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ORIGINAL PAPER

Click chemistry route to covalently link cellulose and clay

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Abstract An efficient method for covalently linking of cellulose and clay using a click chemistry based strategy is reported. Azide and alkynyl derivatives of silane were synthesized and used for silanization of cellulose and clay respectively. Functionalized cellulose and clay were then coupled using Cu(I) catalyzed azide–alkyne cycloaddition reaction, resulting in a covalent linkage between them. Successful synthesis of the silane derivates was established using Fourier transform infrared (FTIR) and nuclear magnetic resonance. Silanization of cellulose and clay with azide and alkynyl derivatives and the formation of a triazole linkage were confirmed using FTIR.

Graphical Abstract
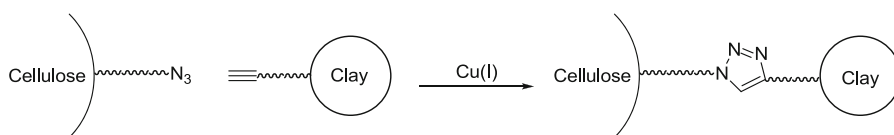
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Abbreviations

APTES	(3-aminopropyl)triethoxysilane
DCC	*N,N'*-dicyclohexylcarbodiimide
DMAP	4-dimethylaminopyridine
DCM	Dichloromethane
DMSO	Dimethylsulphoxide
DMA	Dimethylacetamide
EtOAc	Ethyl acetate
EDC.HCl	1-Ethyl-3-(3-dimethyllaminopropyl) carbodiimide hydrochloride

| PyBOP | Benzotriazol-1-yl-oxytripyrrolidinophosphonium-hexafluorophosphat PyBOP |
| HBTU | O-Benzotriazole-N,N,N',N'-tetramethyl-uronium-hexafluoro-phosphate |

Introduction

Cellulose is the most abundant natural polymer (Bovey and Winslow 1981, Krassig et al. 1986). Due to its high availability, recyclability and biodegradability, cellulose is widely used in many industries, including but not limited to, paper production, pharmaceutics, food, and reinforcement in polymer composites (Okiyama et al. 1992; Bledzki and Gassan 1999; Zimmermann et al. 2004; Orts et al. 2005; Coffey et al. 2006; Czaja et al. 2006; Garcia de Rodriguez et al. 2006; Hoenich 2007; Wan et al. 2007; Maren et al. 2009; Abdul Khalil et al. 2012). Cellulose fibers are used as reinforcement to enhance mechanical properties of polymers (Bledzki and Gassan 1999; Mohanty et al. 2000, 2002; Ludvik et al. 2007). However, poor dispersion of cellulose and limited binding between cellulose and the polymer matrix is the key issue (Eichhorn et al. 2010). Cellulose fibers tend to agglomerate, which reduces their efficacy as reinforcement material. While surface functionalization of cellulose (Abdelmouleh et al. 2002, 2005; Ly et al. 2008; Xie et al. 2010), silanization for example, is used for enhanced binding between fibers and polymer matrix; addition of clay, on the other hand, is employed for better dispersion of cellulose and improved fire retardancy of the composites (White 2004; Ludvik et al. 2007; Liu et al. 2012). Although, addition of clay allow better dispersion of cellulose; mechanical properties of the composites either do not improve significantly (Thunwall et al. 2008) or even degrade (Ludvik et al. 2007). The reason for this discrepancy was attributed to the insufficient binding between clay and cellulose. Hence, for improved mechanical properties, enhanced interfacial interaction between clay and cellulose is desired.

Here we report a possible method for enhancing interfacial binding between cellulose and clay using azide–alkyne cycloaddition based click reaction. Click chemistry is considered as the best method for linking molecular species of different kind (Rostovtsev et al.

2002; Himo et al. 2005). Click reactions received great attention because of the mild reaction conditions, absence of byproducts leading to easy purification of the products and the possibility of using environmentally benign solvents or solvent free conditions. Click reactions are performed even in living system for the detailed study of biochemical reactions (Dam and Caruso 2012; Thirumurugan et al. 2013; Yang et al. 2014). Click reactions have also been used to synthesize functional materials, nanoparticles, catalysts and also in synthesis of a large number of drugs (Qin et al. 2010; Liebert et al. 2006; Binder and Sachsenhofer 2007; Fournier et al. 2007; Moses and Moorhouse 2007; Karaaslan et al. 2013). Click chemistry has found its place in material synthesis, where it has been used mainly for the incorporation of functional groups, which are otherwise difficult to achieve.

Azide and alkynyl derivatives of silane were synthesized and covalently coupled to cellulose and clay respectively. The azide and alkyne groups were then linked by Cu(I) catalyzed click reaction resulting in covalent binding between cellulose and clay.

Surface silanization of clay (Papalos 1966; Manna et al. 1999; Freeman et al. 2000) and cellulose (Abdelmouleh et al. 2002, 2005; Ly et al. 2008; Xie et al. 2010) has been reported previously. Surface functionalization of clay and covalent bonding with polymer (Wheeler et al. 2006) has been demonstrated earlier. Moreover, cellulose is also chemically cross-linked with other polymer (Chang et al. 2008). However, we could not find any literature on covalent coupling between cellulose and clay not to mention any click chemistry between the two. In this paper, click chemistry route to covalently couple cellulose and clay is demonstrated.

Materials and methods

(3-aminopropyl)triethoxysilane (APTES) and propiolic acid were purchased from Thomas Baker (chemicals) Pvt. Ltd (India), N,N'-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP) were purchased from RFCL limited (India), dichloromethane (DCM), dimethylsulphoxide (DMSO), ethyl acetate, silica gel (60-120), citric acid were purchased from Thermo fisher scientific India Pvt. Ltd Mumbai (India), dimethylacetamide (DMA), petroleum ether, sodium sulfate, silica gel (100-200),
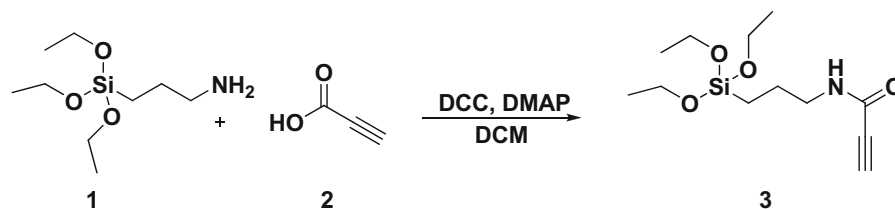
Scheme 1 Synthesis of *N*-(3-(triethoxysilyl)propyl)propiolamide (AMIPTES)

Scheme 2 Synthesis of (3-azidopropyl) triethoxysilane (AZIPTES)
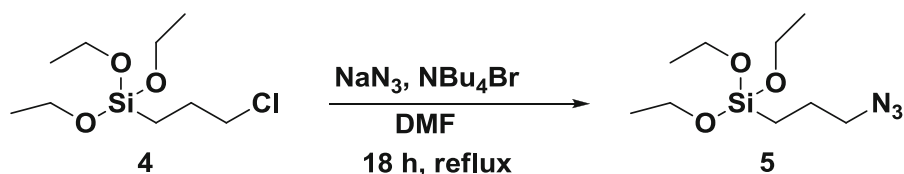
sodium bicarbonate, NaCl saturated solution, N$_2$ gas was purchased from SD fine-chem Limited Mumbai (India). 1-ethyl-3-(3-dimethyllaminopropyl)carbodi-imide hydrochloride (EDC.HCl), benzotriazol-1-yl-oxytripyrrolidinophosphonium-hexafluorophosphat (PyBOP) and *O*-benzotriazole-*N,N,N',N'*-tetram-ethyluronium hexafluorophosphate (HBTU) were purchased from Sigma-Aldrich (USA). Cellulose powder were supplied by Maple Biotech Private Limited Pune (India).

For the characterization of synthesized compounds, Fourier transform infrared (FTIR) (PerkinElmer, Spectrum Two, USA) and nuclear magnetic resonance (NMR) spectra (Jeol spectrometer) were recorded. ^{1}H and ^{13}C NMR spectra were recorded either on a Jeol spectrometer 400 MHz (100 MHz for ^{13}C) or on a 500 MHz (125 MHz for ^{13}C) NMR spectrometer at 25 °C. The ^{1}H NMR signals are referenced to tetramethylsilane (δ = 0.00 ppm) and the ^{13}C NMR peaks are referenced to residual CHCl$_3$ signal (δ = 77.0 ppm).

Synthesis of *N*-(3-(triethoxysilyl)propyl)propiolamide (AMIPTES)

AMIPTES (**3**) was synthesised using (3-aminopropyl) triethoxysilane (**1**) (APTES). APTES, 1.05 mL (4.52 mmol), was dissolved in 20 mL of DCM, followed by the addition of DCC 1.12 g (5.42 mmol), DMAP 0.055 g (0.452 mmol) and 0.3 mL (4.97 m-mol) of propiolic acid (**2**) into the 100 mL round bottom flask and stirred for 18 h at room temperature under inert atmosphere. After completion of the

reaction, the mixture was poured into separating funnel and extracted with 20 mL of saturated sodium bicarbonate solution followed by 5 mL saturated solution of citric acid. The crude reaction mixture was purified via column chromatography (Scheme 1).
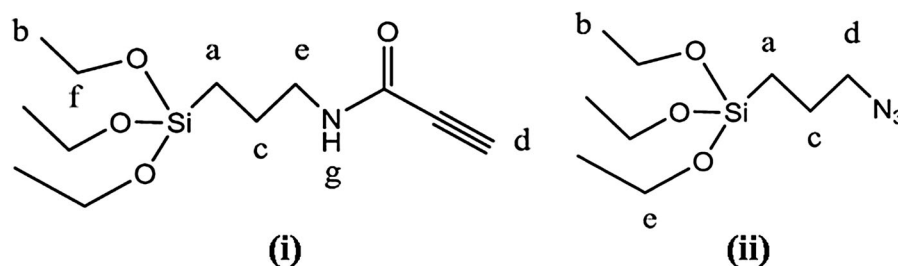
Synthesis of (3-azidopropyl) triethoxysilane (AZIPTES)

The AZIPTES (**5**) was synthesised using (3-chloro-propyl)triethoxysilane (CPTES): 4 mL (16.61 mmol) of (3-chloropropyl)triethoxysilane (**4**) was dissolved in 60 mL of DMA and stirred with 5.35 g (16.61 m-mol) of TBAB and 1.29 g (19.93 mmol) of NaN$_3$, and refluxed for 24 h. After the completion, the reaction mixture was extracted with diethyl ether and water. The organic layer again washed with brine followed by drying over sodium sulphate. The solvents were removed under reduced pressure and the crude reaction mixture purified through column chromatography (Scheme 2).

Silanization of microcrystalline cellulose (MCC) with AZIPTES

Preparation of NaOH treated MCC

Microcrystalline cellulose (33.00 g) was washed in 600 mL solution of 0.1 M NaOH, by ultrasonicating the mixture for 10 min followed by stirring for 30 min. After 30 min, the MCC was washed with DI water (5 cycles) to make it neutral. This step was performed to remove any impurities on cellulose.

Scheme 3 Azide and alkyne derivatives of silane. N-(3-(triethoxysilyl)propyl)propiolamide (AMIPTES) (i) and (3-azidopropyl) triethoxysilane (AZIPTES) (ii)
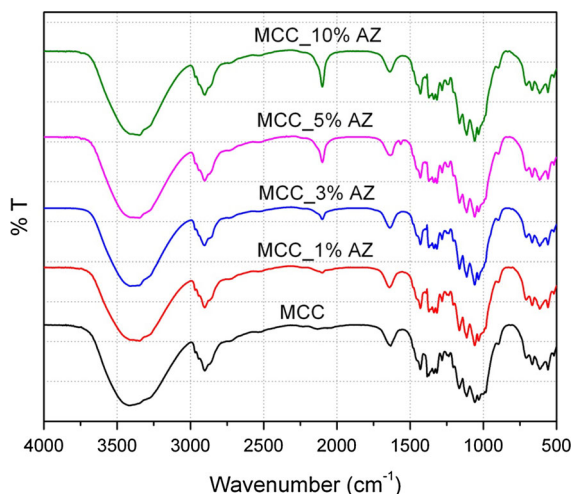

Fig. 1 FTIR confirming the incorporation of azide derivative of the silane on microcrystalline cellulose (MCC)
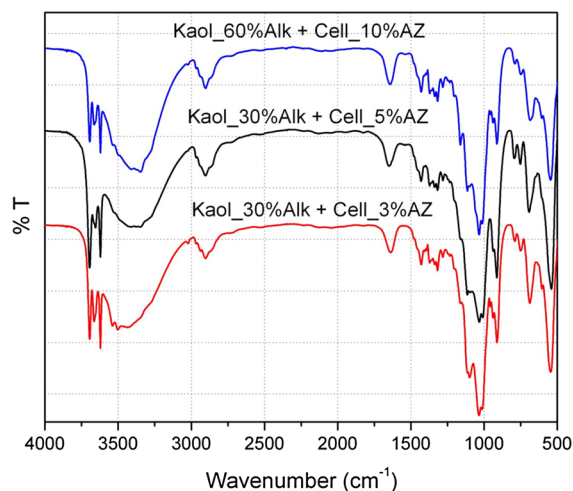

Fig. 3 Successful covalent bonding between cellulose and clay. Alkyne and azide peaks disappeared after the click chemistry reaction
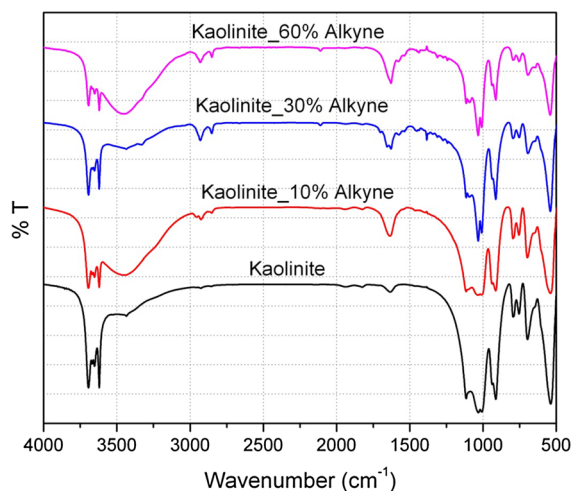
Surface modification of MCC

MCC surface was functionalized with 1, 3, 5 and 10 % (w/w) AZIPTES. Calculated amounts of AZIPTES (1, 3, 5, 10 %, w/w with respect to MCC) were dissolved in 100 mL of 80:20, ethanol–water system separately; afterward 5.00 g of dry MCC was added into each silane solution and stirred at room temperature for 1.5 h, followed by 10 min of ultrasonication. The solution was then transferred in the petridish and kept in oven at 45 °C for 24 h to evaporate ethanol and functionalize the cellulose. After functionalizing, MCC was scratched from petridish and collected in a well stopper bottles.

Silanization of kaolinite clay by AMIPTES

To silanize clay, 10, 30 and 60 % of AMIPTES (w/w with respect to kaolinite clay) was dissolved in

Fig. 2 FTIR spectra confirming successful functionalization of kaolinite clay by alkyne derivative of silane

200 mL of 80:20, ethanol–water system in a 250 mL round bottom flask. Dry kaolinite was added to each solution and the reaction mixture was allowed stir for 2 h. After that the mixture was ultrasonicated for 10 min. The mixture was transferred into petridish and kept in the oven at 100 °C for 24 h to dry after which, the dry modify clay was scratched with spatula and collected into well stopper bottles.

Click chemistry between kaolinite clay and MCC

A double-necked 100 mL round flask equipped with a magnetic stirrer was set and 15 mL of DMSO was added into it. Into that, 0.20 g of 30 % *N*-(3-(triethoxysilyl)propyl)propiolamide treated kaolinite clay and 5 % 3-azidopropyl triethoxysilane treated cellulose were added followed by 0.30 g of CuBr and the mixture was refluxed at 150 °C for 12 h. After stopping the reaction, the mixture was filtered and washed several times by ethyl acetate and water. After

drying the product at 80 °C for 12 h, it was scratched from filter paper and collected for further analysis.

Results and discussion

Spectral characterization of AMIPTES

FTIR spectrum (supplementary information S1) of AMIPTES (Scheme 3i) shows absorption bands at 3257, 2952, 2883, 2823 and 2109 cm^{-1} that are associated with –N–H stretching in secondary amine, alkyl –C–H stretching (2952–2823 cm^{-1}), and –C≡C stretching of alkynyl group, respectively. The spectrum shows a band at 1648 cm^{-1} that is associated with the stretching vibrations of the –C=O of amide group.

^{1}H-NMR (CDCl$_3$, 500 MHz, Fig. 4) δ 0.58 (t, 2H), 1.17 (t, 9H), 1.61 (m, 2H), 2.77 (s, 1H), 3.24(q, 2H), 3.76 (q, 2H), 6.72 (s, 1H); **^{13}C-NMR** (CDCl$_3$,
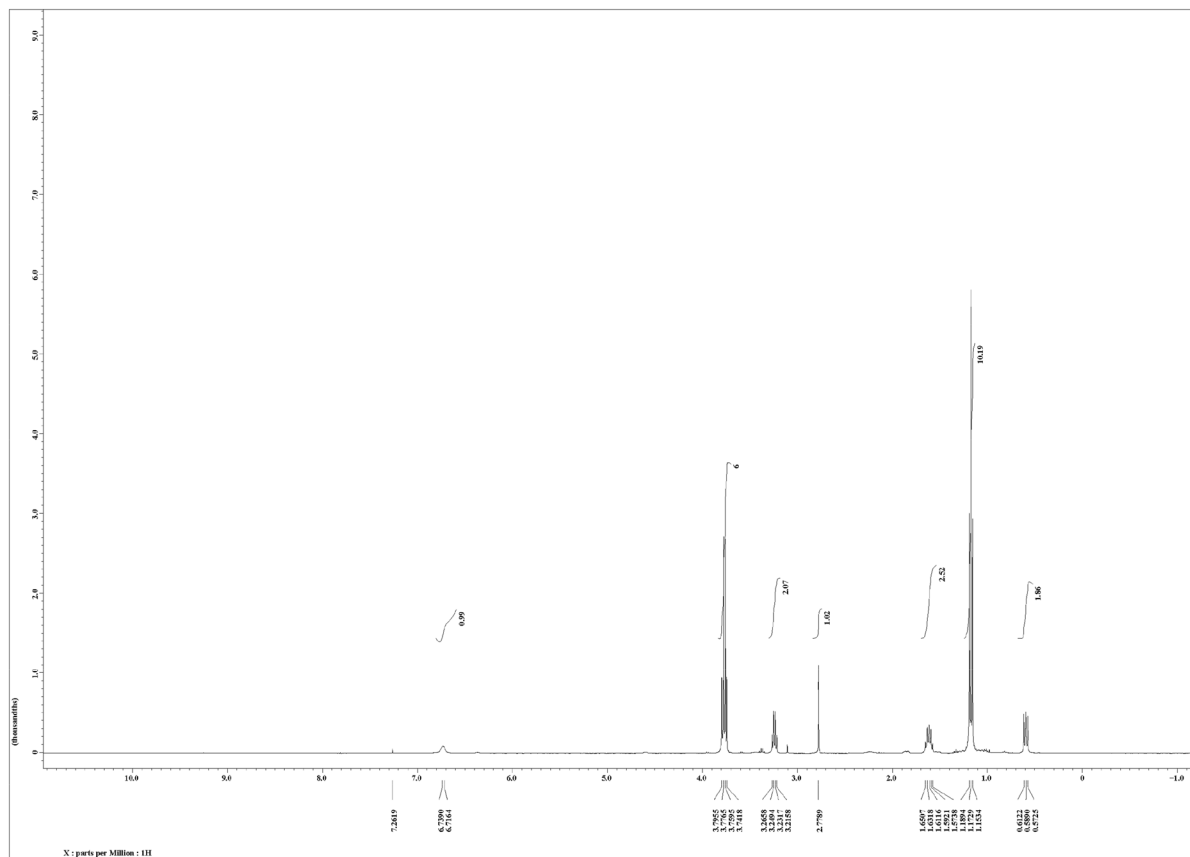

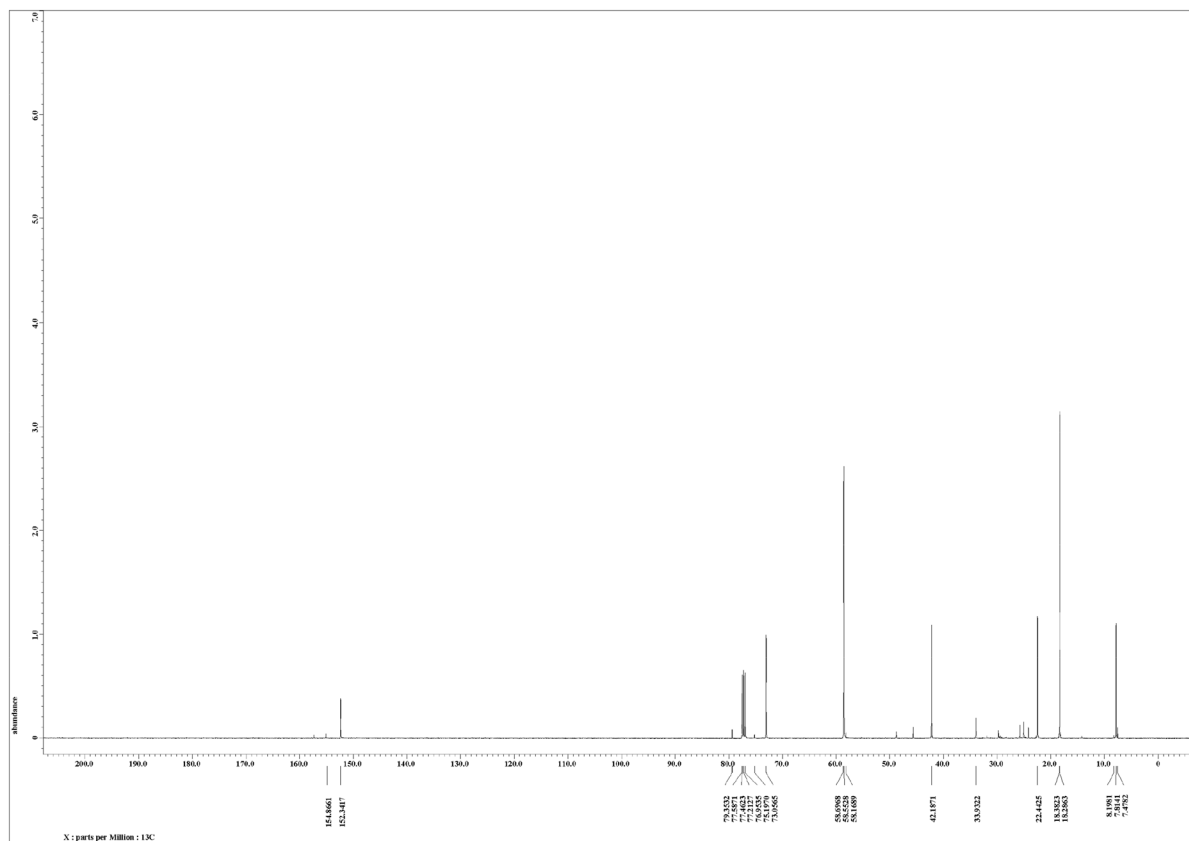**Fig. 4** ^{1}H NMR spectra of *N*-(3-(triethoxysilyl)propyl)propiolamide

Fig. 5 ^{13}C NMR spectrum of *N*-(3-(triethoxysilyl)propyl)propiolamide

100 MHz, Fig. 5), δ 7.81, 18.35, 22.44, 42.18, 58.55, 73.05, 75.19, 77.21, 152.34.

Spectral characterization of AZIPTES

FTIR spectrum (supplementary information S2) of AZIPTES (Scheme 3ii) shows absorption bands at 2977, 2926 cm^{-1} that are associated with –C–H stretching in alkyl groups and 2096 cm^{-1} that corresponds to the –N≡N stretching of nitrile group.

^{1}H-NMR (CDCl$_3$, 500 MHz, Fig. 6) δ 0.67 (t, 2H), 1.19 (t, 3H), 1.23 (m, 2H), 1.66 (t, 2H), 3.79 (q, 2H); **^{13}C-NMR** (CDCl$_3$, 100 MHz, Fig. 7), δ 13.80, 14.18, 18.30, 53.60, 58.43.

Silanization of MCC and kaolinite

The silanization of MCC and kaolinite was achieved by using suitably functionalized silane derivatives. The halogenated silyloxy compound (**4**) was treated with sodium azide and TBAI to get the desired

AZIPTES (**5**) quantitatively. MCC was functionalized with AZIPTES (3, 5, and 10 % w/w) as discussed in "Silanization of microcrystalline cellulose (MCC) with AZIPTES" section and was characterised by FTIR spectra. A stretching band at 2906 cm^{-1} was observed for functionalized MCC, which is the characteristic band for –N≡N group. On increasing the weight percent of AZIPTES from 1 to 10 % in MCC, the band at 2100 cm^{-1} became more intense (as shown in Fig. 1) suggesting successful functionalization of MCC with AZIPES.

Kaolinite was linked with alkyne derivate of silane. AMIPTES was successfully obtained by the coupling between corresponding acid (**2**) and amine (**1**) in the presence of DCC and DMAP. Attempted coupling between the same by using different coupling agents like EDC.HCl, HBTU, PyBOP gave complicated reaction mixtures. Functionalized kaolinite with varying amounts of silane was analysed by FTIR spectra. A stretching band at 2110 cm^{-1} was observed in all the proportion of AMIPTES in kaolinite; which is the
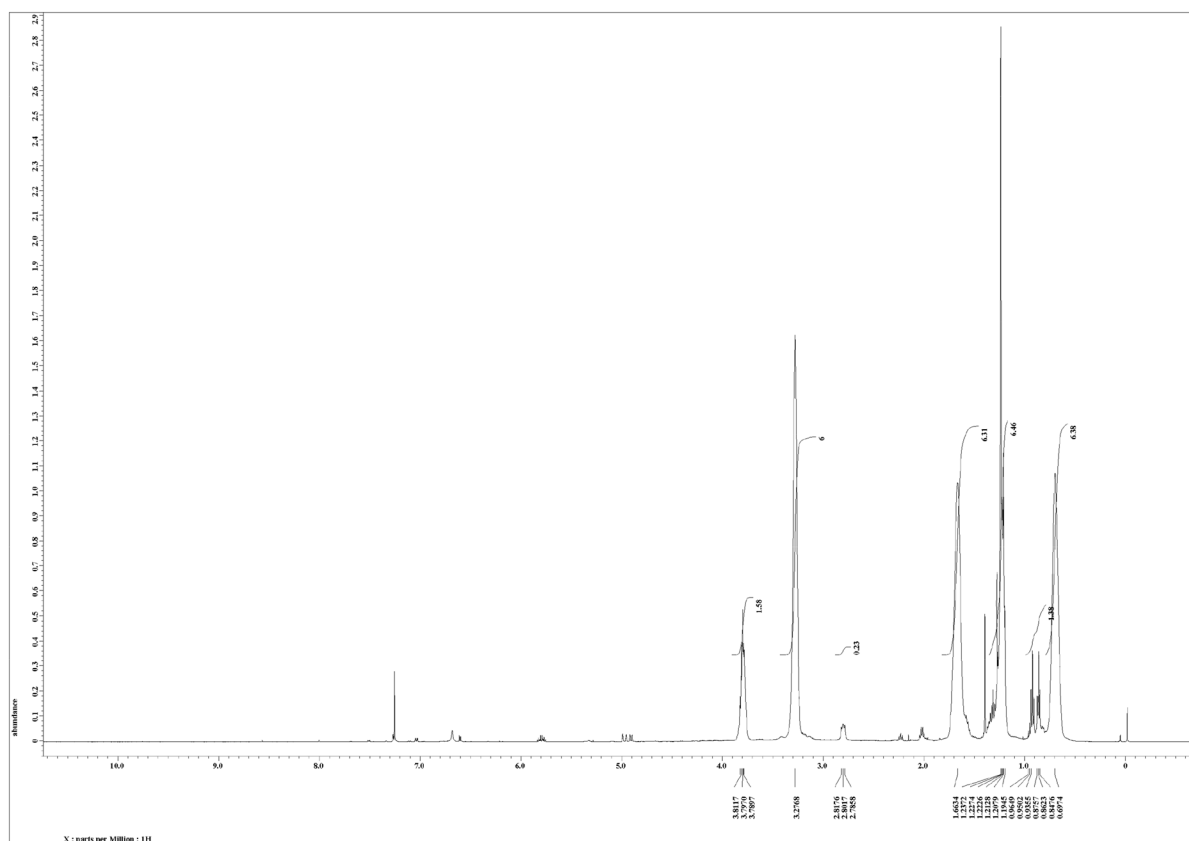
Fig. 6 ^{1}H NMR spectrum of (3-Azidopropyl)triethoxysilane

characteristic peak for –C≡C group (as shown in Fig. 2).

Click chemistry product

After the successful functionalization of cellulose and kaolinite with azides and alkyne respectively, click chemistry was performed by using CuBr as a catalyst in DMSO at 150 °C. The obtained product was washed with organic solvents and water and characterised by FTIR. FTIR spectra (Fig. 3) exhibited the disappearance of alkyne and azide peaks confirming successful reaction. The method is an efficient route for conjugating cellulose to clay.

Discussion

The objective of the presented work was to enhance interfacial interaction between cellulose and clay. In polymer composites, cellulose is added as

reinforcement while clay is used for better dispersion of cellulose. However, poor interfacial interaction between the clay and cellulose leaves us wanting for more (Ludvik, Glenn et al. 2007, Thunwall, Boldizar et al. 2008). Cellulose and clay are separately used as fillers in many polymers and both suffer from their limited interfacial interactions with the polymer matrix. Individually, cellulose and clay have been surface functionalized to enhance their interactions with polymer matrix. Clay, for example, was surface functionalized with silane to enhance its interaction with rubber (Dai and Huang 1999). Silane chemistry on cellulose is also attempted (Abdelmouleh et al. 2002, 2005; Ly et al. 2008; Xie et al. 2010). Considering the prior art in silane based chemistries on cellulose and clay, same was employed to functionalize cellulose and clay.

While functionalization results in surface groups that enhance physical interactions between the components; for enhanced mechanical properties,
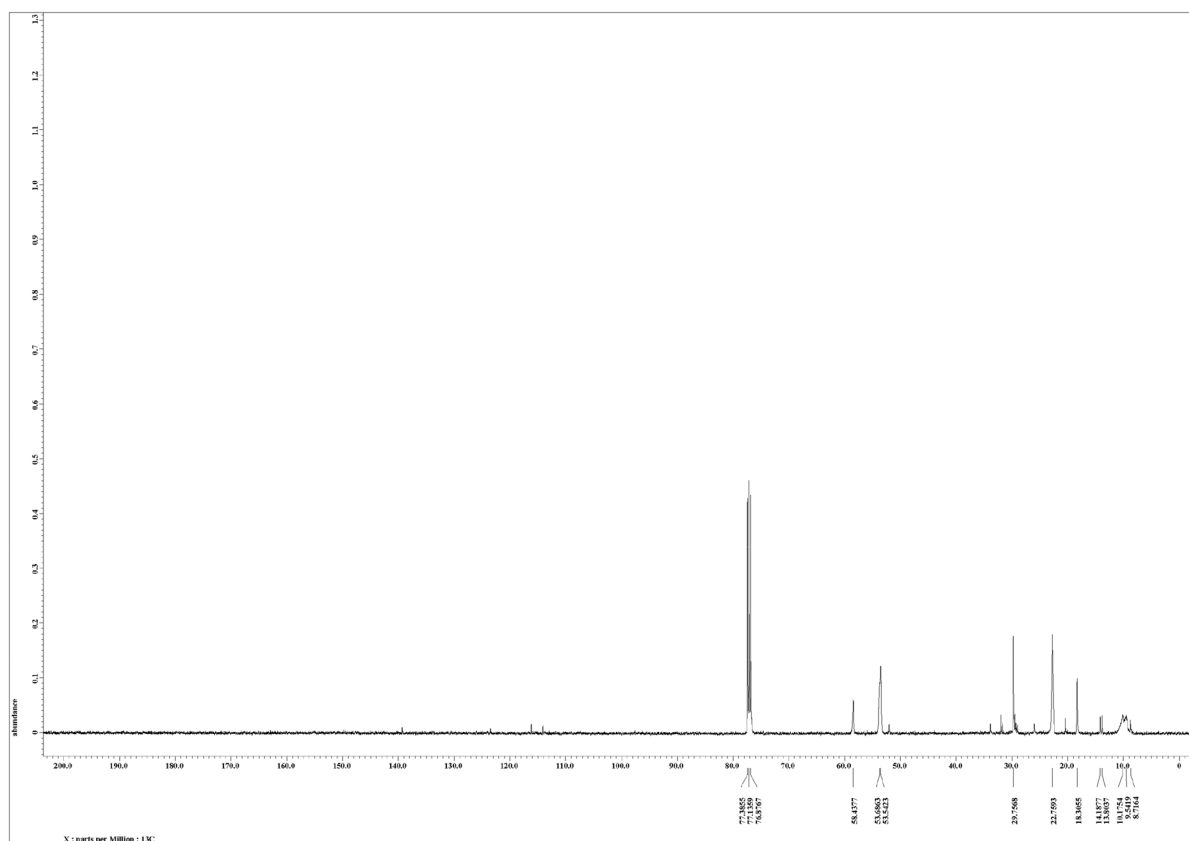
Fig. 7 ^{13}C NMR spectra of (3-Azidopropyl)triethoxysilane

chemical reactions that result in covalent bond are welcomed more. Hence, instead of targeting end groups on silane that would have enhanced only physical interaction between cellulose and clay, azide and alkyne that can form covalent bonds were selected. Moreover, azide–alkyne cycloaddition reaction does not produce any by-product, making the choice of this chemistry further easier.

To realize azide–alkyne cycloaddition reaction, silane derivatives were synthesized as has been mentioned in "Synthesis of *N*-(3-(triethoxysilyl)propyl)propiolamide (AMIPTES)" and "Synthesis of (3-azidopropyl) triethoxysilane (AZIPTES)" sections. The products were characterized using FTIR and NMR (Figs. 4–7). While azide derivative of silane was used to functionalize cellulose, clay was functionalized with alkynyl derivative ("Silanization of microcrystalline cellulose (MCC) with AZIPTES" and "Silanization of kaolinite clay by AMIPTES" sections). FTIR confirmed the successful incorporation of the groups onto the surface of clay and cellulose. Increasing the amount of silane derivatives during functionalization resulted in sharper peaks of the corresponding functional group. For example, the azide peak at ~ 2100 cm^{-1} (Fig. 1) increasingly became stronger when the azide was increased from 1 to 10 % during functionalization of cellulose. Similar results, albeit not as strong, were also observed in alkynyl functionalization of clay (Fig. 2). A weak band could be due to low efficiency of reaction.

Following successful incorporation of azide and alkynyl derivatives of silane on cellulose and clay respectively, click reaction was performed using CuBr as acatalyst in DMSO ("Click chemistry between kaolinite clay and MCC" section). The specific stretching band at ~ 2055 cm^{-1} for azide and at ~ 2117 cm^{-1} alkyne group disappeared from the products confirming successful azide–alkyne cycloaddition reaction. The covalent interaction between cellulose and clay was hence realized. Further studies on the effect of this bond formation on mechanical properties can be performed.

The silane functionalization followed by click reaction to covalently bind two components, cellulose and clay in this case, is presented. It will be interesting to study the mechanical properties of the product. This chemistry can be incorporated in other systems as well where covalent bond between two components is desired.

Conclusion

The present study is focused to incorporate covalent linkage in functionalized MCC and kaolinite using click chemistry. For this, the AMIPTES and AZIPTES were synthesised and used to functionalize kaolinite clay and MCC, respectively. These functionalized kaolinite and MCC were characterized by their specific stretching bands at 2055 and 2117 cm^{-1} respectively. Finally these bands disappear in the FTIR of the conjugate obtained after the click reaction between functionalized MCC and kaolinite.

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