

Review

Nitrocellulose Unveiled: A Brief Exploration of Recent Research Progress

Josmi John¹, K. S. Archana¹, Ashley Mariam Thomas¹, Rose Leena Thomas², Jeena Thomas³, Vinoy Thomas^{1*} , N. V. Unnikrishnan⁴

¹Center for functional materials, Department of Physics, Christian College Chengannur, 689122, University of Kerala, India

²Department of Physics, St. Joseph's College for Women, Alappuzha, 688001, University of Kerala, India

³St. Mary's H.S.S Niranam, Pathanamthitta, 689621, India

⁴School of Pure and Applied Physics, Mahatma Gandhi University, Kottayam, 686560, India
E-mail: vinoythoma@gmail.com

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Abstract: Nitrocellulose is a versatile material with a wide range of applications across various industries. This review article provides an overview of the present state of nitrocellulose technology and explores its future perspectives. It looks at how nitrocellulose is being used in fields like the military, explosives, coatings, inks, and medical equipment. Additionally, it investigates the demand for alternative cellulose raw materials in the manufacture of nitrocellulose, taking sustainability, resource accessibility, and cost-effectiveness into account. The paper also explores the creation of novel nitrating mixtures for the production of cellulose nitrate, focusing on process optimization, environmental concerns, and safety. The study also discusses new developments and ongoing nitrocellulose research. To emphasize the significance of innovation and sustainable practices in determining its future, the article concludes by detailing the future possibilities and developing trends in nitrocellulose applications.

Keywords: nitrocellulose, thermoplastic, nitrogen content, membranes, environmental science

1. Introduction

Environmental consciousness and the depletion of natural resources like fossil fuels, minerals, natural gas, etc. shifted our attention towards renewable products. Among the naturally occurring structures, cellulose is one of the most versatile and abundant natural polymers, which can be obtained from different sources like plants, algae, bacteria, or tunicates.¹ Cellulose ($C_6H_{10}O_5$) is a linear polysaccharide consisting of a long chain of anhydroglucose units connected by β -1, 4 glycoside bonds.² Cellulose is insoluble in water and most common solvents, because of the strong intramolecular and intermolecular hydrogen bonding between the individual chains. Despite this, it has applications in various fields due to its fascinating structure and attractive properties, such as chemical stability, biodegradability, renewability, and biocompatibility.³ While it is biodegradable and derived from renewable resources, cellulose also exhibits resistance to microbial degradation, ensuring long-term stability in certain applications. To increase its utility, cellulose is chemically modified from its native form to yield cellulose derivatives. The commonly used technique for modifying cellulose comprises the esterification, etherification and oxidation of its hydroxyl group.¹ The most prevalent types of cellulose derivatives include cellulose acetates, cellulose ethers, cellulose esters and so forth. These derivatives

exhibit diverse properties, such as improved solubility in various solvents, enhanced film-forming capabilities, and altered rheological characteristics. Due to their versatility, cellulose derivatives find applications in pharmaceuticals, food products, cosmetics, and various industrial processes, contributing to a wide array of innovative and functional materials.⁴ Among the vast varieties of cellulose derivatives, nitrocellulose (NC) is the most explored and sought-after one with a wide range of applications.⁵

Nitrocellulose, also known as cellulose nitrate, is a highly explosive and flammable compound that has been used for various purposes since its discovery in the mid-19th century⁶ (Figure 1). It appears as a white, fibrous, cotton-like material with an ether-like odor. NC's usage as a propellant for explosives and weapons dates back in history, and played a crucial role in the early film industry, as it was used to make photographic film and motion picture reel.⁷ Over time, its usage broadened to encompass various sectors, such as the production of lacquers, varnishes, putty, and paints, providing items with a shiny and protective finish, along with applications in filtration membranes.⁸⁻¹⁰ In recent times, its utilization has expanded into fields like microbiology, biosensors, oil/water separation, emulsions, electrospun nanofibers, microelectronics, and microfluidic devices, among others.¹¹⁻¹⁷ Cotton and wood pulp serve as the traditional precursors for nitrocellulose production. However, there is significant interest in investigating alternate sources for nitrocellulose synthesis due to the increased emphasis on sustainability and the need to reduce reliance on traditional raw materials. Some of the emerging NC sources are bacterial cellulose, agricultural residues, recycled cellulose, etc. Nitrocellulose exhibits unique properties such as high flammability, excellent film-forming ability, and good mechanical strength, which have made it a valuable material. Although it has some disadvantages as well, the explosive nature and flammability of NC pose safety challenges during manufacturing, storage, and transportation. Nitrocellulose tends to absorb moisture from the environment, affecting its stability and properties over time. Moisture absorption can lead to changes in the physical characteristics of nitrocellulose, impacting its performance in certain applications. The limited biodegradability of NC may cause problems for the environment. The production and use of nitrocellulose involve the use of chemical reagents, some of which may have negative effects on the environment and humans. Researchers have been exploring ways to improve the stability, compatibility, and eco-friendliness of nitrocellulose driven by the growing need for sustainable materials.

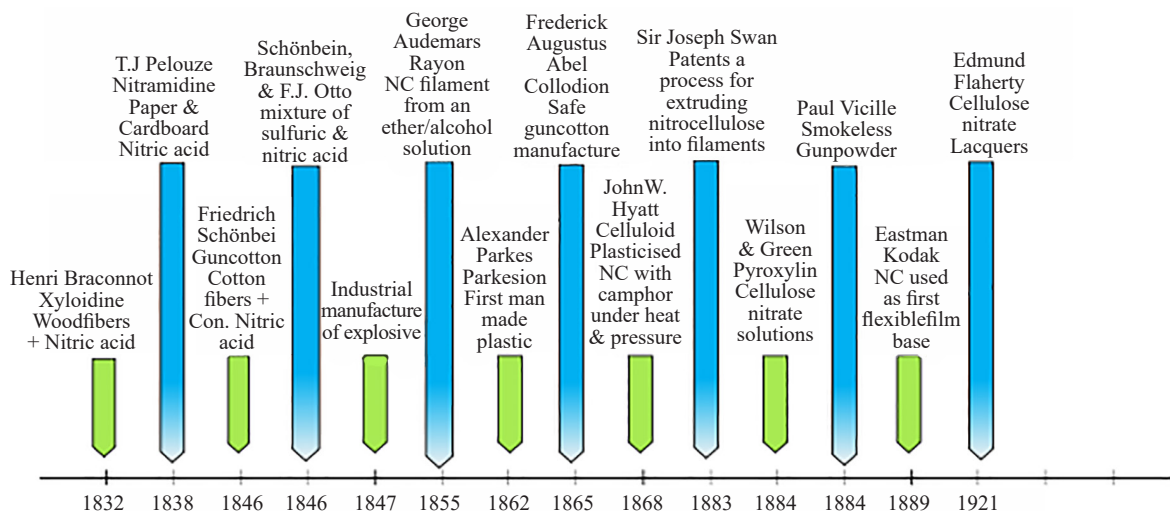


Figure 1. Milestones during the early development of NC^{23,24}

In recent years, various articles have presented the findings of nitrocellulose research, demonstrating the material's rising popularity. However, the majority of these studies have concentrated on the material's thermal properties, explosive behaviour, and medicinal applications.¹⁸⁻²² A detailed investigation into the current state and potential future developments of nitrocellulose is required in order to provide researchers, scientists, business people, and policymakers with useful information that will advance their understanding of the material and promote its responsible use in a

variety of industries. This article aims to provide a comprehensive overview of the existing research on nitrocellulose by examining the latest studies, advancements, and findings related to its properties, synthesis methods, and applications. Here our focus is to analyse emerging trends in the field of nitrocellulose by exploring recent developments, innovations, and novel approaches that have the potential to shape the future applications of nitrocellulose. This multifaceted approach contributes to the uniqueness and relevance of the work in the context of evolving technological and societal demands. Moreover, the purpose is to give readers a look into the growing landscape of nitrocellulose research and its possible implications, as well as to provoke debate and inspire additional research in these promising areas.

2. Current status and emerging trends

2.1 Structure and properties

When examining the composition of nitrocellulose, it is essential to examine its precursor material, cellulose, as they share a similar structure with minor distinctions (Figure 2). The -OH groups of cellulose act as the reactive handles for modification of the polymer, which means that the one primary alcohol at the C6 position and two secondary alcohols at the C2 and C3 positions respectively get substituted with each other during esterification. The resulting products are known as cellulose esters and they are either classified as organic or inorganic depending on the type of substituents. The reaction of cellulose with sulfating agents, phosphating agents, or nitrating agents, yields the inorganic esters cellulose sulfate, cellulose phosphate, and cellulose nitrate respectively.^{25,26}

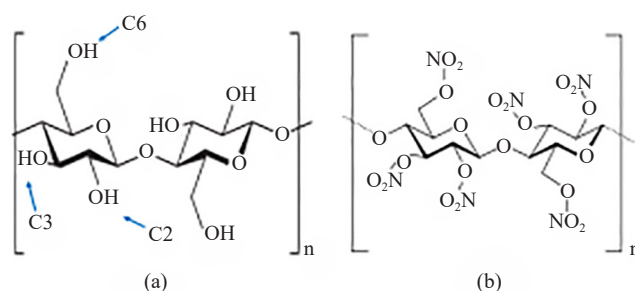


Figure 2. Structure of cellulose (a) & nitrocellulose (b)

Nitrocellulose is formed by the substitution of nitro groups for the three reactive hydroxyl groups in cellulose. However, the nitration rate is different for each carbon because the substitution is more favorable for the C6 carbon, followed by C2 and C3 carbons.²⁷ This difference in nitration rate results in the variation of the nitrogen content of the product. Nitrogen content (N content) is the most important characteristic which determines the properties and applications of nitrocellulose.²⁸ The degree of substitution (DS) is defined as the average number of hydroxyl groups substituted by nitrate groups per glucose unit. DS strongly depends on the synthesis conditions of NC and is most often expressed as nitrogen content. The relationship between the degree of nitration and nitrogen content of NC can be expressed using the equation;

$$DS = \frac{3.6 \times \text{nitrogen content (\%)}}{31.13 - \text{nitrogen content (\%)}} \quad (1)$$

When all the hydroxyl groups are replaced by nitro groups, the degree of substitution is 3 and the maximum nitrogen content is 14.15%. However, fully nitrated nitrocellulose only occurs theoretically since the synthesis is expensive and dangerous due to the formation of unstable compounds such as sulfuric cellulose esters. In practice, the highest attainable nitrogen content is 13.8%.^{29,30}

Although the basic skeleton of NC and cellulose macromolecule are structurally similar there are significant

variances. The replacement of -OH groups by -ONO₂ group reduces the hydrogen bonding. NC is more flexible than cellulose because the steric size of the -ONO₂ group is considerably larger. Furthermore, it also alters the distance between the cellulose backbones and the interaction between the macromolecules, thus affecting the order of arrangement. In addition, the distribution of nitrate groups influences the molecular group structure of NC, when DS is less than or equal to 1 NC does not have any significant difference than that of cellulose. However, when the DS reaches 2-2.25 range, NC exhibits an irregular structure with uneven hydrogen bonds, reduced intermolecular interaction and higher flexibility. Nitrocellulose has a totally repeating and symmetric macromolecular structure with orderly arrangement, reduced chain flexibility, and increased intermolecular interaction when the nitration degree is 2.50 or greater.³¹ The physical and chemical properties of NC is summarized in Table 1.

The nitrogen content affects the solubility, viscosity, stability, flammability and explosibility of NC. Solubility decreases when the nitrogen content decreases. Thus, low-nitrated nitrocellulose is soluble in alcohols, esters, ketones, and glycol ethers, whereas highly-nitrated nitrocellulose is insoluble in alcohols, but can be dissolved in esters, ketones and glycol ethers. The viscosity is inversely related to the degree of substitution and it increases with decreasing nitrogen content.^{32,33} Highly nitrated cellulose with nitrogen content of more than 12.5%, is unstable to heat and will ignite on low-temperature heating itself. The degree of nitration greatly affects the thermal stability and decomposition temperature. Decomposition temperature decreases with the increase of nitrogen percent. Moderately nitrated cellulose is also flammable and explosive, though less violent.³⁴ The nitrogen content rises in direct proportion to the heat of the nitrocellulose explosion. However, it has an inverse relationship with the nitrocellulose-specific volume, formation heat, and combustion heat.^{32,35}

Table 1. Summary of physical & chemical properties of NC^{31,36}

Sl. no	Properties		Comments
1	Molecular Weight		504.3
2	State		Fibrous
3	Color		White
4	Odor		Ether-like
5	Boiling point		83 °C
6	Melting point		160-170 °C (ignites)
7	Solubility	soluble in acetone, esters, ketones, glycol ethers, nitrobenzene, tetrahydrofuran and ethyl-, butyl-, and amylacetate	
8	Electrical conductivity	Poor; conducts in the presence of water (due to the conductivity of water)	
9	Reaction with	Air	No reaction
		Acid	Denitration; decomposition of the NC & catalytic chain process will eventually lead to combustion explosion
		Alkali	Saponification & color change to the product
		Reducing agent	Has highest oxidation state, unstable & strong oxidizing capability; reduced to cellulose via denitration reaction (original cellulose form not achievable)
		Oxidants	very stable

2.2 Synthesis

Nitrocellulose is synthesized by the nitration of cellulose through a highly exothermic esterification reaction.

The synthesis process depends on many factors such as the structure of cellulose, composition of the acidic mixture, temperature, and time of nitration (Table 2).³⁷ The preparation of nitrocellulose with different nitrating mixtures and cellulose obtained from various raw materials has been reported. Figure 3 illustrates the basic extraction mechanisms of cellulose from different biomass followed by the nitration reaction. Cellulose obtained from plants, algae, tunicates or bacteria has different structure, morphology and material properties this will directly influence the structure and properties of NC. For this reason, more crystalline NC is produced by extremely crystalline cellulose. Cellulose is a semi-crystalline material with long thin crystalline domains, these crystalline regions can be combined with amorphous cellulose and other macromolecules such as hemicellulose, lignin and pectin, which vary depending on whether the cellulose is algae- or plant-based. The NC obtained from the nitration process is often in an amorphous state, but it contains regions with a degree of crystallinity. When nitrocellulose is dissolved in a suitable solvent, the polymer chains can reorganize as the solvent evaporates or as the solution cools, leading to the formation of crystalline structures. The rate of crystallization depends on the cooling temperature, that is slower or controlled cooling facilitates the formation of more ordered crystalline structures. The crystalline behaviour of NC can impact the burn rates and combustion rates of propellants and explosives.³⁸

Table 2. Summary of synthesis of NC

Factors influencing NC production		Characteristics
Nitrating Agents	Nitric acid	Highly unstable Easily stabilized Exclusively used in laboratories
	Sulfuric acid, nitric acid & water	Most economical Specific degree of nitration achieved by varying composition of acid Formation of cellulose sulphates is major disadvantage
	Nitric acid & phosphoric acid	Most stable No phosphoric esters are formed Variation in acid composition leads to hardening or crystallization of NC fibers Unable to synthesize low nitrated NC
	Nitric acid & acetic acid	NC with high N content Stabilization needs 3 extractions Acetyl nitrate reaction is the major drawback
	Nitric acid & organic solvents (carbon tetrachloride, methyl nitrate and chloroform)	Non-destruction of polymer chains NC with improved mechanical properties
Raw materials	Cellulose from plants	High alpha cellulose content Comparable with commercially available NC
	Microcrystalline cellulose	Improved properties than ordinary NC Found applications in the industries of propellants, gas generators, and other fields
	Bacterial cellulose	High purity Increased nitrogen content
	Cellulose nanofibers	Low mechanical sensitivity Larger specific surface area and burning rate than NC Higher reactivity and combustion rate
Temperature	High temperature adversely affects the yield, viscosity, and stability of product Cellulose gets destroyed at temperatures above 40 °C	
Time	Influences the quality, consistency, and thickness of NC Prolonged nitration time leads to decrease in viscosity	

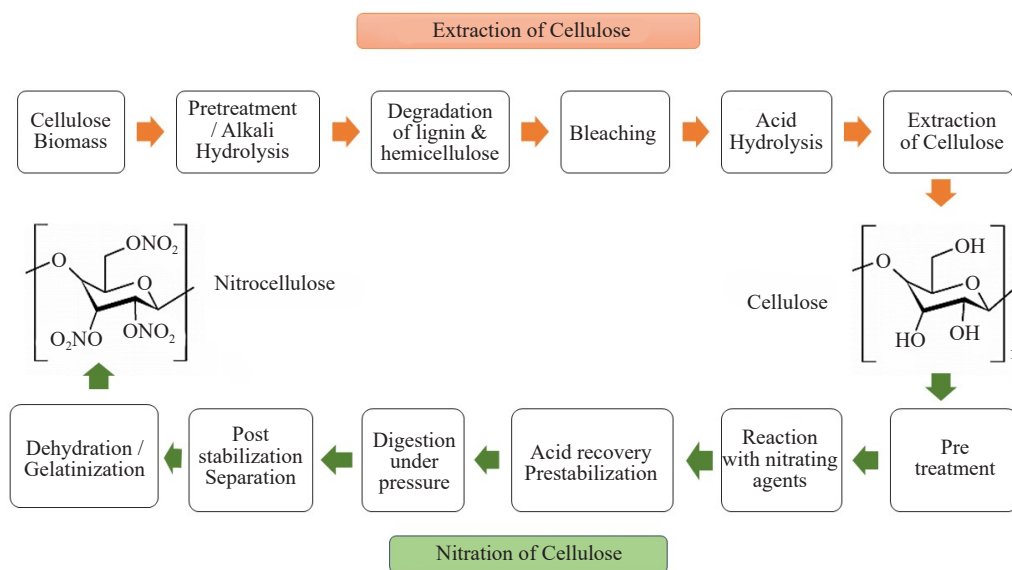


Figure 3. Schematic representation of extraction of cellulose followed by the nitration process

2.2.1 Different nitrating mixtures

2.2.1.1 Nitric acid only

Initially, nitric acid alone was utilized to prepare NC. However, the resulting product was extremely unstable, preventing it from being used in industry. The maximum nitrogen content obtained by using nitric acid as a nitration agent is about 13.6-13.8%. The only advantage of this approach is that NC can be readily stabilized and is exclusively employed in laboratories.³⁹

2.2.1.2 Mixture of sulfuric acid, nitric acid and water

A mixture of sulfuric acid (H₂SO₄) and nitric acid (HNO₃) is found to be the most economical way to produce nitrocellulose. According to the modern theory of nitration, the nitrating agent is the nitronium ion NO₂⁺:



The sulfuric acid present in the nitration mixture first ionizes nitric acid to form nitronium cation. During the nitration, each -OH group produces one H₂O molecule as a byproduct, diluting the acid mixture; hence, a dehydrating agent is necessary to eliminate the produced water molecule. In this case, sulfuric acid binds with released water and at the same time acts as a swelling agent for cellulose and thereby facilitating the subsequent reaction. The main disadvantage of utilizing H₂SO₄ is the creation of cellulose sulphates, which must be eliminated from the product in order to achieve stability.^{29,40} Nevertheless, the industrial manufacturing of nitrocellulose entails a sulfonitric solution comprising nitric acid, sulfuric acid, and water. About 13.9% of nitrogen content is obtained by using this nitration mixture. By carefully varying the composition of the acid mixture, it is possible to achieve specific degrees of nitration, tailoring the properties of the nitrocellulose for desired applications.

2.2.1.3 Mixture of nitric acid and phosphoric acid

Besides the combination of phosphoric acid (H₃PO₄) with nitric acid is employed for NC synthesis. The NC produced by nitric and phosphoric acid mixture brings out the most stable sample, without the formation of phosphoric esters. The main drawback of this method is its inability to synthesize low nitrated NC. Additionally, any deviation from the composition of the nitrating mixture will lead to the hardening or crystallization of the NC fibers.

2.2.1.4 Mixture of nitric and acetic acid

The mixture of nitric and acetic acid is used to obtain nitrocellulose with a high nitrogen content. In order to stabilize the product formed in this reaction three extractions with boiling alcohol are needed. The commercialization of this nitrating mixture is hampered by the acetyl nitrate reaction, which produces a substance that explodes at high temperatures.^{24,27,33}

2.2.1.5 Mixture of nitric acid and organic solvents

Some organic solvents like carbon tetrachloride, methyl nitrate and chloroform were also used as the nitrating medium along with the nitric acid. These solvents will not degrade the polymer chains of the product and help to increase the mechanical properties of NC.^{24,33}

New nitrating mixtures are required in the production of NC due to a number of variables, including safety, environmental concerns, and process improvement. Because of their corrosive and reactive character, commonly used nitration mixtures such as a mixture of nitric and sulfuric acid pose inherent safety issues. So, in order to avoid accidents and reduce the risk of hazardous occurrences, proper handling, storage, and disposal practices should be followed.⁴¹⁻⁴³ Improper disposal of used nitrating mixes can lead to soil and water contamination, posing risks to ecosystems and human health.⁴⁴ Enhancing the safety of workers and minimizing the likelihood of accidents in nitration procedures can be achieved by formulating nitrating mixes that are less hazardous or more stable. Mixtures that produce fewer toxic byproducts or allow for more efficient waste material recycling can help to reduce environmental impact and encourage sustainable manufacturing practices. Optimizing the nitrating mixture composition and properties can lead to more consistent and reliable production of cellulose nitrate with desired characteristics, reducing process variability and enhancing overall manufacturing efficiency. This in turn can open up possibilities for improved product performance, expanding the range of applications and market potential of NC-based materials.

2.2.2 Alternative raw materials

Traditionally, nitrocellulose has been produced from cellulose obtained from wood pulp or cotton fibers.⁴⁵ However, with the growing emphasis on sustainability and the need to reduce reliance on traditional raw materials, there is an increasing interest in exploring alternative sources for nitrocellulose production. This has led researchers and industry experts to investigate and experiment with various unconventional raw materials such as linen flax, hemp, melilot, hogweed, alfalfa, rape, and jute that have the potential to serve as viable alternatives⁴⁶ (Figure 4). These alternative raw materials offer the possibility of not only reducing environmental impact but also diversifying the sources of nitrocellulose production. Exploring various cellulose sources may also offer the potential for cost savings, especially if these sources are locally available, abundant, and less subject to price volatility.

2.2.2.1 Cellulose from plants

Gimutillian et al.⁴⁷ have proposed the formation of high-quality nitrocellulose from miscanthus, a perennial grass species that grows easily without much attention. The miscanthus cellulose consists of 95.4% alpha-cellulose which satisfies the requirements for effective cellulose nitration. This could confirm a yield of 11.85% nitrogen content. Miscanthus nitrocellulose is comparable with basic NC types that are used for the manufacturing of membranes, films, lacquers, paints, nail polish, artificial silk, skin, etc. Yet another work investigated the possibility of using unconventional feedstocks like miscanthus, oat hulls, and intermediate flax straw-derived cellulose nitrates as components of explosive composites.⁴⁸ Cellulose from these feedstocks was isolated by an industrial process using mixed acids. FTIR (Fourier Transform Infrared Spectra) spectra obtained from these samples showed similar absorption bands corresponding to nitro vibrations. The NC samples obtained from the above unconventional feedstocks were compared with the commercially available collosylin cellulose. And the results prove that the basic properties were very much comparable.

Acacia pulp has been widely used in paper manufacturing industries since it contains cellulose with high alpha content (above 92%). In a study conducted by Khai et al.⁴⁹ both low-nitrated and high-nitrated NCs were prepared using acacia pulp. FTIR spectra, nitrogen content, viscosity in acetone, thermal stability, and dissolubility in organic solvents

were examined for the synthesized NCs. Also, a comparative study on the nitrogen content of nitrocellulose obtained from acacia pulp and softwood cellulose was conducted. The conclusion of the study is that the distribution of nitrogen content of those NCs is larger than that of NCs from softwood cellulose.

Lipin et al.³⁴ studied the possibility of using deciduous trees to produce nitrocellulose using samples of deciduous cellulose obtained from a mixture consisting of birch (60%) and aspen (40%). Their rapid renewability, availability and habitats in various climate zones, are the advantages that make them one of the most promising sources of alternative feedstock for nitrocellulose production. Quantitative analysis of the prepared NC by titration with Mohr's salt showed that the N content in the nitrocellulose samples was greater than 10%.

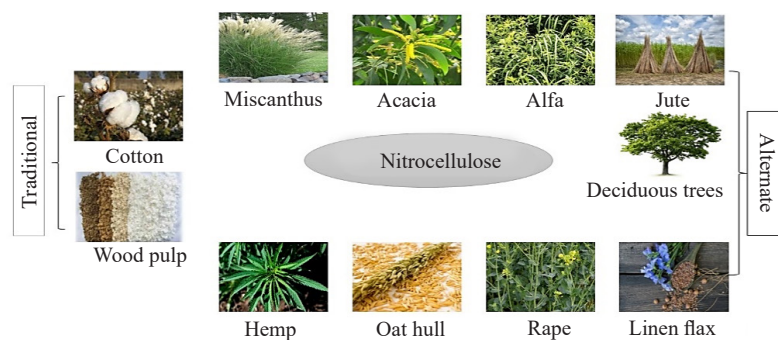


Figure 4. Traditional and alternate feedstocks for NC production

2.2.2.2 Microcrystalline cellulose

Nanometer-scale cellulose has both crystalline and amorphous phases. Without any weight loss, acid hydrolysis can remove amorphous regions and reduce the degree of polymerization of the cellulose chains. These hydrolyzed substances are referred to as microcrystalline cellulose (MCC).⁵⁰ It was published in work⁵¹ that the use of MCC could improve several properties of nitrocellulose rather than using ordinary cellulose.

Trache et al.³⁷ effectively exploited Alfa grass, a non-wood plant that grows in semi-arid habitats in the southern and western Mediterranean basin, to create microcrystalline cellulose nitrate. These easily accessible, low-cost fibers are largely employed in the production of paper. The microcrystalline cellulose nitrate obtained from alfa-MCC, commercial MCC (C-MCC), and pure MCC samples were compared, and the results indicate that the microcrystalline cellulose nitrate obtained from alfa fibers has potential applications in the industries of propellants, gas generators, and other fields.

2.2.2.3 Bacterial cellulose

Several studies discussed have proposed the synthesis of nitrocellulose from various plant sources. However, the cellulose obtained from plants does not exist in pure form, it may contain lignin, hemicellulose, pectin and starch. This signals the necessity of conducting a purification process to remove them. Bacterial cellulose (BC) serves as an alternate substitute to plant cellulose. Many bacteria such as acetobacter, rhizobium, agrobacterium, aerobacter, achromobacter, azotobacter, salmonella, escherichia, sarcina, alcaligenes and pseudomonas^{52,53} have been used to produce BC. BC shows high purity properties compared to cellulose obtained from other sources⁵⁴ and when nitrated, some of the hydroxyl groups of BCs are exchanged with the nitro group to form bacterial cellulose nitrate (NBC). Sun et al.⁵⁵ and Jamal et al.⁵⁶ utilized bacterial cellulose for the preparation of nitrocellulose in their studies. Sun et al., synthesized bacterial cellulose by fermentation using *Acetobacter xylinum* and NBC were prepared with nitro-sulfuric acid under heterogeneous conditions. NBC with the degree of substitution (DS) of 1-2.85 was obtained from *Acetobacter* and the author also discusses the effects of sulfuric to nitric ratio, reaction temperature, and reaction time on the value of DS of NBC. Jamal and his group showed that Nata de coco, a dessert produced by fermenting coconut water with a culture of

bacteria can be used to produce BC. Nata de coco contains cellulose as a major source. The bacteria metabolize glucose as a carbon source in the coconut water and convert it into BC. NBC obtained from bacterial cellulose is expected to contain high nitrogen content, which is essential for advanced energetic materials (Figure 5).

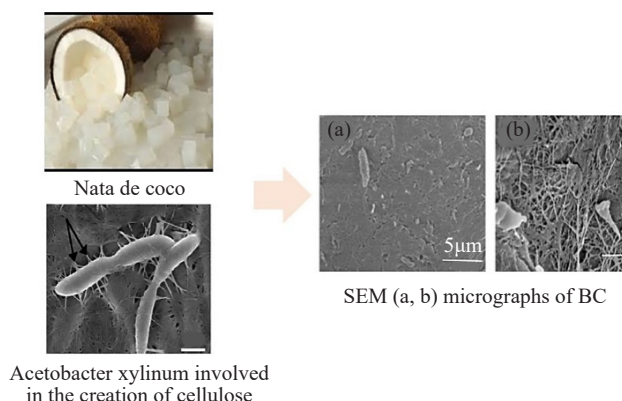


Figure 5. Production of NBC from bacterial cellulose. Reprinted with permission from reference⁵⁶

2.2.2.4 Cellulose nanofibers

Recently, nitrocellulose made from cellulose nanofibers was also reported. In the literature,⁵⁷ microcrystalline cellulose was subjected to pretreatment, hydrolysis, and nitration in order to form spherical NC composite crystals with a diameter of 15 to 30 nm. When compared to conventional NC, the nanosized spherical NC's impact sensitivity dropped by 44.6%. The ladder-like NC produced by isophorone diisocyanate treatment showed that their mechanical sensitivity is lower than that of raw NC.⁵⁸ Zhang et al.⁵⁹ have produced submicron NC particles with a diameter of 500 nm, using dimethylformamide (DMF) solvents. Okada et al.⁴⁰ used cellulose nanofiber (CNF) water suspension, obtained by disk milling of cotton powder as the raw material for NC. The nitrocellulose nanofiber (NCNF) generated has 9%-13.7% nitrogen content, a larger specific surface area and a 3.5 times larger burning rate than that of the NC. The above work concluded that due to its strong combustion performance, NCNF offers potential applications as explosives and has higher reactivity than micro-sized NC. With the aid of electrospinning, Yan et al.⁶⁰ prepared thermite-based nitrocellulose nanofibers while Sovizi et al.⁶¹ prepared two different types of nanofibers; a smooth nanofiber with 90-150 nm and a porous one having 400-500 nm diameters.

2.2.2.5 Recycling cellulose waste

Utilizing alternative cellulose sources can involve repurposing or recycling cellulose waste from various industries, such as agriculture, food processing, paper manufacturing or domestic waste. This approach promotes circular economy principles by reducing waste generation and maximizing resource utilization. It can also contribute to the development of value-added and sustainable supply chains. Muvhiwa et al.⁶² explain a feasible method for the conversion of waste tobacco stalks into nitrocellulose. Here a nitrating mixture of nitric acid and sulfuric acid (1:1 v/v) with a nitration time of 5 minutes was used to produce NC from tobacco stalks by soda pulping method. The obtained nitrocellulose was soluble in acetone, hence characterized by a nitrogen content between 11-11.5%.

2.2.3 Temperature and time of nitration

The nitration temperature and nitration time are also crucial factors in generating high-quality nitrocellulose. An increase in nitration temperature helps in improved nitrating mixture diffusion into the cellulose, which speeds up the rate of nitration reaction but has no effect on the end product's nitrogen content. Conversely, a rise in temperature has several adverse consequences such as oxidation and hydrolysis that have an impact on the yield, viscosity, and stability.

At normal temperatures, nitration happens slowly, reducing the degree of substitution of cellulose nitrate, while the nitrating mixture destroys cellulose at temperatures above 40 °C.³⁴ The exothermic nature of the nitration of cellulose dictates that the temperature of the mixed acid used for the process should be lower than the nitration temperature. The nitration time influences the quality, consistency, and thickness of the NC. During the initial 5-10 minutes of nitration, the nitrogen content in the NC reaches a state of equilibrium. After 30-40 minutes or more, the nitration process has minimal effect on the nitrogen content. However, if the nitration time is less than 30 minutes, it becomes important to consider its impact on the nitrogen content of the NC. Prolonged nitration time leads to increased occurrence of side reactions, as evidenced by the decrease in viscosity of the NC.³¹

2.3 Modifications on NC

Along with polymerization and polycondensation, modification of polymers is one method of physiochemically transforming macromolecular molecules to produce new polymers. Modification can be done either chemically, physically, or biologically (Table 3). The chemical modification of polymers is a process, where the starting polymer is subject to physical or chemical treatment and transforms into a new polymer having a different chemical structure. While physical (structural) modification does not alter the structure of the macromolecules, it is the purposeful alteration of the physical properties of polymers, involving the transformation of their supramolecular structure under the action of physical factors, varying the nature of the solvent, and doping the polymer with small amounts of other substances. Biomodification is a relatively new technique that uses biocompatible, selective interactions with proteins, and bio-inspired surfaces.⁶³

Table 3. Summary of modifications of NC

Type of Modification	Examples	Application/Effects
Chemical	Nucleophilic Substitution Reactions	<ul style="list-style-type: none"> • Dimethylhydrazine, Phthalic Hydrazide, Succinic Hydrazide modified NC products are often used in enamels, varnishes, and other conversion polymer compositions • 2-aminopyridine modified NC is used in bactericidal varnishes and colors • Reacting with Aromatic and Aliphatic Acid Chlorides introduce various functional groups in NC
	Denitration and Esterification	<ul style="list-style-type: none"> • Sodium Carboxymethyl-Nitrocellulose modification offer thermal stability and flame suppression without migration
Physical	Plasticization	<ul style="list-style-type: none"> • Improves mechanical deformability, lowers the brittle point, and facilitates processing • Applicable in coatings, films, and adhesives
	Low Molecular Weight Nitrate Esters	<ul style="list-style-type: none"> • Eg: nitroglycerine (NG), diethylene glycol dinitrate, or trimethylolethane trinitrate • Propulsion applications
	Glycidyl Azide Polymer (GAP) Modification	<ul style="list-style-type: none"> • Improved mechanical properties • Used in propellants
	Insensitive Plasticizers	<ul style="list-style-type: none"> • Eg: N-butyl-N-(2-nitroxy-ethyl) nitramine (Bu-NENA)
	Eco-Friendly Inert Plasticizers	<ul style="list-style-type: none"> • Eg: Acetyl triethyl nitrate (ATEC) and tributyl citrate (TBC) • Employed in applications requiring eco-friendly plasticization
Biological	Silver nanoparticle impregnation	<ul style="list-style-type: none"> • Bacterial filtration and growth suppression in NC membrane filters • Drinking water filtration systems
	Chitosan integration	<ul style="list-style-type: none"> • Improvement of pore size, porosity, and surface groups in NC membrane • Enhanced biomolecule immobilization capacity on paper substrates
	Cellulose nanofiber integration	<ul style="list-style-type: none"> • Increased sensitivity in nucleic acid LFAs for bacterial testing • Modification of paper substrate for enhanced biomolecule adsorption

2.3.1 Chemical modification

In chemical modification, the reactive $-\text{ONO}_2$ groups of nitrocellulose can be replaced by other groups through nucleophilic substitution. Following this, four different types of reactions take place in one or another degree: those involving all the nitrate groups; those involving free OH groups; those involving the glycoside bonds, which break the polymer chain; and those involving the glucopyranose ring opening.³⁹ Dimethylhydrazine, phthalic hydrazide, or succinic hydrazide were employed to modify cellulose nitrate, and the resulting products are excellent candidates for usage as components of enamels, varnishes, and other conversion polymer compositions. This modification of cellulose nitrate with hydrazine derivatives is addressed in.⁶⁴ Another interesting nucleophilic reagent is the heterocyclic molecule found in nature. The product obtained by the reaction of cellulose nitrate with 2-aminopyridine is advised for use in bactericidal varnishes and colors.⁶⁵ Romanova et al.⁶⁶ documented the reactions of cellulose nitrates with aromatic and aliphatic acid chlorides and the cited authors⁶⁷ created a catalyst-free method of chemically modifying nitrocellulose with acetyl chloride in pyridine.

In order to offer thermal stability and flame suppression ions without migration, sodium carboxymethyl function groups were chemically grafted onto the molecular chains of nitrocellulose. Specifically, sodium carboxymethyl-nitrocellulose (CMNC) was produced by denitrifying NC by interacting with hydrazine hydrate to convert some of the nitrate groups into hydroxyl groups, followed by carboxymethylation to esterize these hydroxyl groups in the presence of chloroacetic acid. Both denitration and etherification had an impact on the quantity of sodium carboxymethyl groups attached to nitrocellulose chains. The findings demonstrated that the thermal stability of CMNC was superior to that of the original NC. Meanwhile, the decomposition products and thermal decomposition behaviors of CMNC are comparable to those of NC.⁶⁸

2.3.2 Physical modification

Plasticization is the most common physical modification of NC, which improves the mechanical deformability of the plasticized polymer and, as a result, extends the service temperature range to lower temperatures, lowers the brittle point, and facilitates processing. NC can be plasticized by incorporating additives such as camphor, dibutyl phthalate, or other plasticizers and is suitable for applications requiring flexibility, such as coatings, films, and adhesives.⁶⁹ In propulsion applications, low molecular weight nitrate esters such as nitroglycerine (NG), diethylene glycol dinitrate, and trimethylolethane trinitrate are typically utilized with NC. Nitrate esters, such as NG, are effective, but they have a number of limitations, including significant migration and stability concerns throughout the propellant's life cycle. Furthermore, NG is hazardous to both users and the environment. Glycidyl azide polymer (GAP) has recently been suggested as a potential substitute for nitrate esters in propellant formulations and other solid propulsion applications.⁷⁰ GAP was absorbed on NC to increase the plasticizing performance of NC spherical powders, and a new variety of GAP-modified single-base spherical powders was first made using an internal solution approach.⁷¹ It was discovered that nitrocellulose powders treated with GAP exhibit high round, no bonding between the particles, and excellent fluidity. Nitrocellulose powders with GAP modifications can enhance the propellant's mechanical properties. The influences of insensitive plasticizer N-butyl-N-(2-73 nitroxy-ethyl) nitramine (Bu-NENA) plasticizers on the dynamic mechanical properties of NC base propellants have been investigated by Xiaofei Qi et al.⁷² Nitrocellulose granules containing the proposed new eco-friendly inert plasticizers, such as acetyl triethyl citrate (ATEC) and tributyl citrate (TBC) were discussed in.⁷³

2.3.3 Biological modification

In biomodification, silver nanoparticles biosynthesized from *Aspergillus niger* (AgNPs-Asp), *Cryptococcus laurentii* (AgNPs-Cry), and *Rhodotorula glutinis* (AgNPs-Rho) were impregnated in the nitrocellulose membrane filter to investigate their influence on bacterial filtration and bacterial growth suppression. *Escherichia coli*, *Enterococcus faecalis* and *Pseudomonas aeruginosa* were used for the test and nitrocellulose membrane filters impregnated with 1 mg/L of biosynthesized AgNPs inhibited bacterial growth completely, making it appropriate for use in a drinking water filtration system.⁷⁴ Tang et al. devised a simple approach for modifying paper materials by introducing chitosan into the NC membrane, which has a favorable influence on the pore size, porosity, and surface groups of NC membrane, hence

improving biomolecule immobilization capacity on paper substrate.⁷⁵ A simple method for modifying the characteristics of paper substrate by integrating CNFs into a nitrocellulose membrane to improve the sensitivity of nucleic acid LFAs is also given. This approach alters the pore size, porosity, surface groups, and surface area of the paper substrate, hence increasing biomolecule adsorption on the paper substrate. The results show that nucleic acid LFAs have a 20-fold increase in sensitivity in *Staphylococcus aureus* testing.⁷⁶

2.4 Applications

The nitrogen content of nitrocellulose plays a crucial role in determining its applications and performance characteristics. NC with varying levels of nitrogen content is utilized in a wide range of industries, each requiring specific properties for optimal functionality. Low nitrogen content nitrocellulose, typically around 10-12%, finds application in products like lacquers, wood finishes, and printing inks. These formulations require a nitrocellulose base with good adhesion, flexibility, and film-forming properties. As the nitrogen content increases, reaching approximately 12-13%, the nitrocellulose becomes suitable for propellant applications. Nitrocellulose with higher nitrogen content, ranging from 12.6% to 13.4%, possesses excellent energy release and stability properties, making it an ideal ingredient in ammunition, fireworks, and blasting agents.⁷⁷ Additionally, nitrocellulose with a specific nitrogen content is used in the pharmaceutical sector.⁷⁸ Manufacturers can cater to the unique needs of numerous sectors by tailoring the nitrogen content of nitrocellulose, assuring optimal performance and safety in each application.

2.4.1 Military applications

Nitrocellulose holds a significant role in military fields due to its rapid decomposition upon ignition, releasing a large amount of energy. NC with a nitrogen content of about 12.95%-13.35%, usually called gun cotton is employed in military sector.⁷⁹ The controlled combustion of nitrocellulose-based propellants generates high-pressure gases that propel projectiles with precision and velocity.⁸⁰ As a result, it plays a crucial role in the ammunition used in heavy artillery, rifles, and handguns. Furthermore, nitrocellulose finds use in the formulation of explosive materials. When combined with suitable ingredients, such as stabilizers and sensitizer compounds, nitrocellulose can be employed to create a range of explosives, including dynamite, and blasting agents. These explosives are vital for mining operations, demolition, and construction activities where controlled and efficient detonation is required.⁸¹ Another significant application of nitrocellulose in the military and explosive industry is in the production of pyrotechnics.^{82,83} Pyrotechnic devices, such as fireworks and flares, utilize nitrocellulose as a binder or matrix material. Its fast-burning characteristics and ability to produce vibrant colours make it ideal for creating visually stunning displays and signaling devices.

The low bond energy of the nitrate groups, however, makes NC chemically unstable and prone to autocatalytic breakdown when stored. Additionally, these decomposition by-products include nitroxyl radicals and nitrogen oxides, which speed up the process of breaking down NC by autocatalysis and release a lot of heat that can lead to unstable propellants or even explosions.^{84,85} Improved qualities, such as greater stability and burn rate, have been the subject of ongoing research on highly nitrated NC.

Compounds that contain energetic groups such as nitro-, azido-, and other groups, and whose burning products contain a lot of nitrogen gas are known as energetic polymers.⁸⁶ NC is one of the first known and remains the most widely used energetic polymer in gunpowder and solid propellant compositions due to its unique properties. However, their low density, high friability, limited combustion, and high sensitivity limit their energetic application. Studies show that physical modification or chemical surface functionalization can be utilized to overcome the drawbacks and produce alternative energetic polymers with improved properties. Literature reveals the use of different precursors towards the formation of a novel class of energetic polymers. Tarchoun et al. proposed a novel methodology for the synthesis of nitrogen-rich energetic polymers based on tetrazole-acetate modification of pristine cellulose and microcrystalline cellulose, as well as their nitrated derivatives.⁸⁷ This study shows that microcrystalline cellulose is a better precursor than pristine cellulose. Later the same group explored the use of aminoethyl-nitramine explosophoric functional groups and the newly synthesized energetic polymers exhibited high nitrogen contents, elevated densities, and good thermal stability compared to the traditional ordinary cellulose nitrates and MCC nitrates.⁸⁸ They investigated azide-functionalized microcrystalline cellulose-based energetic polymer and compared its properties with azidodeoxy pristine cellulose nitrate, microcrystalline cellulose nitrate and conventional cellulose nitrate.^{89,90} Ongoing research in this field

focuses on developing innovative formulations that improve performance, reduce sensitivity, and address environmental concerns

2.4.2 Medical field

Nitrocellulose also finds application in the medical field, primarily in the realm of controlled-release drug delivery systems.⁹¹ NC membranes are utilized to create transdermal patches, wound dressings, and other devices that facilitate the sustained release of medications. In transdermal patches, nitrocellulose serves as a permeable membrane that allows for the controlled diffusion of drugs into the bloodstream through the skin. The porosity and structure of nitrocellulose can be tailored to regulate the release rate of the medication, ensuring a steady and consistent delivery over a prolonged period.⁹² This method of drug administration offers several advantages, including improved patient compliance, reduced side effects, and optimized therapeutic efficacy.

Wound dressings incorporating nitrocellulose play a crucial role in promoting healing and preventing infection. Nitrocellulose-based dressings can create a protective barrier over the wound while allowing for the exchange of oxygen and moisture. Moreover, the controlled-release properties of nitrocellulose enable the gradual release of antimicrobial agents or other therapeutic substances, aiding in the healing process.^{93,94} A recent study⁹⁵ developed a very efficient wound healing dressing using nanoporous graphene (NPG) mixed with nitrocellulose to create a composite membrane with a moderate water vapour transmission rate, outstanding toughness performance and good biocompatibility. Furthermore, the membrane has great broad-spectrum antibacterial properties and can lower the risk of microbial infection in the body following trauma.

Further, nitrocellulose is utilized in diagnostic applications, such as lateral flow assays. These tests, commonly used for rapid detection of various medical conditions, employ nitrocellulose membranes as the solid support for capturing and detecting target molecules. The high surface area and uniform pore size distribution of nitrocellulose membranes make them ideal for immobilizing biomolecules, facilitating efficient and sensitive detection.^{20,96} Ongoing research and advancements in nitrocellulose technology continue to expand its applications in medical devices and therapeutics, contributing to improved patient care and outcomes.

2.4.3 Industrial applications

Nitrocellulose was one of the earliest materials used in the production of lacquers and coatings in the late 19th century. The film-forming property of NC makes it an ideal candidate in the coating industry. Later NC lacquers gained popularity for automobile finishes due to their fast-drying time and the ability to achieve a smooth, high-gloss appearance (Figure 6). The development of alkyd resins in 1930 was a substantial breakthrough in coatings technology. Alkyds, combined with nitrocellulose, offered improved durability, flexibility, and adhesion. These formulations became widely used in various coatings applications. Weather resistance and color retention were enhanced with the introduction of thermoplastic acrylic resins. However, environmental and safety considerations have led to the exploration of alternative binders and the development of nitrocellulose-free formulations. Although, NC continues to be used as a key ingredient in coatings and paints, particularly in automotive clear coats, wood finishes, printing inks, and specialty coatings.⁹⁷ NC is rarely used as a solid substance in coatings, but when mixed with amyl acetate and industrial wood alcohol, it produces pyroxylin, which is subsequently used to make lacquers, waterproofing solutions, leather constructions, and artificial silk. Sani M. Gumel and Bello B. Dambatta compared the performance of nitrocellulose, polyvinyl alcohol (PVA), and a PVA/NC blend as topcoats on colored goatskin leather. Their findings revealed that a PVA/NC coating had better characteristics than the PVA coat alone.⁹⁸ Current research in the coating industry focuses on novel formulations, alternative binders, and approaches to improve performance without compromising environmental concerns.

Nitrocellulose-based inks were employed in letterpress printing, flexography and offset printing during the 20th century due to their ability to adhere well to various substrates and produce sharp, defined images. The digital printing revolution posed challenges for traditional ink formulations. While the demand for nitrocellulose-based inks persisted in some applications, especially in packaging and label printing.⁹⁹ Nitrocellulose's solubility in organic solvents and ability to dry quickly makes it ideal for high-speed printing processes. NC-based inks provide vibrant colours, good printability, and resistance to smudging. According to recent studies, nitrocellulose-based graphene inks represent a

promising avenue in the field of printable electronics and advanced coatings. NC is demonstrated to be a synergistic polymer stabiliser for graphene inks. For compatibility with a wide range of deposition processes, graphene treated with nitrocellulose is formed into inks with viscosities ranging over 4 orders of magnitude. Furthermore, nitrocellulose residue outperforms state-of-the-art graphene inks based on ethyl cellulose in terms of mechanical and environmental stability.¹⁰⁰

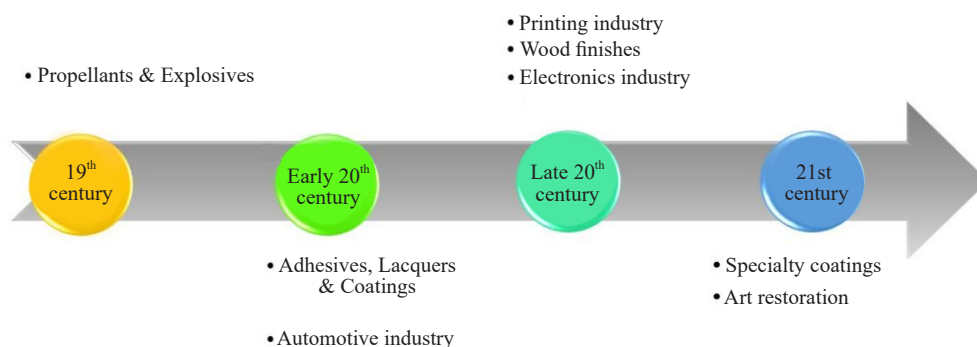


Figure 6. Key developments in the industrial applications of nitrocellulose

NC-based adhesives are widely used in various industrial applications. They offer strong bonding properties for materials such as wood, paper, plastics, and textiles.¹⁰¹ Nitrocellulose films and tapes find application in the packaging and labelling industry. In the leather and textile industries NC coatings are used to enhance the surface appearance, impart water resistance, and improve durability. They are commonly used for leather finishes, shoe polishes, and textile coatings. Nitrocellulose-based coatings are also used in the electronics and electrical industries to insulate and protect electrical components from moisture and corrosion.¹⁰²

2.4.4 Other applications

In addition to the aforementioned uses, NC is currently exploring other fields of applications. This article section covers a few of them.

2.4.4.1 Oil/water separation

For effective oil/water separation, dual-scaled porous nitrocellulose (NC) membranes with underwater superoleophobicity were fabricated using a desktop robot punch system outfitted with a homemade needle with a conical tip. A series of p-NC membranes with various pore diameters were produced by adjusting needle punching depths. Due to high separation efficiencies (> 99%), the p-NC membranes were able to selectively separate water from a variety of oil/water mixtures, including gasoline, diesel, hexane, petroleum ether and even high-viscosity crude oil/water mixtures. These membranes are quite promising in oil spill cleanup and oily wastewater treatment applications.¹¹ Zhang and Guo presented an immersion technique for achieving super amphiphilic in-air and under-liquid dual superlyophobicity on a hydrophobic nitrocellulose membrane at the same time (Figure 7). PDA-modified NC membrane was created using a straightforward impregnation approach with polyamine and polyethyl enimine as modification reagents. To generate a dense polymer layer, dopamine was deposited on the nitrocellulose membrane. The dopamine layer increased the NC membrane's underwater oleophobicity/under-oil hydrophobicity to underwater superoleophobicity/under-oil superhydrophobicity. The under-liquid dual superlyophobicity of the NC membrane is mostly due to the synergistic impact of the nitrocellulose and the dopamine coating. The PDA-modified NC membrane can efficiently separate an emulsion as well as an oil/water mixture on demand. A light oil/water mixture and a heavy oil/water mixture can be efficiently separated using the produced NC membrane.¹⁰³

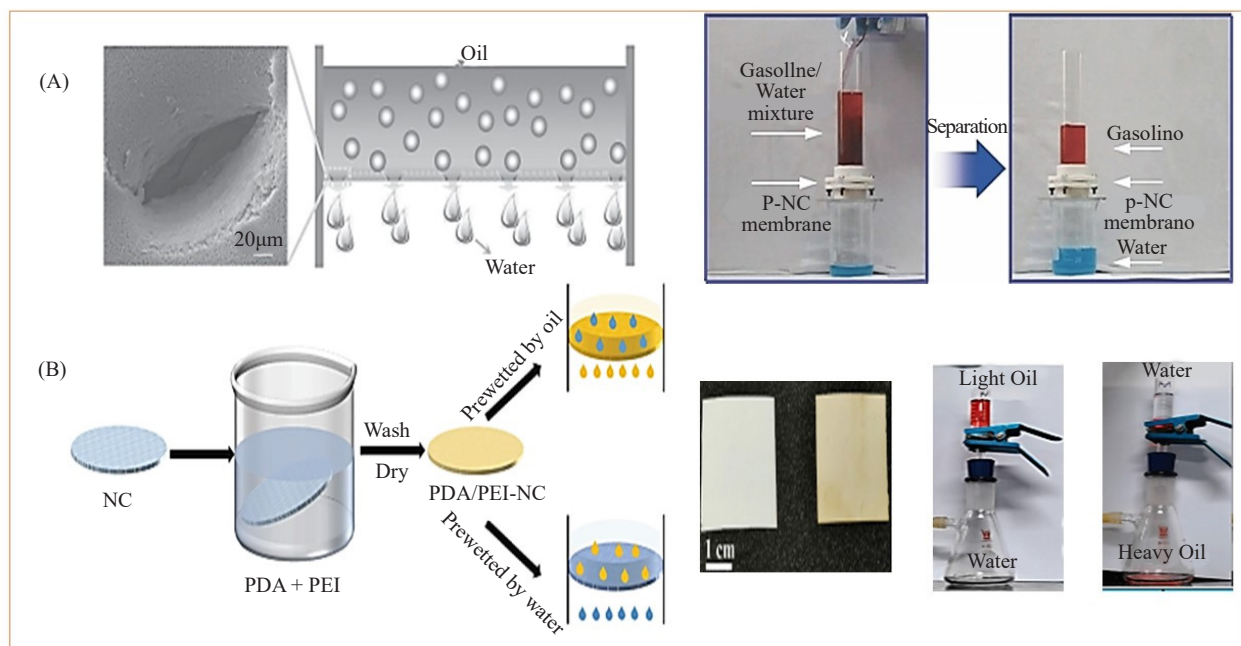


Figure 7. (A) oil/water separation studies using p-NC membrane (Reprinted with permission from reference.¹¹) (B) Dopamine-modified NC membranes on demand separation of oil/water mixtures (Reprinted with permission from¹⁰³)

2.4.4.2 Sensors

The development of a nitrocellulose membrane biosensor with a simple fluorescence technique facilitated the sensitive detection of lead (II) in spiked river water. Streptavidin was conjugated to the nitrocellulose membrane's surface using glutaraldehyde, and a DNA probe was then immobilized using a biotin modifier. In the presence of potassium ions, the biotinylated DNA probe can fold into a G-quadruplex structure, which selectively binds to N-methyl mesoporphyrin IX and produces a bright fluorescence signal. Lead (II) can cause the G-quadruplex to alter conformation and adopt a more compact shape. This causes the release of the potassium ion and N-methyl mesoporphyrin IX with a corresponding decrease in the fluorescence signal. The biosensor showed exceptional selectivity for lead (II) over other metal ions and a detection limit as low as 10 nM.¹⁰⁴

In the manufacturing of polycarbonate, polystyrene resins, epoxy resins, plastics, polysulfones, and polyesters used as plasticizers, fire retardants and coating agents, bisphenol A (BPA) is an essential organic component. BPA is reported to have alarming health impacts including adult reproductive problems, obesity, cancer, and neurotoxicity, even at low doses. A fluorometric nanosensor for BPA detection was developed in literature.¹⁰⁵ On molecularly imprinted nanoparticles, graphene quantum dots (GQDs) were immobilized and subsequently applied on nitrocellulose paper to fabricate the fluorometric nanosensor. The GQDs exhibit blue fluorescence, which is diminished in the presence of BPA. The stripe was used to determine BPA in (spiked) tap water and seawater. It is also mentioned that, by using alternative functional monomers for the molecular imprinting processes, the sensing system can be easily extended to monitor not only contaminants but also biomolecules. Wu et al. also investigated the factors affecting the degradation of BPA by NC membrane under illumination.¹⁰⁶

Similarly, nitrocellulose and multilayer graphene were utilized for the preparation of tunable temperature alarm sensors to monitor early high-temperature risks (Figure 8). The graphene/NC alarm sensor remains electrically insulated at low temperatures but becomes electrically conducting when exposed to high temperatures, such as during a flame assault. The fast chemical reaction of NC limits its response time to a few seconds. The alarm sensor also has prospective uses in both indoor and outdoor settings since the response temperature and time of the alarm sensor can be adjusted by graphene/NC ratios to lower the fire risk of various combustible materials in different fire-prone conditions. Due to its better flame retardancy property, the sensor is efficient in functioning in paint, wallpaper, and other composites as well as in harsh environments like underwater and vacuum.¹⁰⁷

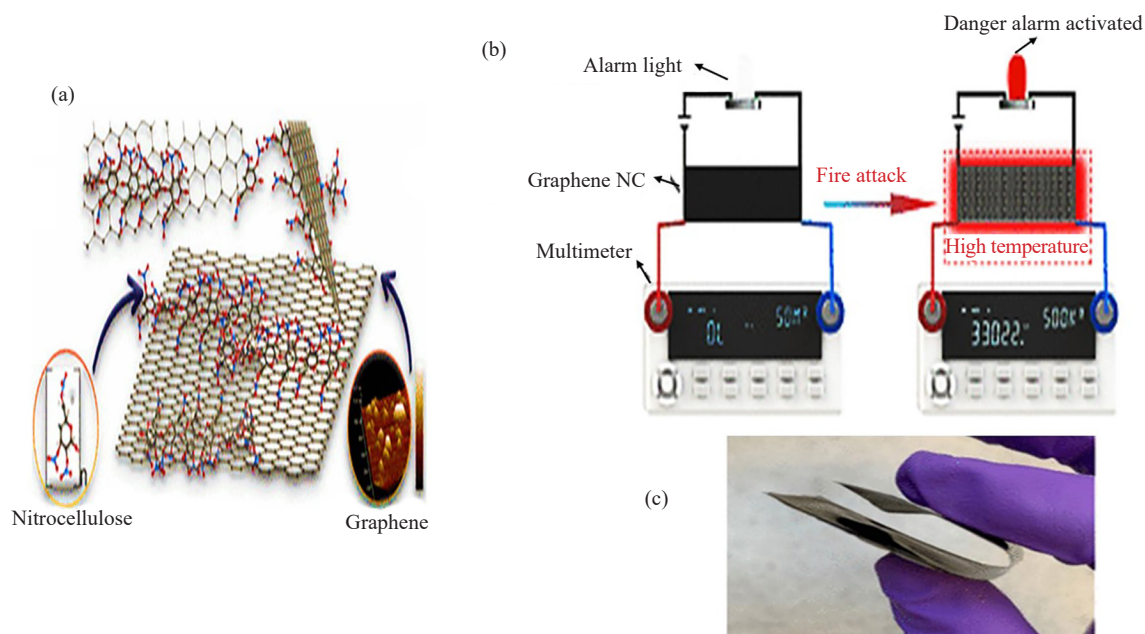


Figure 8. (a) Schematic illustration of GNC membrane and (b) flame detection processes using the alcohol burner and (c) photograph showing the flexibility of graphene/NC sensor. Adopted from reference¹⁰⁷

2.4.4.3 Triboelectric nanogenerator (TENGs)

A novel power-generation technique called a triboelectric nanogenerator transforms mechanical energy into electrical energy. The paper-based Triboelectric nanogenerator (P-TENG), which generates a current and voltage utilizing a sustainable kind of green electronics, is described in literature¹⁰⁸ employing multiple triboelectric polarities (Figure 9). As the friction layers of the PTENG, crepe cellulose paper (CCP) and nitrocellulose membrane (NCM) are employed. It was possible to attain excellent voltage, current, power, and robustness values. The characteristics of P-TENG were greatly improved using NCM as the negative triboelectric material to achieve voltage outputs of about 194 V, when paired with CCP as positive triboelectric material and layered in 3 layers.

2.4.4.4 Dye removal

Environmental pollution from the discharge of azo dye wastewater has increased over the past few years, leading to major environmental issues. The topic of organic wastewater treatment offers a wide range of potential applications for NC membranes. For practical applications and understanding the degradation mechanism, an in-depth study on the organic pollutant degradation by NCM is of major value.¹⁰⁹ Li Wu and his team investigated a new advanced oxidation technology to treat azo dyes. They set up a photodegradation experiment under a simulated light source, using acid orange 8 as the target pollutant and NCM as the source of active oxygen (Figure 10). The effects of light intensity, solution pH, temperature, membrane area, initial concentration, and water composition on NCM photodegradation were also investigated. With a rate constant of $1.94 \times 10^{-3} \text{ min}^{-1}$, the hydroxyl radicals generated by NCM accelerated the photodegradation of acid orange 8 under simulated sunlight. Within a particular range, the degradation effect reduced as light intensity decreased, and acidic conditions were helpful for acid orange 8 photolysis. The ideal reaction conditions sustained by the team were: a membrane area of 17.35 cm^2 , a light intensity of 481 mW/m^2 , a water bath temperature of 30°C , and a pH value of 3.¹¹⁰

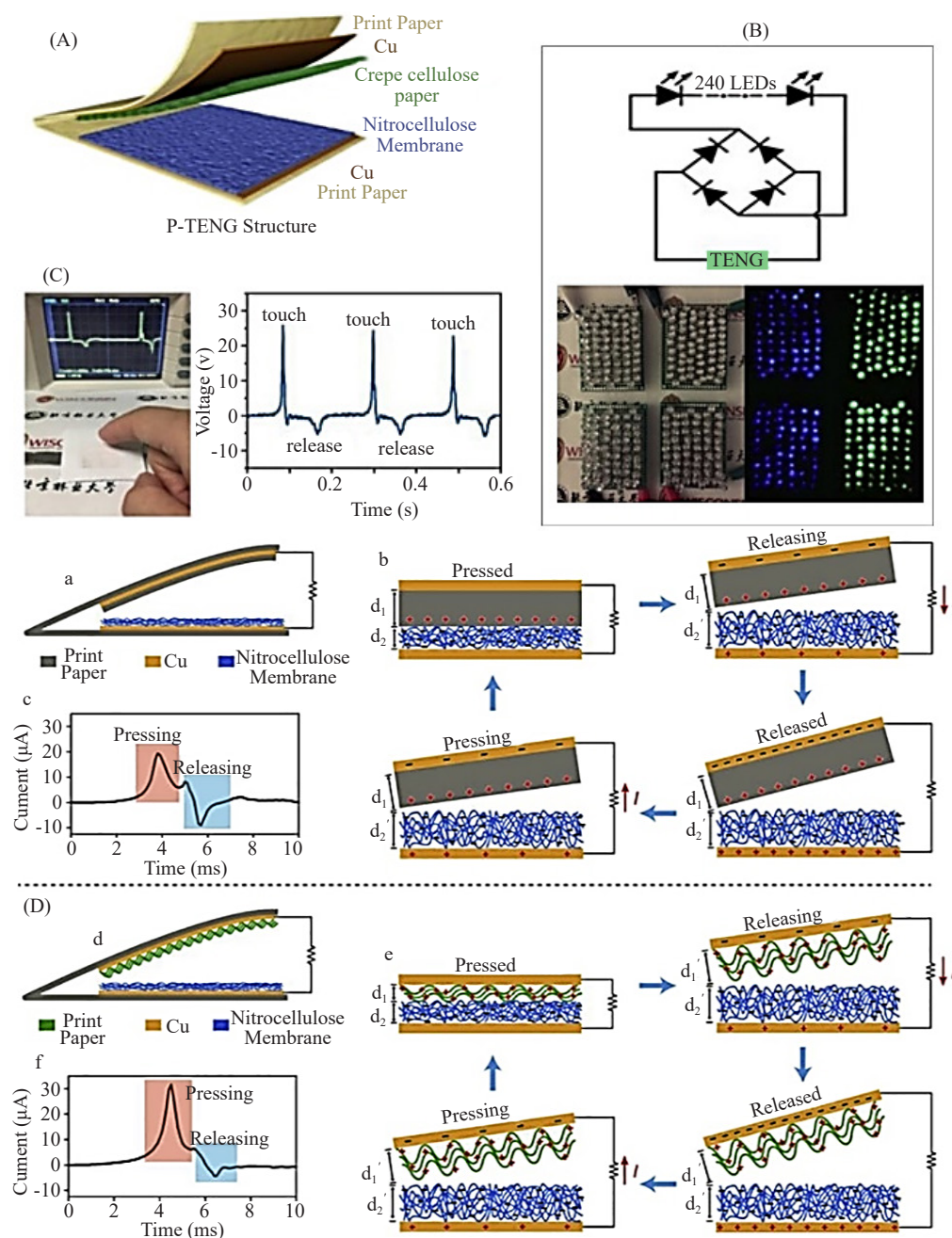


Figure 9. (A) Structure of p-TENG, (B) P-TENG lit up 240 LEDs through a bridge rectifier under repeated pressing, (C) Demonstration of self-powered touch sensing using the P-TENG and (D) Schematic illustration of the P-TENG working principle. (a, b) Working principle of the P-TENG containing print paper as the positive friction layer, and its (c) short-circuit current output under one cycle of pressing and releasing. (d, e) Working principle of the P-TENG containing three layers of CCP as the positive friction layer and its (f) short-circuit current output under one cycle of pressing and releasing. Reprinted with permission from reference¹⁰⁸

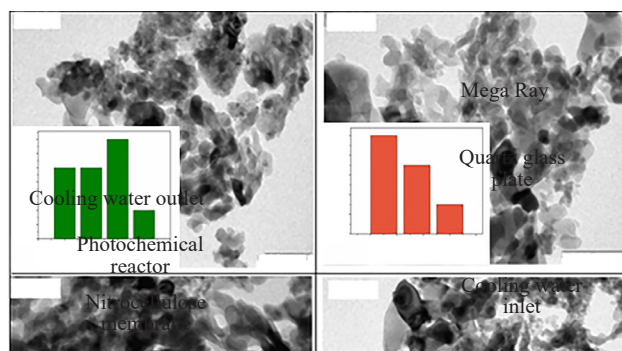


Figure 10. Schematic illustration of photoreactor. (Adopted from ref¹⁰²)

3. Future perspectives of NC

The most recent nitrocellulose research discoveries and innovations have demonstrated promising advancements in a variety of fields, including synthesis, characterization, functionalization, and applications. Scientists have been exploring eco-friendly and sustainable methods for synthesizing nitrocellulose, including the adoption of environmentally friendlier solvents, alternative energy sources, and improved reaction conditions. These innovations seek to reduce the environmental footprint associated with nitrocellulose production while preserving its desired properties. Another topic that has received a lot of attention is the functionalization of nitrocellulose, which involves introducing nanoparticles, polymers, or additives to change its mechanical, thermal, or chemical properties.^{111,112} Improved adhesion, flame retardancy, antibacterial activity, and responsiveness to external stimuli have all been demonstrated with functionalized nitrocellulose. These advancements pave the way for customized applications in fields such as improved coatings, flexible electronics, smart materials, and biomedical devices. Because of its biocompatibility and regulated breakdown, nitrocellulose has received interest in the biomedical field. Researchers have investigated its application potential in tissue engineering scaffolds,¹¹³ wound dressings,^{94,95} drug delivery systems,^{114,115} and biosensors.¹¹⁶ Nitrocellulose-based materials have shown potential in promoting cell development, delivering medicinal drugs in controlled doses, and detecting specific biomarkers. Using nitrocellulose-based materials, additive manufacturing, including 3D printing,¹¹⁷ has been used to construct complicated structures. In addressing concerns regarding printability and material characteristics, researchers fine-tuned printing parameters, developed suitable ink formulations, and explored post-processing techniques. This investigation utilizes nitrocellulose to craft intricate designs, tailored shapes, and functional devices, offering potential applications in microfluidics, electronics, and tissue engineering.

4. Challenges and limitations

While nitrocellulose holds significant potential in various applications, there are several limitations and challenges that need to be addressed for its current use and future applications: NC is highly flammable and poses significant safety risks if not handled properly. Its explosive nature requires stringent safety protocols and regulations, increasing the complexity and cost of its handling, storage, and transportation.³¹ Ensuring safe practices and mitigating potential hazards remain crucial challenges in utilizing nitrocellulose. Developing more biodegradable and environmentally friendly formulations of nitrocellulose is essential to reduce its long-term environmental footprint. Nitrocellulose is prone to degradation over time due to factors such as moisture, temperature fluctuations, and exposure to light. Expanding its applications requires enhancing its stability and aging resistance. Achieving compatibility with certain polymers, additives, or fabrication techniques may require careful formulation design or modifications. The selection of suitable processing methods and optimization of process parameters for specific applications can be complex and also require extensive research and development. Nitrocellulose production involves several steps and requires specialized equipment and raw materials. The cost associated with manufacturing, purification, and quality control can be relatively

high, limiting its widespread use in certain industries. Ensuring a consistent and affordable supply of high-quality nitrocellulose remains a challenge.

5. Conclusions

In conclusion, this review article has given a comprehensive overview of the properties, synthesis, modifications, and applications of nitrocellulose. Nitrocellulose, with its unique properties and versatility, has found diverse applications across industries such as military, coatings, healthcare, and electronics. This study reviewed, recent advances in the application fields of nitrocellulose research. A new development in the realm of research is that scientists are investigating uses for nitrocellulose other than utilizing its explosive properties. Further research is needed to develop safer, more environment-friendly formulations, improve stability and aging resistance, enhance compatibility with other materials, optimize processing techniques, and reduce costs. Finally, establishing clear regulatory frameworks and standards that balance safety and innovation will be crucial to facilitating the responsible use and future applications of nitrocellulose.

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Conflict of interest

The authors declare no competing financial interest.

References

- [1] Lavanya, D.; Kulkarni, P.; Dixit, M.; Kanth Raavi, P.; Vamsi Krishna, L. *IJDFR* **2011**, *2*, 19-38.
- [2] Xu, J.; Sagnelli, D.; Faisal, M.; Perzon, A.; Taresco, V.; Mais, M.; Giosafatto, C. V.; Hebelstrup, K. H.; Ulvskov, P.; Jørgensen, B.; et al. *Carbohydr Polym.* **2021**, *253*, 117277.
- [3] Eichhorn, S. J.; Dufresne, A. A.; Aranguren, A. M.; Marcovich, A. N. E.; Capadona, A. J. R.; Rowan, A. S. J.; Weder, A. C.; Thielemans, A. W.; Roman, A. M.; Renneckar, A. S.; et al. *J. Mater. Sci.* **2010**, *45*, 1-33.
- [4] Stephen, A. M.; Phillips, G. O.; Williams, P. A. *Food Polysaccharides and Their Applications*; CRC/Taylor & Francis, 2006.
- [5] Gensh, K. V.; Kolosov, P. V.; Bazarnova, N. G. *Russ. J. Bioorg. Chem.* **2011**, *37*, 814-816.
- [6] Akhavan, J. *The Chemistry of Explosives, Royal Society of Chemistry, 4th Edition*; UK, 2022.
- [7] Bussiere, P. O.; Gardette, J. L.; Therias, S. *Polym. Degrad. Stab.* **2014**, *107*, 246-254.
- [8] Liu, Y.; Shao, Z.; Yuan, J.; Jia, S.; Wang, F.; Li, Y.; Guo, B.; Yang, Z.; Zuo, Y. *Cent. Eur. J.* **2021**, *18*, 448-476.
- [9] Sullivan, F.; Simon, L.; Ioannidis, N.; Patel, S.; Ophir, Z.; Gogos, C.; Jaffe, M.; Tirmizi, S.; Bonnett, P.; Abbate, P. *Ind. Eng. Chem. Res.* **2018**, *57*, 1883-1893.
- [10] Chiang, L. K. *Prospects and Utilization of Tropical Plantation Trees*; CRC Press: London, 2019.
- [11] Gao, X.; Xu, L. P.; Xue, Z.; Feng, L.; Peng, J.; Wen, Y.; Wang, S.; Zhang, X. *Adv. Mater.* **2014**, *26*, 1771-1775.
- [12] Hwang, H.; ho Shin, J.; Lee, K. Y.; Choi, W. *Appl. Surf. Sci.* **2018**, *428*, 422-431.
- [13] Weng, X.; Neethirajan, S. *Microchimica Acta.* **2017**, *184*, 4545-4552.
- [14] Li, Y.; Yang, H.; Hong, Y.; Yang, Y.; Cheng, Y.; Chen, H. *J. Therm. Anal. Calorim.* **2017**, *130*, 1063-1068.

- [15] Song, Y.; Kim, S.; Heller, M. J. *ACS Appl. Mater. Interfaces* **2017**, *9*, 42302-42312.
- [16] Su, X.; Chen, Z.; Zhang, Y. *Chem. Pap.* **2017**, *71*, 2145-2152.
- [17] Gismatulina, Y. A.; Budaeva, V. V.; Sakovich, G. V. *Russ. Chem. Bull.* **2015**, *64*, 2949-2953.
- [18] Luo, L.; Jin, B.; Xiao, Y.; Zhang, Q.; Chai, Z.; Huang, Q.; Chu, S.; Peng, R. *Polym. Test.* **2019**, *75*, 337-343.
- [19] Ahmad, A. L.; Low, S. C.; Abd Shukor, S. R.; Ismail, S. R. *Ind. Eng. Chem. Res.* **2009**, *48*, 3417-3424.
- [20] Jia, P.; Li, Z.; Wang, X.; Xu, F.; You, M.; Feng, S. *ICHMT* **2023**, *143*, 106729.
- [21] Yao, E.; Zhao, N.; Qin, Z.; Ma, H.; Li, H.; Xu, S.; An, T.; Yi, J.; Zhao, F. *Nanomater* **2020**, *10*, 725.
- [22] Liu, C.; Zhu, S.; Wu, J.; Tao, L.; Wang, W. *IOP Conference Series: Earth and Environmental Science*; IOP Publishing, 2020.
- [23] Cheung, C. *Studies of the Nitration of Cellulose-Application in New Membrane Materials*; Doctoral dissertation, University of British Columbia. 2014.
- [24] Saunders, C. W.; Taylor, L. T. *J. Energ. Mater.* **1990**, *8*, 149-203.
- [25] Heinze, T.; El Seoud, O. A.; Koschella, A. *Cellulose Derivatives: Synthesis, Structure, and Properties*; Springer, 2018.
- [26] Wang, Y.; Wang, X.; Xie, Y.; Zhang, K. *Cellulose* **2018**, *25*, 3703-3731.
- [27] Ángeles Fernández de la Ossa, M.; López-López, M.; Torre, M.; García-Ruiz, C. *TrAC Trends in Anal. Chem.* **2011**, *30*, 1740-1755.
- [28] Grau, H. *Surface Chemistry and Surface Properties of Energetic Surface Chemistry and Surface Properties of Energetic Nitrocellulose (NC)*; Doctoral dissertation, 2020.
- [29] Alinat, E.; Delaunay, N.; Archer, X.; Mallet, J. M.; Gareil, P. *J. Hazard Mater.* **2015**, *286*, 92-99.
- [30] Li, Y. Y.; Wang, B.; Ma, M. G.; Wang, B. *Int. J. Polym. Sci.* **2018**, *13*, 2018.
- [31] Liu, J. *Nitrate Esters Chemistry and Technology*; Springer. 2019.
- [32] Luo, Q.; Ren, T.; Shen, H.; Zhang, J.; Liang, D. *Combustion Science and Technology* **2018**, *190*, 579-590.
- [33] Mattar, H.; Baz, Z.; Saleh, A.; Shalaby, A. S.; Elsayed Azzazy, A.; Salah, H.; Ismail, I. *WEFEJ* **2020**, *1*, 1-15.
- [34] Lipin, V. A.; Petrova, I. I.; Sofronova, E. D. *Fibre. Chem.* **2020**, *52*, 201-204.
- [35] Liu, Y.; Shao, Z.; Wang, W.; Li, L.; Lv, Y.; Sun, J. *Cent. Eur. J.* **2018**, *15*, 554-571.
- [36] Quinn, M. J. *Wildlife Toxicity Assessments for Chemicals of Military Concern*; Elsevier, 2015, pp 217-226.
- [37] Nikolsky, S. N.; Zlenko, D. V.; Melnikov, V. P.; Stovbun, S. V. *Carbohydr. Polym.* **2019**, *204*, 232-237.
- [38] Trache, D.; Khimeche, K.; Mezroua, A.; Benziane, M. *J. Therm. Anal. Calorim.* **2016**, *124*, 1485-1496.
- [39] Golubev, A. E.; Kuvshinova, S. A.; Burmistrov, V. A.; Koifman, O. I. *Russ. J. Gen. Chem.* **2018**, *88*, 368-381.
- [40] Okada, K.; Saito, Y.; Akiyoshi, M.; Endo, T.; Matsunaga, T. *PEP* **2021**, *46*, 962-968.
- [41] Tsai, Y. T.; Yang, Y.; Huang, H. C.; Shu, C. M. *AIChE J.* **2020**, *66*, e16888.
- [42] Zhao, B. *Nat. Hazards* **2016**, *84*, 707-713.
- [43] Luo, Q.; Ren, T.; Shen, H.; Zhang, J.; Liang, D. *Combust. Sci. Technol.* **2018**, *190*, 579-590.
- [44] Raeisi, M.; Najafpour, G. D. *IJEE* **2011**, *2*, 221-228.
- [45] Stovbun, S. V.; Nikol'skii, S. N.; Mel'nikov, V. P.; Mikhaleva, M. G.; Litvin, Y. A.; Shchegolikhin, A. N.; Zlenko, D. V.; Tverdislov, V. A.; Gerasimov, D. S.; Rogozin, A. D. *Russ. J. Phys. Chem.* **2016**, *10*, 245-259.
- [46] Gismatulina, Y.; Korchagina, A.; Budaeva, V.; Sakovich, G. *MATEC Web of Conferences*; EDP Sciences, 2018; pp 243.
- [47] Gismatulina, Y. A.; Budaeva, V. V.; Sakovich, G. V. *PEP* **2018**, *43*, 96-100.
- [48] Gismatulina, Y. A.; Budaeva, V. V.; Sakovich, G. V. *Russ. Chem. Bull.* **2016**, *65*, 2920-2924.
- [49] Khai, D. M.; Nhan, P. D.; Hoanh, T. D. *The 5th Academic Conference on Natural Science for Young Scientists*; Master and PhD, 2017.
- [50] Beroual, M.; Boumaza, L.; Mehelli, O.; Trache, D.; Tarchoun, A. F.; Khimeche, K. *J. Polym. Environ.* **2021**, *29*, 130-142.
- [51] Nickel, R.; Walker, R. *Method for Manufacture of Microcrystalline Nitrocellulose*; U.S. Patent Application No. 11/058,677, 2006.
- [52] Chawla, P. R.; Bajaj, I. B.; Survase, S. A.; Singhal, R. S. *Food Technol. Biotechnol* **2009**, *47*, 107-124.
- [53] Islam, M. U.; Ullah, M. W.; Khan, S.; Shah, N.; Park, J. K. *Int. J. Biol. Macromol.* **2017**, *102*, 1166-1173.
- [54] Blanco, A.; Monte, M. C.; Campano, C.; Balea, A.; Merayo, N.; Negro, C. *HNIA* **2018**, *74*-126.
- [55] Sun, D. P.; Ma, B.; Zhu, C. L.; Liu, C. S.; Yang, J. Z. *J. Energ. Mater.* **2010**, *28*, 85-97.
- [56] Jamal, S. H.; Roslan, N. J.; Shah, N. A. A.; Noor, S. A. M.; Ong, K. K.; Yunus, W. M. Z. W. *Mater. Today: Proc. Elsevier* **2019**, *29*, 185-189.
- [57] Meng, X.; Pu, C.; Cui, P.; Xiao, Z. *PEP* **2020**, *45*, 1194-1203.

- [58] Meng, X.; Xiao, Z. *PEP* **2018**, *43*, 300-307.
- [59] Zhang, X.; Weeks, B. L. *J. Hazard Mater.* **2014**, *268*, 224-228.
- [60] Yan, S.; Jian, G.; Zachariah, M. R. *ACS Appl. Mater. Interfaces* **2012**, *4*, 6432-6435.
- [61] Sovizi, M. R.; Hajimirsadeghi, S. S.; Naderizadeh, B. *J. Hazard. Mater.* **2009**, *168*, 1134-1139.
- [62] Muvhiwa, R.; Mawere, E.; Moyo, L. B.; Tshuma, L. *Heliyon* **2021**, *7*, e07598-e07598.
- [63] Fabbri, P.; Messori, M. *Modification of Polymer Properties*; Elsevier, 2017; pp 109-130.
- [64] Romanova, S. M.; Mukhetdinova, A. M.; Fridland, S. V. *Izvestiya Vysshikh Uchebnykh Zavedenii, Khimiya i Khimicheskaya Tekhnologiya* **2012**, *55*, 68.
- [65] Romanova, S. M.; Treskova, V. I.; Gilmanov, R. Z. *Bulletin of Kazan Technological University*, **2012**, 67-70.
- [66] Romanova, S. M.; Madyakina, A. M.; Fatykhova, L. A.; Fridland, S. V. *Russ. J. Gen. Chem.* **2013**, *83*, 58-62.
- [67] Romanova, S. M.; Fatykhova, L. A. *Izvestiya Vysshikh Uchebnykh Zavedenii. Seriya Khimiya i Khimicheskaya Tekhnologiya*. **2014**, *57*.
- [68] Li, S.; Li, Y.; Ding, Y.; Yuan, Y.; North, L.; Xiao, Z. *Cellulose* **2022**, *15*, 8103-8115.
- [69] Gotlib, E. M. *Plastifikatsiya Polyarnykh Kauchukov, Lineinykh I Setchatykh Polimerov (Plasticization of Polar Rubbers, Linear and Network Polymers)*; Gos. Tekhnol. Univ. 2008.
- [70] Comtois, E.; Favis, B. D.; Dubois, C. *Polym. Eng. Sci.* **2020**, *60*, 2301-2313.
- [71] Wu, Y.; Ge, Z.; Luo, Y. *J. Therm. Anal. Calorim.* **2016**, *124*, 107-115.
- [72] Qi, X.; Yan, N.; Li, H. Y.; Zhao, Y.; Liu, P. J.; Yan, Q. L. *Cellulose* **2022**, *29*, 1307-1314.
- [73] Gańczyk, K.; Specjalska Cieślak, K.; Jakubczak, M.; Drożdżewska, K.; Szymańska Tomaszewski, W.; Prasula, P. *PEP* **2023**, *48*, e202200305.
- [74] Fernández, J. G.; Almeida, C. A.; Fernández-Baldo, M. A.; Felici, E.; Raba, J.; Sanz, M. I. *Talanta*. **2015**, *146*, 237-243.
- [75] Tang, R.; Xie, M. Y.; Li, M.; Cao, L.; Feng, S.; Li, Z.; Xu, F. *Appl. Mater. Today* **2022**, *26*, 101305.
- [76] Tang, R. H.; Liu, L. N.; Zhang, S. F.; Li, A.; Li, Z. *Microchimica Acta*. **2019**, *186*, 1-8.
- [77] Moniruzzaman, M.; Houlihan, E.; Parker, M.; Wilson, I. *Journal of Energetic Materials* **2023**, 1-12.
- [78] Shokri, J.; Adibki, K. *Cellulose-Medical, Pharmaceutical and Electronic Applications*; InTech, 2013.
- [79] Agrawal, J. P. *High Energy Materials: Propellants, Explosives and Pyrotechnics*; John Wiley & Sons, 2010.
- [80] Sullivan, F.; Simon, L.; Ioannidis, N.; Patel, S.; Ophir, Z.; Gogos, C.; Jaffe, M.; Tirmizi, S.; Bonnett, P.; Abbate, P. *AIChE Journal* **2020**, *66*, e16234.
- [81] Tarchoun, A. F.; Trache, D.; Klapötke, T. M.; Abdelaziz, A.; Derradj, M.; Bekhouche, S. *Def. Technol* **2022**, *18*, 537-546.
- [82] De Klerk, W. P. C. *PEP* **2015**, *40*, 388-393.
- [83] Li, G.; Jin, B.; Chai, Z.; Ding, L.; Chu, S.; Peng, R. *Polym. Degrad. Stab.* **2020**, *172*, 109061.
- [84] Sun, Z. D.; Fu, X. L.; Yu, H. J.; Fan, X. Z.; Ju, X. H. *J. Hazard. Mater.* **2017**, *339*, 401-408.
- [85] Lindblom, T. *Propellants, Explosives, Pyrotechnics: An International Journal Dealing with Scientific and Technological Aspects of Energetic Materials* **2002**, *27*, 197-208.
- [86] Sabatini, J. J.; Johnson, E. C. *ACS Omega*. **2021**, *6*, 11813-11821.
- [87] Tarchoun, A. F.; Trache, D.; Klapötke, T. M.; Khimeche, K. *J. Chem. Eng.* **2020**, *400*, 125960.
- [88] Tarchoun, A. F.; Trache, D.; Klapötke, T. M.; Krumm, B. *Fuel* **2020**, *277*, 118258.
- [89] Tarchoun, A. F.; Trache, D.; Klapötke, T. M.; Krumm, B.; Khimeche, K.; Mezroua, A. *Carbohydr. Polym.* **2020**, *249*, 116820.
- [90] Tarchoun, A.; Trache, F.; Thomas, D.; Klapötke, M.; Slimani, K.; Belouettar, B.; Abdelaziz, A.; Bekhouche, S.; Bessa, W. *PEP* **2022**, *47*, e202100293.
- [91] Zhong, Y.; Ravi, V. B. *JCR* **2005**, *106*, 309-318.
- [92] Gönüllü, Ü.; Şaki, D. *Trop. J. Pharm. Res.* **2017**, *16*, 2785-2792.
- [93] Hussain, Z.; Thu, H. E.; Shuid, A. N.; Katas, N.; Hussain, F. *Curr. Drug. Targets*. **2017**, *19*, 527-550.
- [94] Pudžiuvelytė, L.; Drulytė, E.; Bernatoniienė, J. *Polymers (Basel)* **2023**, *15*, 1057.
- [95] Du, S.; Liu, B.; Li, Z.; Tan, H.; Qi, W.; Liu, T.; Qiang, S.; Zhang, T.; Song, F.; Chen, X.; et al. *ACS Appl. Bio. Mater.* **2021**, *4*, 4522-4531.
- [96] Wang, X.; Xue, C. H.; Yang, D.; Jia, S. T.; Ding, Y. R.; Lei, L.; Gao, K. Y.; Jia, T. T. *RSC Adv.* **2021**, *11*, 26493-26501.
- [97] Stoye, D. *Freitag, Eds. W. Paints, Coatings and Solvents*; John Wiley & Sons, 2008.
- [98] Gumel, S. M.; Dambatta, B. B. *IJCEA* **2013**, 249-253.
- [99] Apolinário, L. D.; Colonetti, E.; Cercená, R.; da Silveira Santos, F.; Cargnin, M.; Dal-Bó, A. G. *J. Appl. Polym.*

Sci. **2020**, *137*, 49237.

- [100]Secor, E. B.; Gao, T. Z.; Islam, A. E.; Rao, R.; Wallace, S. G.; Zhu, J.; Putz, K. W.; Maruyama, B.; Hersam, M. C. *Chem. Mater.* **2017**, *29*, 2332-2340.
- [101]Keimel, F. A. *Handbook of Adhesive Technology*; USA, 2003; pp 1-12.
- [102]Tian, Y.; Guo, K.; Bian, X. F.; Wang, T. W.; Chen, S. H.; Sun, J. X. *Surf. Coat. Technol.* **2017**, *328*, 444-450.
- [103]Zhang, R.; Guo, Z. *Biomater Sci.* **2021**, *9*, 5559-5568.
- [104]Peng, L.; Xi, Q.; Wang, X.; Kan, Y.; Jiang, J.; Yu, R. *Anal. Lett.* **2014**, *47*, 2341-2349.
- [105]Üzek, R.; Sari, E.; Şenel, S.; Denizli, A.; Merkoçi, A. *Microchimica Acta.* **2019**, *186*, 1-10.
- [106]Wu, L.; Jin, X.; Zhao, T.; Wang, H.; Dai, Z. *J. Environ. Sci.* **2021**, *100*, 193-202.
- [107]Wei, W.; Yi, Y.; Song, J.; Chen, X.; Li, J. *ACS Appl. Mater. Interfaces* **2022**, *14*, 13790-13800.
- [108]Chen, S.; Jiang, J.; Xu, F.; Gong, S. *Nano Energy* **2019**, *61*, 69-77.
- [109]Tai, C.; Zhang, S.; Yin, Y.; Dai, Z.; Li, Y. B.; Jiang, G. B.; Cai, Y.; Huang, C. H.; Shi, J. B. *ChemSusChe* **2018**, *11*, 843-847.
- [110]Wu, L.; Fu, J.; Song, B.; Zhao, T.; Liu, H.; Li, X. *Front. Environ. Sci.* **2022**, *10*, 992202.
- [111]Ramar, P.; Samanta, D. *ACS Appl. Polym. Mater.* **2022**, *4*, 8900-8912.
- [112]Grau, H.; Fadeev, H. J. *Colloid. Interface. Sci.* **2019**, *547*, 145-152.
- [113]Li, A.; Wang, Y.; Deng, L.; Zhao, X.; Yan, Q.; Cai, Y.; Lin, J.; Bai, Y.; Liu, S.; Zhang, Y. *Cytotechnology* **2013**, *65*, 71-81.
- [114]Sumantakul, S.; Harley, W. E.; Remcho, V. T. *Sens. Actuators B Chem.* **2023**, *389*, 133867.
- [115]Pawar, K.; Rajendra Shinde, D.; Dhondu Shivgan, D.; Namdev Sherker, S.; Devdendra Sharma, S.; Ramasare Sharma, R.; Takarkhede, S. *WJBPHS* **2020**, 2582-5542.
- [116]Tang, R.; Xie, M. Y.; Li, M.; Cao, L.; Feng, S.; Li, Z.; Xu, F. *Appl. Mater. Today* **2022**, *26*, 101305.
- [117]Jurischka, C.; DInter, F.; Efimova, A.; Weiss, R.; Schiebel, J.; Schulz, C.; Fayziev, B.; Schierack, P.; Fischer, T.; Rödiger, S. *Clin. Hemorheol. Microcirc.* **2020**, *75*, 57-84.