

Review on the Use of Mono- and Di-Isocyanates to Modify the Surface of Cellulose and Nano-Cellulose

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Abstract

To increase its potential in particular fields of interest, cellulose and Nanocellulose have undergone a wide range of chemical modifications. These changes either altered the composition of the nanocellulose itself or added various functional groups—ranging from simple molecules to polymers—to its surface. Among many other chemicals, aliphatic and aromatic mono- and di-isocyanates are a class of compounds that have been applied to surface modification of cellulose for a century. Although they have just recently been employed with nanocellulose, they have demonstrated significant promise as chemical linkers and surface modifiers to graft certain functional chemicals and polymers onto the nanocellulose surface. This article examines the modification of cellulose and nanocellulose utilising isocyanates, such as hexamethylene diisocyanate (HMDI), toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI) and phenyl isocyanate (PI), as well as their derivatives and polymers. Additionally, it outlines the most popular methods for modifying nanocellulose, along with their benefits and drawbacks. The difficulties of employing isocyanates generally for nanocellulose modification are finally covered.

Keywords

cellulose,
nanocellulose,
isocyanate,
nanocrystal,
modification

Introduction

The most abundant biopolymer on Earth is cellulose. Nearly 10^{12} tonnes of cellulose are produced annually by plants. Plants have around 33% of the cellulose found in wood and cotton, compared to wood's 50% and cotton's 90%. It makes up 40–60% of the mass of the wood and, after pulping, can be obtained as fibres 20–40 mm thick^{1,2}. Natural or synthetic fibres made from

wood pulp are referred to as cellulose fibres. It can also be made utilising plant-based resources such the esters of plant materials including bark, leaves, and wood. The remaining natural fibres come from sources including cotton, jute, flax, hemp, and ramie, while the main artificial fibres are lyocell, viscose, and modal. Due to their high strength, high moisture absorption, and extreme

light weight, these fibres are mostly utilised to make chemical filters, biocomposites, house textiles, and textiles for everyday use. The market for cellulose fibre is estimated to be worth US\$33.003 billion in 2019 and is expected to grow at a CAGR of 5.53 percent to reach US\$48.088 billion by 2026. The demand for cellulose fibres is increasing globally due to growing concerns about environmental degradation and climate change, which is expected to drive the growth of the cellulose fibre market during the forecast period. Companies are looking for alternatives to fibres sourced from petrochemicals and are moving toward environmentally friendly and biodegradable fibres. Additionally, since cellulose fibres are widely utilised in the textile and garment industries, the expansion of these sectors globally is boosting demand for cellulose fibre and is anticipated to accelerate the growth of the cellulose fibre market in the upcoming years. The market for cellulose fibre suffered from the recent new coronavirus disease outbreak. The pandemic caused a fall in the textile and garment sector, which had a detrimental effect on the market expansion for cellulose fibres. The rising global focus on developing an environmentally friendly and biodegradable fibre is one of the major reasons supporting the market expansion for cellulose fibre.

More and more companies are attempting to switch to a green choice for fibres from the conventionally used petrochemical based fibres that cause significant environmental carbon emissions as the topic of climate change, environmental pollution, and sustainability has taken a storm. As a result, the demand for cellulose fibres is increasing. This demand is expected to continue to expand over the course of the forecast period, accelerating the expansion of the cellulose fibre market.

Cellulose fibres have an advantage over other materials because they can be recycled. Additionally, cellulose fibres are rapidly being considered to reinforce and replace plastics in numerous applications due to their eco-friendly qualities.

Cellulose nano-fiber is such a material that demonstrates similar properties to plastic, such as being lightweight, strong, transparent, and with high impermeability to water and gas, which is the reason it is being seen as a substitute to plastics not only in the food industry but also in numerous other industries like medicine, cosmetics, and electronics.

Research and development on cellulose fibres have increased due to the need for a biodegradable and environmentally friendly fabric, and new fibres are being developed as alternatives to currently-used fibres.

For instance, German Institutes for Textile and Fiber Research Denkendorf (DITF) created a substance called PURCELL while searching for a replacement for glass-fiber-reinforced plastics. Since the substance is made entirely of cellulose, it is 100% recyclable. The market for cellulose fibre is expected to expand in the upcoming years due to the increasing opportunity that the ongoing advancement of research is presenting to replace environmentally harmful fibres with environmentally favourable ones³.

In 2019, the percentage of cellulose fibres derived from wood that was consumed globally increased to 7%, a 17 percent rise from the previous year. Lyocell, Modal, and viscose are cellulose fibres made from wood⁴. Figure 1 shows the percentage of wood-based cellulose fibre consumed globally between 2016 and 2019.

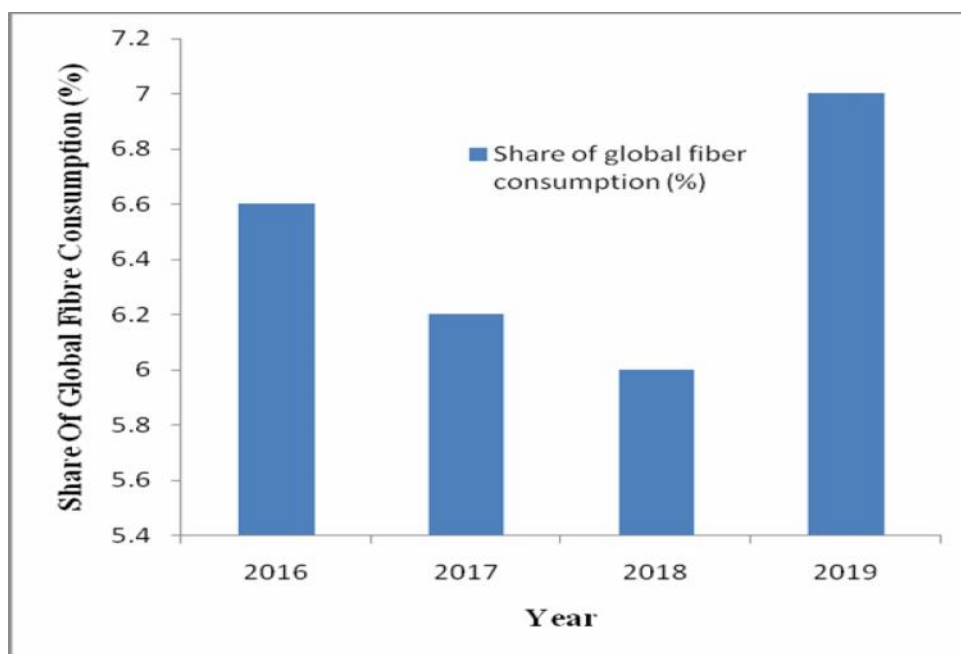


Figure 1. Year wise consumption share of wood based cellulose fiber

Besides its conventional application in the paper and packaging sectors and its expanding transformation into textile fibres, cellulose can be treated, synthesised into useful nanoparticles⁵. Cellulose nanocrystals (CNCs) are among them; they are crystalline nano-rods with a thickness of 3–10 nm and a length of a few hundred nm⁶. They are taken from pulp fibres using an established industrial process that involves the use of acids⁷. Using a variety of chemicals and procedures, they can also be isolated directly from wood and lignocelluloses⁸⁻¹⁰. Additionally, tunicate cellulose can be used to produce CNCs with micrometer-lengths¹¹. Another type of nanocellulose is cellulose nanofibrils (CNFs), which are semi-crystalline spaghetti-like nanoparticles with a thickness of 5 to 30 nm and a length of only a few micrometres⁶. They are created by mechanically fibrillating pulp fibres using a variety of methods, such as homogenization and microfluidization⁵. Along with having strong mechanical qualities, being biodegradable, and having a large surface area, CNCs and CNFs are well known for the ability to

change their surfaces because to the many hydroxyl groups. Additionally, they can position themselves in functional liquid crystalline formations that are formed in 1D, 2D, and 3D nanostructures¹². The automotive sector¹³, medication delivery¹⁴, tissue engineering¹⁵, packaging¹⁶, and water filtering¹⁷ are just a few of the applications where CNCs and CNFs have demonstrated considerable potential as a result of these intriguing features. As a result, from 208 in 2009 to 2372 in 2018, nanocellulose-related publications and patents grew each year. Figure 2 shows the amount of articles published on nanocellulose in the previous ten years demonstrates the growing demand for nanocellulosic materials (Web of Science, July 2019, cellulose nanocrystals/whiskers/fibers/fibrils; micro/nanofibrillated cellulose, nanocellulose; nanocrystalline cellulose)¹⁸. Over 20 nanocellulose production facilities, including CelluForce, Innventia, and Blue Goose Biorefinaries, have been established as a result in the past 20 years⁵.

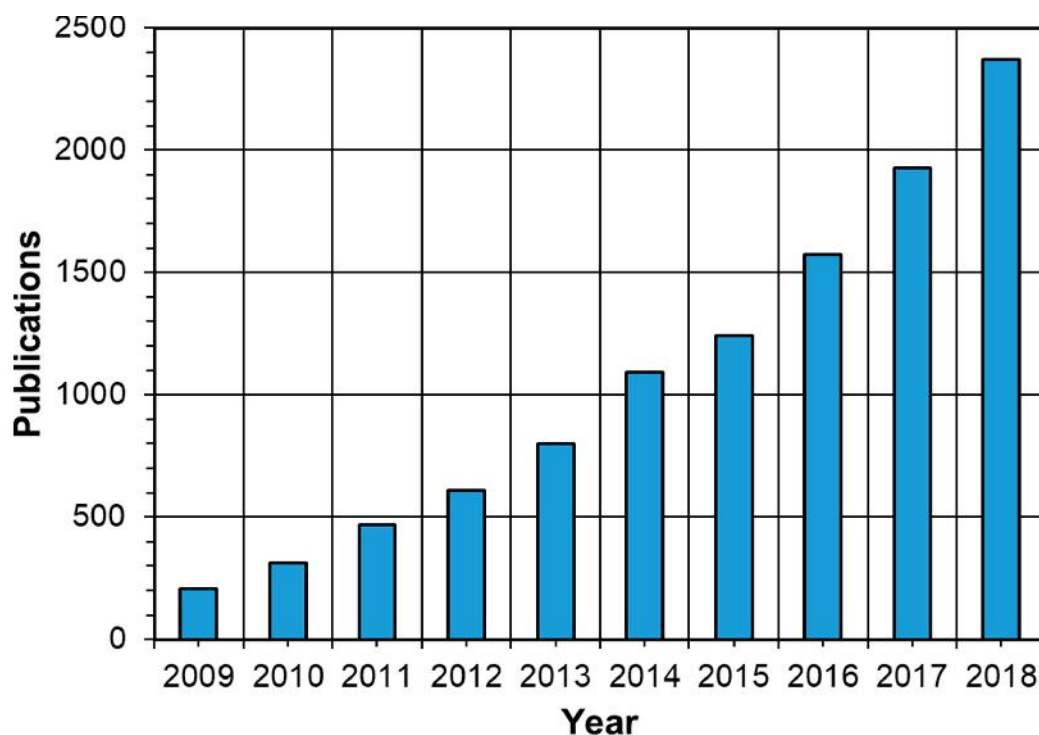


Figure 2. The amount of articles published on nanocellulose in the previous ten years¹⁸

Nanocellulose's potential has substantially increased due to the hydroxyl groups on its surface. Through conventional reactions like acetylation and oxidation, a wide variety of chemical functionalities have been added to nanocellulose surfaces^{19, 20}. Functional materials and polymers were occasionally grafted onto the surface as part of the reaction. These adjustments sought to alter the surface characteristics of nanocellulose in order to enhance its processing with nonpolar matrices²¹⁻²³ or alter its affinity for specific polar and nonpolar molecules^{24, 25}. In other cases, the modification intended to add functional groups to the surface of nanocellulose to focus on certain applications²⁶. In this situation, whether they were simple chemicals or polymers, a chemical linker was frequently required to connect these functional groups to nanocellulose. Despite being used with cellulose for a century, aliphatic and aromatic isocyanates have gained more interest recently among other modifiers and linkers for nanocellulose modification. They are a highly fascinating class of compounds that are best known for their interactions with polyols to produce polyurethanes²⁷.

For the modification of cellulose and nanocellulose, aliphatic and aromatic mono- and di-isocyanates, including phenyl isocyanate (PI), toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), and hexamethylene diisocyanate (HMDI), as well as their polymeric forms, have all been employed²⁸⁻³¹, are depicted in figure 3. PI and n-octadecyl isocyanate (OI) were mainly used to decrease the hydrophilicity of cellulose and nanocellulose as they do not have the necessary second isocyanate to function as a linker, while TDI, PPDI, MDI, and HMDI have been used both as surface modifiers and chemical linkers^{32, 33}. The fundamental difference between TDI, MDI, and HMDI is in their molecular stiffness, which is mostly determined by the benzene rings. Due to its two benzene rings, MDI is the hardest, but HMDI is the most flexible due to its aliphatic chain. For instance, polyurethane foams based on MDI are stiffer than those based on TDI³⁴. TDI is a very remarkable di-isocyanate since its 2,4-isomer's isocyanates respond differently.

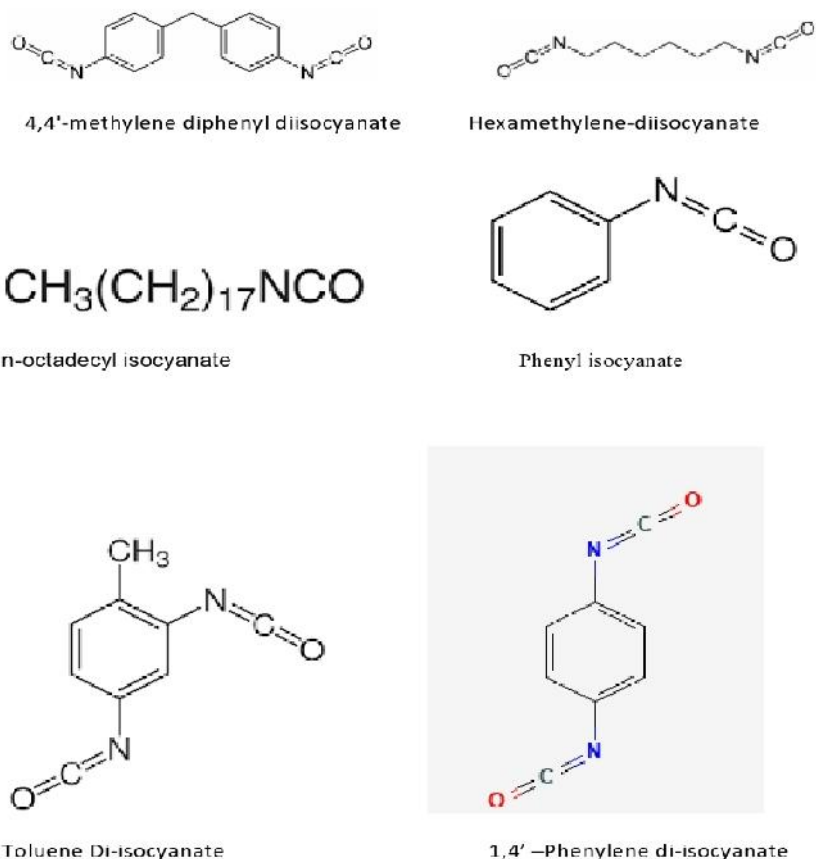


Figure 3. The most commonly used aromatic and aliphatic mono- and di-isocyanates for cellulose and nanocellulose modification

Due to steric hindrance from the nearby methyl group, the ortho isocyanate is 5–10 times less reactive than the para isocyanate^{35,36}. Due to the ability of one material to react with the para isocyanate first, followed by the interaction of the other material with the ortho isocyanate, 2,4-TDI is extremely useful for binding components to one another.

Amines like triethylamine were discovered to be efficient catalysts for the reaction between isocyanates and the hydroxyl groups of nanocellulose and the subsequent formation of polyurethane linkages³⁷. However, they could also promote the self-polymerization of isocyanates as a side reaction.

This review examines the application of molecular and polymeric aliphatic and aromatic

mono- and di-isocyanates to the surface modification of cellulose and nanocellulose. The literature reports for each material will be divided into groups according to the purpose of the surface modification. Some of these reports used application-oriented methodologies, concentrating on altering the properties of cellulose and nanocellulose to function in particular applications, while other reports used property-oriented methodologies, aiming to enhance the properties of cellulose and nanocellulose generally, such as hydrophobic nature and heat resistance, without focusing on a particular application. However, the majority of research concentrated on using isocyanates to accelerate up the process of cellulose and nanocellulose in nonpolar thermoplastic and thermoset matrices to produce reinforced composites with better interfacial adhesion.

Aliphatic and Aromatic Isocyanates in the Modification of Cellulose

The earliest study³⁸ on the reaction between isocyanates and cellulose appears to have been written by Charles in 1920. Subsequent reports³⁹⁻⁴¹ focused on the use of the reaction in the textile industry to create cellulose fibres with enhanced mechanical and thermal qualities. With an emphasis on Phenyl Isocyanate, Ellzey et al. and Ohno et al., respectively, in 1962 and 1970, further investigated the interaction between cellulose and isocyanates^{42, 43}. Later, Ohno investigated how cellulose interacted with diisocyanates (2,4-TDI and HMDI)^{44, 45}.

Isocyanates were used to treat cellulose, mostly to lessen its hydrophilicity or increase its biocompatibility. PI, cyclohexyl isocyanate, HMDI, and oxime-blocked isocyanate oligomers were used to react with cellulose to lessen its hydrophilicity^{28, 46, 47}. Botaro et al. used a more involved method to achieve the same result, in which cellulose fibres were treated with alkenyl isocyanate and then radical polymerized with additional monomers (styrene or methylacrylate) to form hydrophobic polymeric brushes around the fibres^{48,49}. By submerging cellulose fabric in an aqueous polyethylene glycol solution, impregnating it with an organic 2,4-TDI solution, and then thermally pressing it, Badanova et al. were able to hydrophobize the material⁵⁰.

The biocompatibility of cellulose with human blood was also enhanced by the application of isocyanates. One of its isocyanates, for instance, was used to react with cellulose sheets before the other isocyanate was used to react with molecules that contained betaine⁵¹. Similar to this, cellulose fabric was treated with 2-methacryloyloxyethyl isocyanate to enable phosphoryl choline to be grafted onto it afterwards. This increased the fabric's biocompatibility for use as a hemodialysis substrate for blood purification⁵². The reaction of cellulose acetate membranes with phenyl, propyl, and butyl isocyanates improved their mechanical, chemical, and thermal properties^{53, 54}.

Utilizing aliphatic and aromatic isocyanates to modify nanocellulose

In general, there are three main categories of nanocellulose: nanofibrillated cellulose (NFCs), nanocrystalline cellulose (NCCs), and bacterial nanocellulose (BNCs). This nanocellulose can be made using top-down or bottom-up techniques⁵⁵. NCCs and NFCs are typically isolated and extracted from crops, higher plants, and by-products of forestry and agriculture such as banana stems, rice straws, pineapples, oil palm, rubber, lalang, and sugar palm fibres using top-down approaches such as enzymatic, chemical, or physical techniques. Contrarily, bacterial nanocelluloses (BNCs) are created by a specific bacterial family (*Glueconoacetobacter xylinus*) and are grown as microfibrils in a culture medium using a bottom-up method⁵⁶.

Recently, researchers have become increasingly interested in using nanocellulose as a reinforcing agent. Basically, because nanocellulose is hydrophilic, it can disperse easily in polar polymers. The three hydroxyl groups that are joined to each glucopyranose ring are responsible for this characteristic. Additionally, some aggregates are produced as a result of their huge surface area and strong hydrogen bonding, which makes compounding with the majority of hydrophobic polymers ineffective⁵⁷. The surface of nonpolar polymers must be altered through physical, chemical, and biological methods in order to expand the applications of nanocellulose⁵⁸. There are numerous physical methods that can be used, including electric discharge (plasma treatment), ultrasonic treatment, irradiation, and surface fibrillation, according to a prior paper review by Islam et al.⁵⁹. However, among other surface modification techniques, chemical procedures such as esterification, carboxylation, cationization, silylation, and polymer grafting are the most often used⁶⁰. The procedure involves replacing the hydroxyl groups on nanocellulose's surface with other chemical groups. By increasing the amount of stable positive or negative charges on its

surface, this procedure seeks to enhance the compatibility and dispersion of nanocellulose⁶¹. It is necessary to carry out chemical alteration in a way that preserves nanocellulose's original morphology and the structural integrity of its crystal⁵⁹.

Isocyanates⁶² have been used to change cellulose for almost a century, but they were only utilised to modify nanocellulose for the first time in 2008. Isocyanates were employed to graft polymers onto the surface of starch nanocrystals two years prior^{63, 64}. Since then, isocyanates have been used more frequently to modify nanocellulose. Compared to cellulose, modification of nanocellulose only occurred in heterogeneous circumstances, which implies that it primarily occurred on the surface of the material. Except for the inert C3 hydroxyls, nanocellulose has up to 15% of its hydroxyls on the surface⁶⁵⁻⁶⁷. Nanocellulose is more interesting than cellulose for producing functional cellulosic materials because it allows a more significant grafting of molecular structures on its surface due to the high percentage of surface hydroxyls.

Nearly every report in this collection focused on nanocellulose hydrophobization. In contrast to cellulose nanocrystals (CNCs), which were hydrophobized by a reaction between 2,4-TDI⁶⁸ and castor oil as well as a reaction between 2,4-TDI and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and 2,4-TDI, Cellulose nanofibrils (CNFs) were hydrophobized by a reaction with OI⁶⁹. Better heat stability and hydrophobicity were seen in the modified CNCs⁷⁰. When CNFs are reacted with HMDI and certain alkyl diamines, CNFs having amine groups on the surface are produced⁷¹. A CNF aerogel was cross-linked with HMDI to enhance its mechanical qualities by submerging it in a HMDI in acetone solution⁷².

It has also been reported to employ nanocellulose to reinforce thermosets in various forms (foams, films, coatings) consisting of lignin, castor oil, poly(ethylene glycol), polyether polyols, or other polyols. Adding nanocellulose to the polyol/di-isocyanate mixture to crosslink the mixture as

a whole was done in some of these investigations⁷³⁻⁷⁵. In other studies, the nanocellulose was reacted with the di-isocyanate utilising one of its isocyanates, and then cross-linked with a solution of the polyol and the same di-isocyanate⁷⁶⁻⁸³. These publications' principal finding was that nanocellulose alteration improved the thermoset's mechanical or thermomechanical capabilities. There was also evidence of a rise in the thermoset's glass transition temperature.

Issues Associated with Isocyanates

It is obvious that mono- and di-isocyanates have a lot of potential for modifying nanocellulose. However, there are other obstacles restricting their utilisation in addition to their documented toxicity^{84,85}. The necessity of moisture-free settings for isocyanate reactions to occur is one of the key difficulties. The isocyanates will be hydrolyzed and cross-linked to generate a polyurea in the presence of moisture. In addition, before the process, the nanocellulose must be swapped to organic solvents. In general, this is a concern because nanocellulose, particularly CNFs, has a propensity to clump in these solvents, which affects the uniformity of the reaction. Ultrasonication is typically used to reduce aggregation, however this method is problematic since it may partially destroy the nanocellulose and/or change its surface properties⁸⁶.

Controlling the reaction between di-isocyanates and nanocellulose is another problem. Only one of the two isocyanates in di-isocyanates is supposed to interact with the surface hydroxyl groups of nanocellulose. This may not be viable in practise since a sizeable portion of the di-isocyanate reacts with both of its isocyanates, rendering the graft ineffective. Since the isocyanates in 2,4-TDI are not all similarly reactive, this problem might be more difficult to overcome for HMDI. Furthermore, both of HMDI's isocyanates have a higher chance of reacting with nanocellulose because of its more flexible molecular structure than 2,4-TDI. Due to steric hindrance, the ortho isocyanate of 2,4-TDI

has a 5–10 times lower reactivity than the para isocyanate^{35, 36}. Despite this difference in reactivity, the reaction conditions significantly affect the selectivity between para and ortho. In response to its reaction with 2,4-TDI, Abushammala has developed an useful technique to quantify the ortho isocyanates on the nanocellulose surface⁸⁷. The 2,4-TDI and nanocellulose reaction could be optimised using this technique to achieve a maximum para/ortho selectivity of 93 percent, which means that 93 percent of the 2,4-TDI molecules that reacted with the nanocellulose surface have their ortho isocyanates available for a subsequent grafting⁸⁸. The research also demonstrated that reaction temperature reduced the difference between the reaction kinetics of para and ortho isocyanates, which has a negative impact on selectivity⁸⁹.

Isocyanate self-polymerization, whether it occurs in the reaction mixture or on the surface of nanocellulose, is a major problem. With the help of a catalyst and heat, isocyanates can dimerize to generate uretidinediones and carbodiimides, or they can trimerize to form isocyanurates or even larger oligomers. The effectiveness of nanocellulose modification is negatively impacted by the numerous opportunities for isocyanates to self-polymerize⁹⁰⁻⁹².

Conclusion

For the surface modification of nanocellulose, numerous alkyl and aryl mono- and di-isocyanates have been employed. Numerous of these adjustments up to this point have been geared on making nanocellulose compatible with nonpolar thermoplastic and thermoset matrices for the creation of composites with improved interfacial adhesion. The primary goal was to enhance the composites' mechanical features. The effect of nanocellulose alteration on the composite's thermal characteristics, including thermal stability and crystallisation kinetics, has occasionally been studied. To boost the potential of nanocellulose for specific applications like water filtration and biotechnological ones, a few more modifications incorporated functional

groups to the surface of the material. Despite the reported potential of isocyanate compounds as chemical linkers and surface modifiers, their interactions with nanocellulose are complicated by a number of factors, such as the need for a moisture-free environment, the agglomeration of nanocellulose during solvent exchange, the adaptability of the reaction, and isocyanate self-polymerization.

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