries 6 and 7). The highest turnover number (TON) and turnover frequency (TOF) were observed when the reaction was carried out using 0.005 mol% of **CuN@PHA** (entry 5).

Table 2. Optimization of Michael Addition Reaction



Entry	Catalyst	CuN@PHA (mol%)	Time (h)	TON	TOF (h ⁻¹)	Yield (%)
1	CuN@PHA	1.6 (32 mg)	1.5	57.5	38	92
2	CuN@PHA	0.08	4	1125	281	90
3	CuN@PHA	0.04	4.5	2175	483	87
4	CuN@PHA	0.02 (0.4 mg)	5.5	4500	818	90
5	CuN@PHA	0.005 (0.1 mg)	6.5	17600	2707	88
6	PHA 2	(1 mg)	6	-	-	15
7	CC 3	(1 mg)	6	-	-	19

Note: Reactions contained 10 mmol of piperidine and 11 mmol of butyl acrylate in 10 mL of MeOH at room temperature.

The **CuN@PHA** was then examined for its wide applicability in Michael addition reactions. The addition reaction between dibutylamine (10 mmol) and methyl acrylate (11 mmol) was carried out using 0.02 mol% (0.4 mg) of **CuN@PHA** at room temperature in methanol for 5.5 h. These conditions yielded 91% of *N*-alkylated product (**xvii**) (Fig. 9). The aliphatic heterocyclic amines, *e.g.*, morpholine, piperidine, and dibenzyl amine, were also reacted smoothly with methyl acrylate under the same reaction conditions to give the corresponding *N*-alkylated addition products (**xviii**)-(**xx**) with 90% to 93% yield. The Michael addition reaction of dibenzyl amine with butyl acrylate and acrylonitrile produced (**xxi**) and (**xxii**) with 92% and 90% yield, respectively. The reactions of pyrrolidine, morpholine, and dibutylamine with butyl acrylate were also effective and yielded corresponding addition products (**xxiii**)-(**xxv**) with 89% to 91% yield. Thus, the **CuN@PHA** catalyst efficiently explored the Michael addition reaction of both open chain and cyclic secondary amines with different Michael acceptors. Interestingly, the sterically hindered secondary dibenzylamine readily gave corresponding addition products (**xx**) and (**xxii**) with excellent yield. Importantly, the primary amine, ethylenediamine, also effectively took part in the Michael addition reaction with butyl acrylate and acrylonitrile, providing poly-alkylated products (**xxvi**) and (**xxvii**) with 87% and 86% yield, respectively.

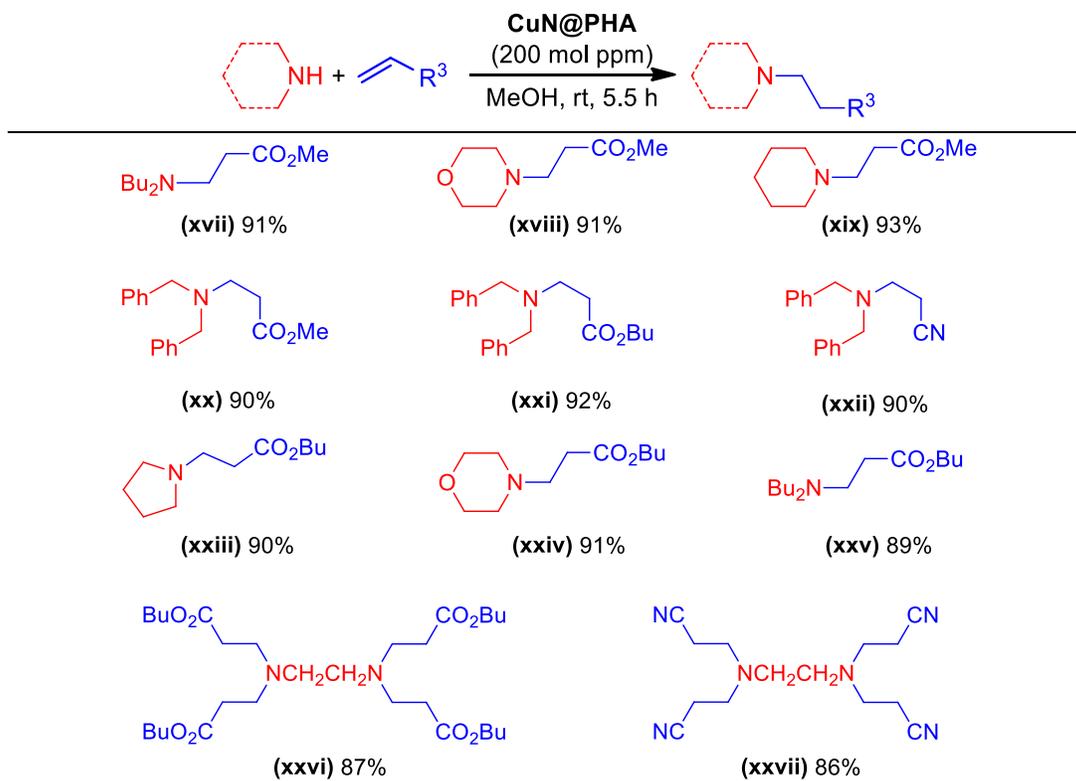


Fig. 9. Michael addition reactions using 10 mmol of amine, 11 mmol of Michael acceptor, and 0.02 mol% of **CuN@PHA** in 10 mL MeOH at room temperature for 5.5h

Recycling of the Catalysts

From the standpoint of economical and green chemistry, the reusability of catalysts in heterogeneous catalysis systems is very important. The results of recycling and reusing of **CC 3** (5 mol%) and **CuN@PHA** (0.25 mol%) are shown in Figs. 10 and 11, respectively. When the first run was completed, the catalysts were separated from the reaction mixture by filtration and were washed with ethyl acetate and methanol. The solid catalysts were dried at 80 °C under vacuum and then reused in the next run in the same reaction conditions.



Fig. 10. Recycling of **CC 3** in the Click reaction

Both **CC 3** and **CuN@PHA** were active up to seven times without notable loss of catalytic activity. The only negligible decrease in catalytic activity was found under the same

reaction conditions as the initial run. The small reduction in activity was found after five cycles due to the loss of catalysts during the filtration process. However, ICP-AES analysis showed that a trace amount of copper species (< 0.11 mol ppm of Cu) was leached into the reaction medium for the Click reaction. Therefore, the prepared catalysts can be recycled as well as reused repeatedly without significant reduction in their catalytic activity.

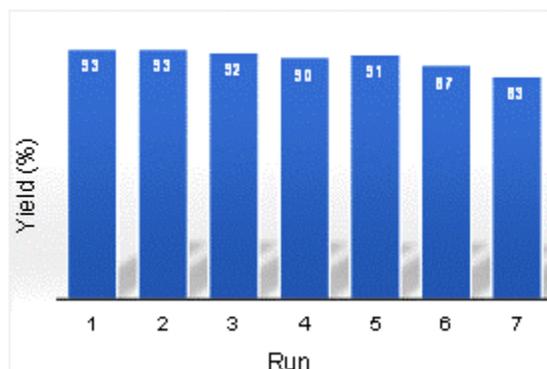


Fig. 11. Recycling of **CuN@PHA** in the Aza-Michael reaction

Heterogeneity Test of the CC 3

A hot filtration test was conducted to prove the insolubility of **CC 3** during reaction progress (Fig. 12). After 2 h of the reaction between phenylacetylene and benzyl azide, the catalyst was separated at hot condition and the filtrate was allowed to run for another 3 h but no further starting material was converted into product. The ICP-AES analysis of the filtrate also indicated no copper leaching in the reaction mixture.

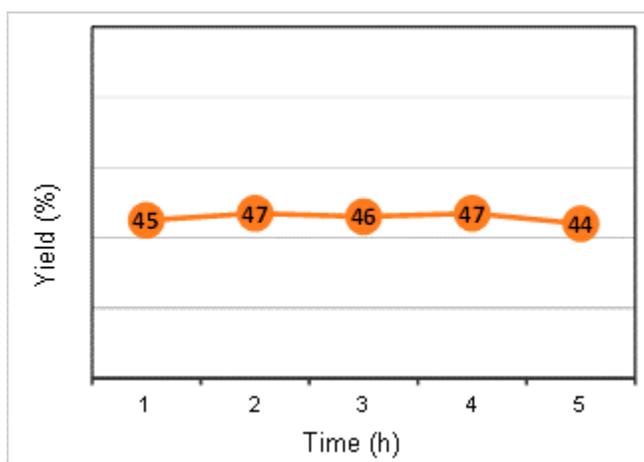


Fig. 12. Heterogeneity test of **CC 3** in the Click reaction

The leaching experiments were done for the first, fourth, and fifth run of the catalyst. Thus, it is assumed that the catalytic reaction proceeded under heterogeneous conditions.

Chemoselectivity Test of Aza-Michael reaction

Because chemoselectivity is an important issue in synthetic applications, the chemoselectivity of **CuN@PHA** in the *N*-alkylation reaction was investigated. For this reaction, a mixture of aniline and piperidine were exposed with methyl acrylate (3 mol

equiv) according to Table 1, entry 3. Interestingly, aniline did not undergo the reaction; rather, the mono-Michael adduct of piperidine (**xix**) was produced exclusively. This result clearly showed that **CuN@PHA** was chemoselective for aliphatic amines and the comparatively lower reactivity of aromatic amines could have been responsible for this (Fig. 13).



Fig. 13. Chemoselectivity of the Michael addition reaction

CONCLUSIONS

1. Kenaf cellulose anchored poly(hydroxamic acid) copper complex and copper nanoparticles were synthesized and characterized.
2. The kenaf cellulose anchored poly(hydroxamic acid) copper complex and copper nanoparticles were successfully applied as catalysts for C–N bond formation reactions.
3. The catalysts efficiently (0.05 mol% for Click and 0.02 mol% for Aza-Michael reaction) promoted the Click reaction of organoazides with alkynes, and Michael addition of amines with α,β -unsaturated carbonyl/cyano compounds to afford the corresponding products with high yields. Moreover, catalysts were recovered from the reaction mixtures and reused several times without significant loss of their catalytic performance.

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