Crosslinking of fibers via azide–alkyne click chemistry: Synthesis and characterization

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ABSTRACT: There has been growing interest in fiber modification for several industrial applications. The modifications have mostly been done to improve the fiber properties. However, the information regarding fiber modification via click chemistry is still limited. In this work, two strategies of click chemistry are evaluated for modifying commercial paper without the addition of copper catalyst. The first strategy is the direct reaction between azidated fiber and propargylated fiber, and the second strategy is to bridge azidated fiber with a self-made alkyne terminal crosslinker. Native and chemically modified fibers were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, and ^{1}H-NMR spectroscopy. The effects of the two clicking strategies on the fiber were further investigated by making handsheets. In terms of mechanical properties, the bridge-clicking strategy was found to produce better handsheets than the direct-clicking strategy. These modified fibers would be an interesting application for the packaging and printing industries. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43576.

INTRODUCTION

In recent years, new fibrous material such as carbon nanotube fibers[1,2] and other kinds of functional electrospun nanofibers[3,4] have been developed and have attracted a lot of attention because of their ultimate mechanical and electronic properties. However, the high costs and growing global concerns for environmental issues have caused researchers from various backgrounds to develop new products based on sustainable and ecofriendly materials.[5] Recently, cellulose has been identified as one of the most promising materials because it is very abundant and has unique properties that have led to widespread industrial use today.[6–8] By virtue of its structure and functional groups, cellulose has become an ideal starting material for defined modifications and specific applications.[9–12]

Recently, cellulosic materials have been modified under many conditions depending on the final application, such as packaging, coating, cosmetic formulation, absorbents in wastewater treatment, and other industrial fields.[13–18] The strong hydrophilic nature of the fiber surface is the main reason why cellulose fiber is chemically modified.[19–21] Cellulose fibers tend to agglomerate into bundles due to hydrogen bonds forming between the hydrophilic fibers, and they cannot be dispersed uniformly in most nonpolar polymer media.[22,23] The most common approaches for cellulose modifications are esterification and etherification.[24] Zhou and coworkers[25] reported that by modifying the cellulose using an esterification process, a fully transparent film with high hydrophobic properties was obtained.

The introduction of the "click" concept by Sharpless and coworkers[26] has certainly had a large impact, especially in the biomaterial area.[27] The term "click" describes a reaction that should be wide in scope, modular, stereospecific, high yielding, and simple to perform, creating only inoffensive byproducts (which can be removed without chromatography) and requiring benign or easily removed solvents, preferably water.[7] It was highlighted that the chemistry can be used to efficiently link or click together two components, instead of focusing on the tedious construction of different bonds.[27]

Based on the specifications established for click reactions, the three most popular options are thiolyne, thiolene, and azide–alkyne chemistry. The chemistry of thiols is normally influenced by the basic structure of the thiol, whether radical or catalyst mediated.[28] However, the classic radical-based photopolymerization has several critical problems, including complex polymerization kinetics.[23,29] Normally for both thiolyne and thiolene chemistry, the -ene or -yne structure dictates whether the
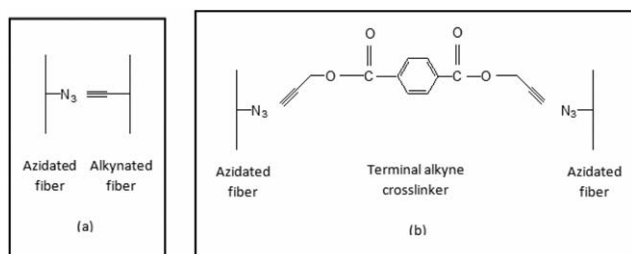
Figure 1. Illustration of (a) direct-click fiber (b) bridge-click fiber.

reaction is chain-transfer limited or not.[28] The use of thiolene chemistry has also been reported as a convenient way to synthesize functional polymeric materials.[30–33]

In this study, azide–alkyne click chemistry has been utilized since it is a very selective reaction, where the reaction takes place only between the azide and alkyne components.[34] Normally the crosslinking process has been performed by using a Cu(I) catalyst, a type of Huisgen's 1,3-dipolar azide–alkyne cycloaddition.[35] However, since the Cu(I) catalyst was found to be harmful and poses a potential toxicity risk, the use of copper has been dropped.[34,36] Recently, Yhaya and coworkers[37] successfully performed Huisgen's 1,3-dipolar azide–alkyne cycloaddition without a catalyst between β- cyclodextrin azide and propargyl alcohol as a model reaction in a drug-delivery system. The result showed the formation of two stereoisomers via NMR, and the reaction is complete in 24 h at 100 °C. As compared to Huisgen's 1,3-dipolar azide–alkyne cycloaddition with Cu(I), there is quite a complicated problem, in which there is significant product loss and traces remaining of Cu(I) ions, even after several procedures were attempted to remove all of the copper.

To the best of our knowledge, no crosslinking of cellulose fibers using alkynated crosslinker has been reported in the literature. In this study, the experiment has been divided into two different methods. For the first method, azidated and alkynated fibers were crosslinked to form a direct-click fiber [Figure 1(a)]. For the second, azidated fibers were crosslinked with bifunctional bispropargyl terephthalate alkyne crosslinker as a bridge to form a bridge-click fiber [Figure 1(b)]. The properties of both crosslinked fibers were analyzed and compared with the untreated fibers.

EXPERIMENTAL
Materials
The fibers used in this research were commercial fibers (with 10% moisture content) purchased from Hasrat Bestari Sdn Bhd., Penang, Malaysia, and were treated before use. Para-toluene sulfonyl chloride (tosyl chloride) was purchased from Sigma-Aldrich, St Louis, Missouri, and other chemicals such as triethylamine, sodium azide, N,N-dimethylformamide were purchased from R&M Co. (Essex, United Kingdom). The bispropargyl crosslinker was synthesized using terephthaloyl chloride, propargyl alcohol, dichloromethane, sodium hydrogen carbonate, and magnesium sulfate purchased from R&M Co. All of the chemicals were used as received unless stated otherwise.

The FTIR (Fourier transform infrared) spectroscopy was performed using a Perkin Elmer 1000 FTIR spectrometer (Waltham, Massachusetts) that was equipped with spectrum software. The investigated samples were mixed with dried KBr during the sample preparation stage before being scanned over the range 4000–50 cm^{-1} to obtain the spectra.

The ^{1}H-NMR (proton nuclear magnetic resonance) spectra were analyzed using a Bruker Ascend 500 spectrometer (Billerica, Massachusetts) with CDCl$_3$ as solvent. The ^{13}C-NMR was performed using solid-state NMR because cellulosic fiber does not dissolve in common NMR solvents. The spectra were recorded using NMR Topspin 3.0 with a total of 32 spins. All chemical shifts are stated in ppm with reference to the chemical shifts of the residual nondeuterated solvent.

Scanning electron microscopy (SEM) images were obtained with a Carl-Zeiss Leo 1450 VP (Oberkochen, Germany) using secondary electron imaging. Before the samples were tested, the samples were coated with gold.

Methods
Fibers from commercial paper were used as raw material to differentiate the two strategies of click chemistry, direct clicking and bridge clicking. First, commercial papers were disintegrated by continuous stirring overnight to remove other additives, such as starch and filler. Then the fibers were filtered off and washed with water and acetone. The resulting fibers were used for the preparation of clicked fibers.

Preparation of Tosylated Fibers. The synthesis was carried out according to Elchinger et al.,[35] with a few modifications. A 4 g portion of fiber was mixed with 160 mL distilled water, 9.44 g tosyl chloride, and 11.84 mL of triethylamine under stirring for 24 h at room temperature. The mixtures were then filtered off and washed with hot distilled water (200 mL) followed with hot ethanol (200 mL). Then the filtered product was dried at 40 °C.

Azidation of Fibers. The azidation of tosylated fibers was carried out by mixing the 2 g of tosylated fibers with 3.85 g of sodium azide in 60 mL of N,N-dimethylformamide (DMF) for 48 h at 75 °C. Then the reaction was cooled down to room temperature, followed by a filtration process. During the filtration process, the product was washed using hot distilled water and hot ethanol. The product was dried at 40 °C.

Propargylation of Fibers. First, 1.0 g of fibers, 2.5 g sodium hydroxide, and 26.9 mL of distilled water were mixed and stirred. After 30 minutes, 12 mL of propargyl bromide was added slowly into the mixture solution and kept stirring for overnight. The solution was then filtered off and washed with distilled water and acetone. The propargylated fiber was dried at 50 °C overnight. Caution must be taken because propargyl bromide is toxic.

Preparation of Bispropargyl Terephthalate. First, 5.13 g (0.031 mol) of terephthaloyl chloride was added slowly to a stirred solution of 5 g (0.086 mol) of propargyl alcohol, 15 mL of triethylamine, and 400 mL of dichloromethane (DCM). The reaction mixture was kept stirred at room temperature overnight while the color slowly turned dark. The next day, the resulting
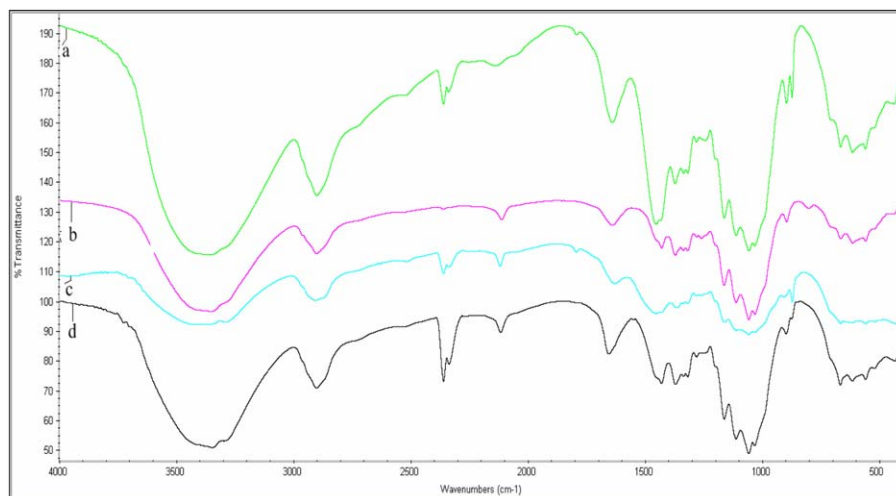
Figure 2. FTIR spectra of (a) untreated fiber, (b) azidated fiber, (c) propargylated fiber, and (d) direct-click fiber. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mixture was quenched with a saturated sodium hydrogen carbonate solution. The organic layers were extracted with 10% hydrochloric acid (3×30 mL), saturated sodium hydrogen carbonate solution (1×30 mL), and distilled water (1×30 mL). After extraction, the solution was dried over magnesium sulfate, and the remaining DCM was removed with reduced pressure. The product was dried at 50 °C overnight.

Preparation of Direct-Clicked Fibers. The clicking of fibers was carried out by dissolving 0.5 g of azidated fibers and 0.5 g of propargylated fibers in 75 mL of DMF. The mixture was then left to react under continuous stirring for 24 h at 100 °C. The resulting mixture was washed with hot distilled water and hot ethanol. The clicked fibers were dried at 50 °C overnight.

Preparation of Bridge-Clicked Fibers. First, 0.133 g (1 mol) of azidated fiber and 0.2 g (2 mol) of bispropargyl terephthalate were mixed in 75 mL of DMF. Under continuous stirring, the mixture was left to react for 24 h at a temperature of 100 °C. The resulting mixture was filtered off and washed with hot distilled water and hot ethanol, followed by drying at 50 °C overnight.

RESULTS AND DISCUSSION

Characterization of Raw and Chemically Modified Fibers

Infrared Spectroscopy. The crosslinked cellulose was characterized by FTIR spectroscopy, as shown in Figure 2. FTIR spectroscopy was used to study the chemical changes of the fibers before and after the click reaction. The differences between the FTIR spectra of the untreated and treated commercial paper fibers were investigated. In Figure 2(a), the absorbance bands at 3356 cm^{-1}, 2901 cm^{-1}, 2360 cm^{-1}, 2339 cm^{-1}, and 1641 cm^{-1} were associated with native fibers. Figure 2(b) shows a band around 2113 cm^{-1}, corresponding to the azide groups. When tosylated fibers reacted with sodium azide, the FTIR spectrum of azidated fiber showed the appearance of a new intense band typical of the azide groups, which clearly confirms that azide molecules covalently couple to the fiber chains.[23] The FTIR spectrum of propargylated fiber in Figure 2(c) shows two new adsorption bands at 3286 cm^{-1} and 2119 cm^{-1}, corresponding to $\equiv$C—H stretching and C$\equiv$C stretching, respectively, indicating the successful incorporation of terminal alkynes onto the fiber chains.[29] In the spectrum of direct-click fibers in Figure
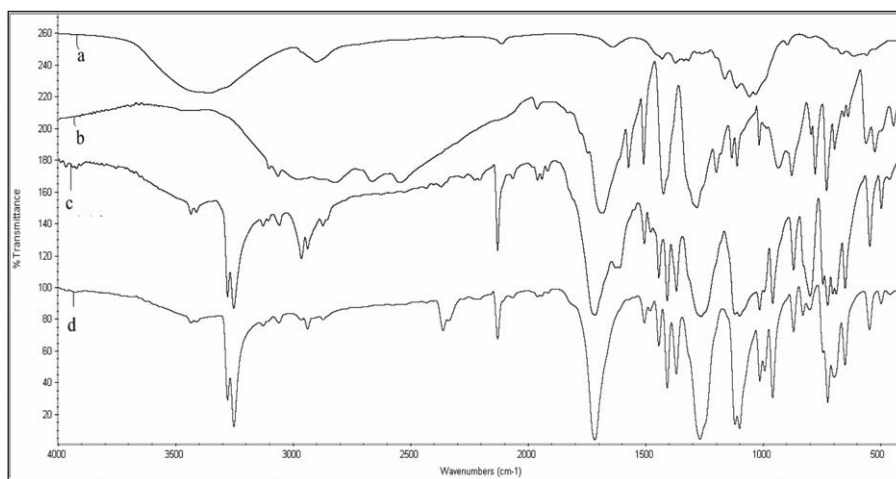
Figure 3. FTIR spectra of (a) azidated fiber, (b) terephthaloyl chloride, (c) bispropargyl terephthalate, and (d) bridge-click fibers.
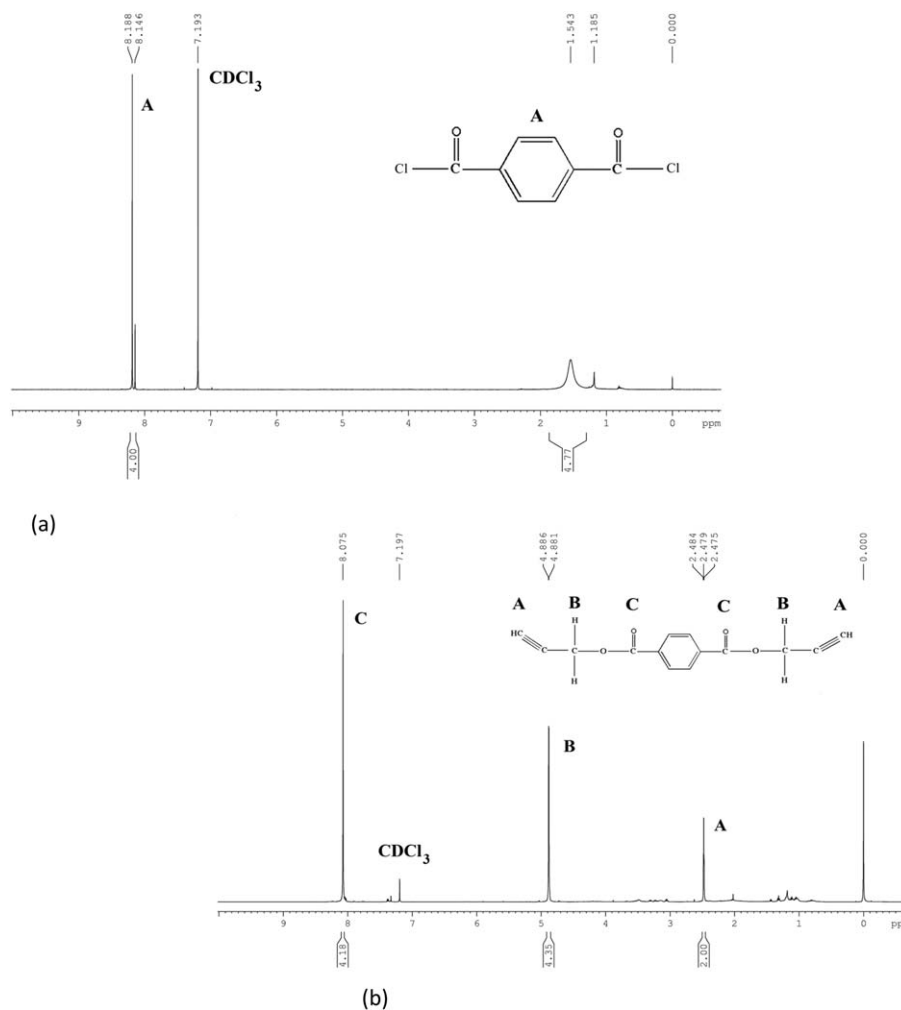
Figure 4. ^{1}H-NMR spectra of (a) terephthaloyl chloride and (b) bispropargyl terephthalate.

2(d), the band evidences a decrease of N_3 (azide group) after crosslinking of azidated and propargylated fibers. This indicates that a low degree of "clicking" occurred during the reaction, verifying that the reaction between azidated and alkyne groups fibers was incomplete. The stretching vibration of N=N is forbidden in IR.[38]

For the bridge-click chemistry, the alkyne terminal crosslinker bispropargyl terephthalate was synthesized and is displayed in Figure 3(b). The FTIR spectrum of terephthaloyl chloride in Figure 3(a) was used as a control for bispropargyl terephthalate. As presented, the C≡C stretching, C=C stretching, and C=O stretching bands appear at 2129 cm^{-1}, 1505 cm^{-1}, and 1714 cm^{-1}, respectively. The successful bispropargyl terephthalate synthesis is proven by ^{1}H-NMR in Figure 4(b). Figure 3(c) clearly displays a decrease of N_3 after the click reaction. Bridge-click fibers have the same results as the direct-click fibers, where the clicking was incomplete due to the dissimilarities in the physical state of the raw materials involved (i.e., solid and liquid).[24]

NMR Spectroscopy. The ^{1}H-NMR spectrum of bispropargyl terephthalate is shown on Figure 4(b). Terephthaloyl chloride in Figure 4(a) was used as a control for the synthesis of bispro-

pargyl terephthalate. Based on the ^{1}H-NMR spectra in Figure 4(a), the aromatic group in terepthaloyl chloride is assigned at 8.2 ppm. The peak observed at 1.5 ppm is due to the presence of moisture. However, in Figure 4(b), the chemical shift at 8.1 ppm is attributed to the aromatic carbons, while the chemical shift at 4.9 ppm is assigned to H—C—H. It also clearly shows the appearance of a peak at 2.5 ppm, associated with the alkyne pendant groups (HC≡CH).[39]

The occurrence of the click reaction, azidated fiber, and propargylated fiber were further investigated by ^{13}C-NMR spectroscopy, as shown in Figure 5. Each of the ^{13}C-NMR spectra present different shapes, which could be taken as an indication that the chemical modification took place. Unfortunately, every spectrum of ^{13}C-NMR displayed overlapping peaks, causing difficulties in peak assignments.

Scanning Electron Microscopy. The SEM images in Figure 6 illustrate the changes in surface morphologies during fiber modification and the clicking process. The unmodified fiber [Figure 6(a)] has a smooth surface and exhibits visible cylindrical shapes.[29] However, after the azidation [Figure 6(b)], the fibers
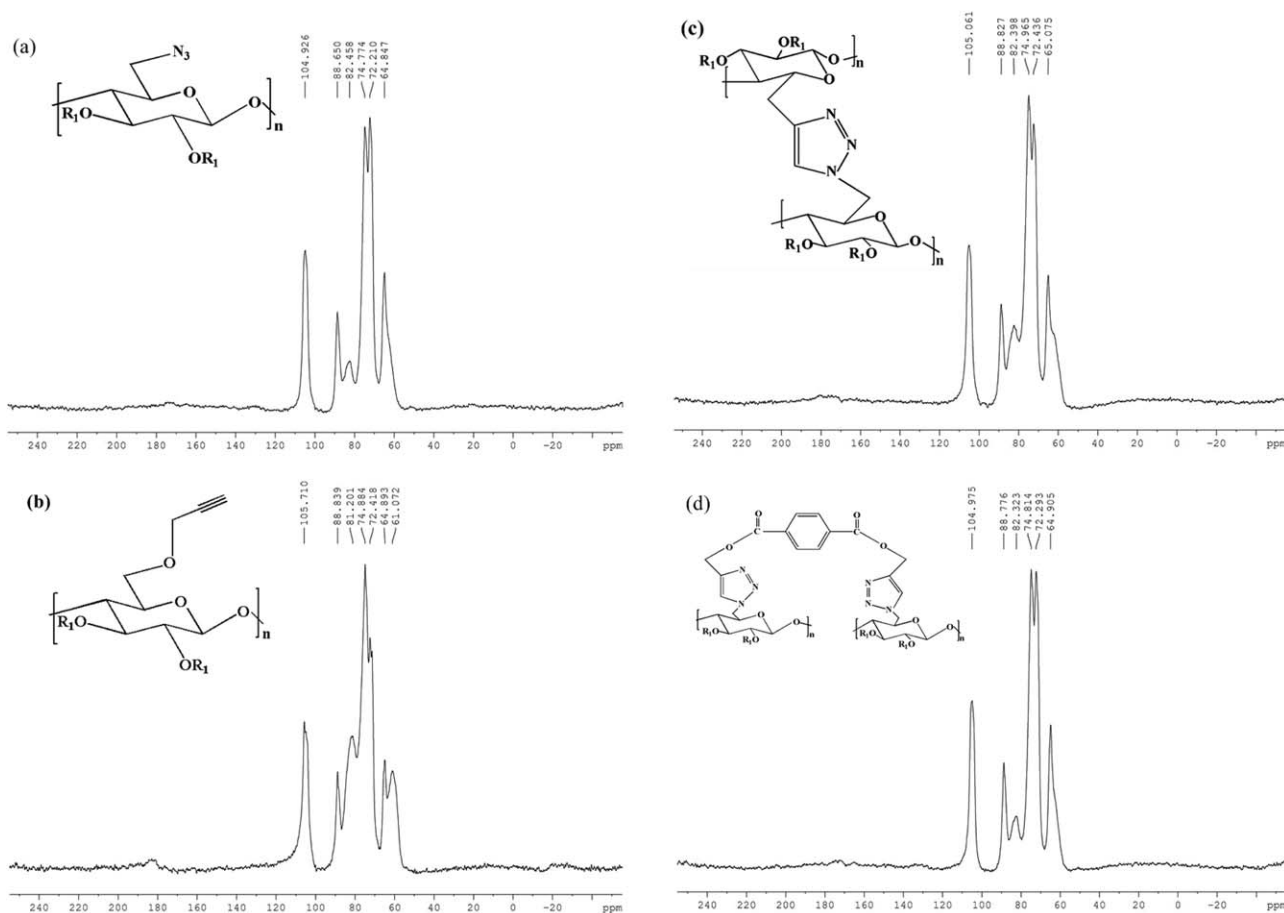
Figure 5. ^{13}C-NMR spectra of (a) azidated fiber, (b) propargylated fiber, (c) direct-click fiber, and (d) bridge-click fibers.
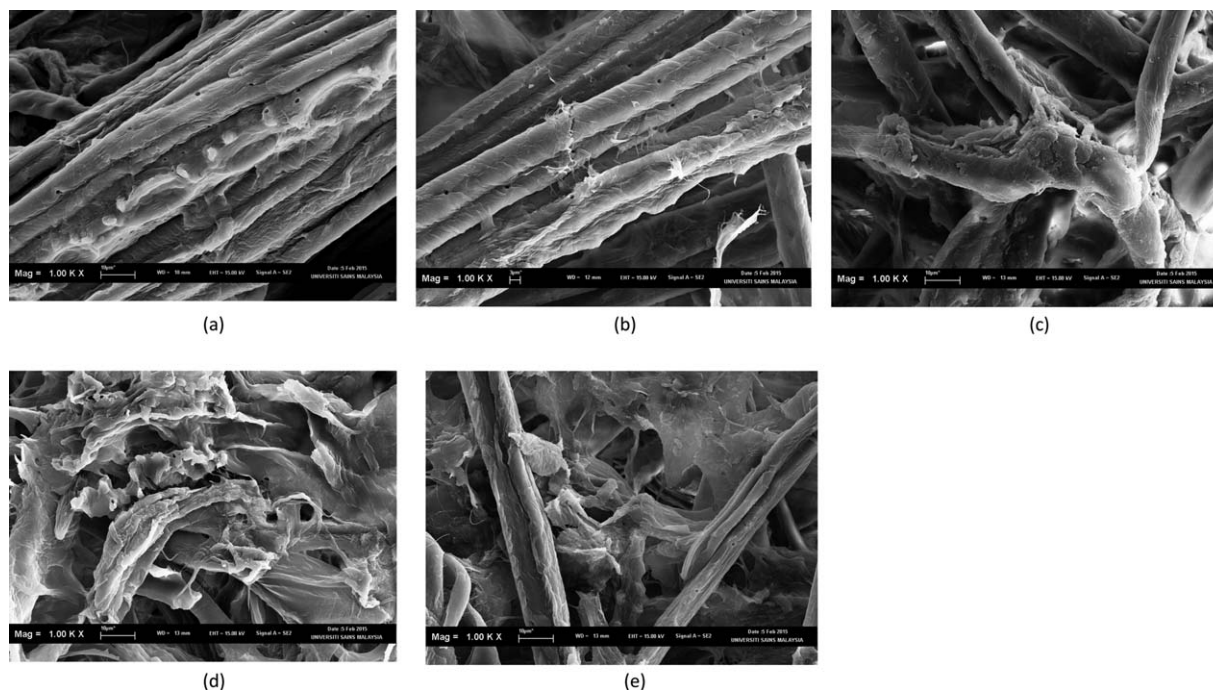
Figure 6. SEM micrographs of (a) unmodified fiber, (b) azidated fiber, (c) propargylated fiber, (d) direct-click handsheet fiber, and (e) bridge-click handsheet fiber.

Table I. Mechanical Properties of Untreated, Direct-Click, and Bridge-Click Handsheets

	Untreated fiber handsheet	Direct-click handsheet	Bridge-click handsheet
Tensile index (N m/g)	16.7331	19.1981	56.1930
Tearing index (N m/g)	7.1837	8.1419	33.3546
Bursting index (kPa m²/g)	0.00132	0.00197	0.00152
Wet tensile index (N m/g)	0.8749	13.0189	37.1379

were swollen, and their surface aspect has a less smooth and stringier surface.

After the propargylation of the fiber [Figure 6(c)], the surface became rough. This was probably due to the cracking and effects from the solvent during the modification process and the partial collapse of fiber after solvent removal, which is in accordance with the dissolution behavior and mechanism of fiber modification described by Henninges et al.[40]

The successful crosslinking between the fiber (for the direct-click handsheet) is confirmed in Figure 6(d), where it is worth noting that a self-curling behavior occurred during the clicking process. The surface structure of the click fiber is also slightly different from the azidated fiber [Figure 6(b)] and alkynated fiber [Figure 6(c)], clearly showing that the fibers are bonded to each other.

For the bridge-click fiber [Figure 6(e)], the clicking process was a success, based on the changes that occurred in the surface morphologies of the azide fiber [Figure 6(b)] and the bridge-click fiber [Figure 6(e)]. The presence of bispropargyl terephthalate crosslinker (between the fibers) helped to click the fibers together.

Interestingly, in the SEM images, the difference between the direct-click handsheet and the bridge-click handsheet is clearly shown. For the direct-click handsheet, it shows that the fibers were self-bonded to each other by self-curling, whereas for the bridge-click handsheet, no curling is observed because the fibers were held together by the bispropargyl terephthalate crosslinker.

Mechanical Properties

Some mechanical properties have been measured in order to observe the effects of crosslinking for both direct-click and bridge-click fibers.

The results for the direct-click handsheet are presented in Table I. From the tensile index result, the direct-click fibers show a significant improvement over the untreated fiber. The strong interconnected network between azide and alkyne fibers may well lead to an increase in the mechanical stability of the modified fiber.[35,41] Moreover, the increase of the tensile index was also due to the fibers being chemically bonded, and more force was needed to break the bonds.[42] This can be seen in the SEM image [Figure 6(d)], where the strong curvature of the treated fibers may also be involved in increasing the tensile index properties.[35,41]

Based on the analysis in Table I, the tensile properties of the bridge-click handsheet are significantly affected by the crosslink method and seem to show a better improvement compared to the direct-click handsheet. The presence of bispropargyl terephthalate as crosslinker helps to enhance the fiber-to-fiber bonding and make the fibers more flexible.[43] Thus, when forces are applied, the force can be distributed evenly, and more load is needed to break the bonds. Furthermore, the biocompatibility between the crosslinker and the fiber also plays an important role in determining the mechanical properties. This could be explained by analyzing the SEM image of the tensile test specimen [Figure 6(e)]. There it can be seen that the crosslinker was strongly attached and holds the fibers together.

The tearing index properties were also observed for both click handsheets. Normally, the tearing strength is related to the fiber strength, which depends on the fiber length and fiber flexibility. Based on the results in Table I, the tearing index for the direct-click handsheet showed a higher performance as compared to the control handsheet. The fiber-to-fiber links formed during the modification process help to improve the tearing properties of the direct-click handsheet. When a force was applied to tear the handsheet, more energy was needed to tear the handsheet. Overall, the bridge handsheet shows a better tearing performance since it is more flexible than the others.

Referring to the results for bursting strength in Table I, the direct-click fiber showed an increase compared to the control handsheet. This was due to an increase in the bonding between the fibers.[42] The modification processes (azidation and alkylation fiber) also help increase the internal bonding between the fibers. The same result was also observed for the bridge-click fiber. The presence of bispropargyl terephthalate as crosslinker helped improve the fiber bonding. However, in comparing the direct-click and bridge-click with the untreated fiber handsheet, the direct-click handsheet showed the highest bursting strength index. This may attributed to several factors where the direct-click handsheet has better properties, such as lower embrittlement and fiber stiffening, as compared to the bridge-click handsheet.

Wet tensile testing was done to measure how well the fiber-to-fiber bonding can resist a force of rupture when the paper was in a wet condition. Based on the results in Table I, the wet tensile index for the untreated handsheet was dropped very low compared to the dry handsheet. According to Su et al.[44] and Rowland Standley,[45] the tensile strength of paper is directly affected by the swelling behavior of the fibers interacting with

water. The fiber-to-fiber interaction that develops during the paper formation and drying process is one of the factors that controls the paper strength.[44] Hydrogen bonding acts as the dominant adhesive force in dry paper, and since the bonds are sensitive to water, the penetration of water into the dry paper may lead to a rapid weakening of the fiber-to-fiber bonding.[44,46] However, for the direct-click and bridge-click handsheets, the percent reduction in wet tensile strength is lower if compared to the dry handsheet. This is probably related to the high cross-linking effect from the chemical bonds forming between the azi-dated and alkylated functional groups. Therefore, when water was added, the bonding between those fibers was not so easily disrupted.

CONCLUSIONS

A new strategy for crosslinking fibers via azide–alkyne chemistry was performed to generate a new material. Based on the analysis done using FTIR, NMR, and SEM, a new fiber-to-fiber clicking was successfully performed via direct clicking and via bridge crosslinker clicking. The differences between the products were highlighted in both their chemical and mechanical properties. Comparing the clicking methods, bridge clicking led to a significant increase in mechanical properties. These results can open a new route to preparing new material via the click-chemistry method. In addition, it also proved that the alkylation and azi-dation processes can be conducted using natural fibers and at the same time can be used for grafting molecules of interest.

ACKNOWLEDGMENTS

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