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An Overview of Unlocking the Potential of Carboxymethyl Xylan

Samit Kumar[1*], Amit Kumar[2], Sundaram Khare[1], Shailendra Yadav[1], Dinesh Kumar Mishra[1] and Nand Kishor bhagat[3]

[1]Department of Chemistry, Faculty of Basic Sciences, AKS University, Satna-485001 (MP), India

[2]Department of Dairy Chemistry, G.N. Patel College of Dairy Science, Kamdhenu University, Gandhinagar, India

[3]Department of Chemistry, Govt. (Auto) PG College, Satna, (M.P.), India

*Corresponding author: samitiitr07@gmail.com; Mb No.: +91-9407858347

ORCID: Samit Kumar: https://orcid.org/0009-0002-1563-6995

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Abstract

Xylan is the second most abundant and renewable biopolymer component of plant cell walls, has attracted a lot of attention in a variety of industrial uses. Chemical alteration known as carboxymethylation has been identified as a key strategy for improving xylan's functional characteristics and expanding its range of applications. This review explores the principles, techniques, and applications of xylan carboxymethylation. First, the basic ideas behind the structure and characteristics of xylan are explained. Next, carboxymethylation techniques are thoroughly examined, along with reaction mechanisms and important variables. This review highlights the importance of carboxymethylation as a tactical method for customizing xylan for a variety of industrial uses, opening the door for more developments and breakthroughs in this field.

Keywords: Xylan; Carboxymethyl xylan (CMX); Degree of Substitution (DS); sodium monochloroacetate (SMCA); Thermal stability

1. Introduction

1.1. Briefly introduce xylan and its derivatives

Utilization of renewable resources is a desirable substitute for lowering the need for materials derived from fossil fuels. The primary renewable source of raw materials for the production of biofuels, chemicals, and biomaterials is biomass residues which is primarily derived from plant sources. Among all renewable resources, lignocellulosic biomasses are the most abundant as they come from lower plants, forests, and agro-industry residues [1,2]. The primarily lignocellulosic materials present in plant cell walls are consist of cellulose (40–50%), hemicelluloses (25–35%), and lignin (15–25%), along with other lignocellulosic components such as extractives, inorganics, pectins, proteins, etc. The development of biopolymers and chemically modified functional materials, which can be utilized in films, coatings, and hydrogels, is becoming more and more important. Hemicelluloses are the second most abundant polysaccharides in nature, after cellulose [3-5]. Hemicelluloses have a lower degree of polymerization (DP) than cellulose. They are composed of branching amorphous chains that comprise pentoses, hexoses, and acids. Hemicellulose also have pitiable chemical and thermal stabilities than cellulose [6]. The primary source of hemicelluloses is xylan, which comes from softwood (7–12%), grasses and grains (20–35%), and hardwood (15–30%). It means it comprises almost half of the weight of non-woody plants and 25–35 percent of the weight of woody biomass [7]. The polymeric backbone of xylan is composed of xylose repeating units, which are connected by β-1-4 linkage [8]. Recently, xylan has gained attention as a potential valuable biopolymeric material due to its abundance of hydroxyl groups and variety of hardwood species [9-10].

Xylans have less industrial uses than cellulose and starch because of their high water solubility [11], albeit this could be remedied by the characteristics and use of the finished product. If xylans are made as insoluble materials via chemical modification, then they can be used to make biopolymer films, drug release products, viscosity-improving additives, hydrophobic barriers, packaging films, paper additives, emulsifiers for food and cosmetics and adsorbents for water purification [11]. The chemical modification of xylan leads to value-added products. Oleoylation [12], laurolyation [13], acetylation [14], carboxymethylation [15], and cationization [16-17] are some of these chemical alteration processes.

1.2. Importance of carboxymethyl xylan in various industries

Carboxymethylation is the most adaptable and appealing method among chemical modifications of xylans for producing high value-added products from bio-based materials that can be used in the paint, paper, textile, and pharmaceutical industries [18-19]. This is because carboxymethylation does not require the use of severe modifying conditions or solvents (such as ethanol), making it an industrially desirable procedure. Thus, carboxymethylation represents a useful way to produce soluble derivatives with anionic functions from hemicelluloses, when carried out in different suspension media. The carboxymethyl xylan is an anionic polymeric ether derived from the xylan, in which the hydroxyl groups of xylan are partially substituted by carboxymethyl groups. Total substitution is not possible because of the branched D-xylopyranose units. The degree of substitution (DS) reaches variable values and the final product usually contains non-substituted, mono- or di-substituted in the xylan chain [2]. Thus, the purpose of the present review paper is to provide a comprehensive overview on important derivatives of xylan, with a focus on its synthesis, properties, applications, and potential impact on various industries.

2. Isolation, chemical composition and chemical Structure of xylan

2.1. Isolation of xylan

Holocellulose was produced by delignifying agricultural waste materials—such as maize cobs, wheat straw, and sugarcane bagasse (SCB)—in an acidic solution at a high temperature using sodium chlorite. The xylan components of holocellulose were dissolved in an alkaline KOH/NaOH solution at 25°C for a predefined period of time, with fixed ratios of solid to liquid, in order to extract the xylan-rich hemicelluloses [3,14, 20,21].

2.2. Chemical Compositions

Hemicelluloses are classified as polymeric carbohydrates that include five or six carbon atoms per sugar unit and repeat to form polymeric chains. The primary sugars found in hemicelluloses include L-arabinose, D-xylose, D-glucose, D-galactose, D-mannose, D-glucuronic acid, 4-O-methyl-D-glucuronic acid, D-galacturonic acid, and, to a lesser extent, L-rhamnose, L-fucose, and various O-methylated neutral sugars. Hemicelluloses are low molecular weight, branching polymers having 80–200 degrees of polymerization [22]. The main hemicelluloses found in hardwood are partially acetylated (4-O-methyl-D-glucuronopyranosyl)-D-β-xylans, or simply "xylans." The backbone of Gramineae hemicelluloses such as cereal straws, consists of β-(1→4)-linked β-D-xylopyranosyl units. While some xylan chains are linked to D-glucopyranosyluronic acid units, the two most significant acidic hemicelluloses are O-acetyl-4-O-methyl-D-glucuronoxylans and L-arabino(4-O-methyl-D-glucurono)xylans. O-acetyl groups are present in graminaceous plant xylans at levels of 1% to 2%. Grass cell walls also contain 1%–2% substituents for phenolic acid [8]. Water solubility is typically higher in xylans with high side chain substitution [23].

2.3. chemical structure of xylan

Since xylan is made up of several monosaccharide units joined together, it is classified as a polysaccharide. A seemingly limitless supply of hemicelluloses is available from a variety of sources, including wheat straw, corn cobs, and maize fibers, for the creation of high-quality, value-added products. Being an abundant byproduct of the agro-industry, their cost is another factor that makes them competitive. Xylan can vary in its degree of branching, side chain composition, and substitution patterns depending on its botanical source and processing methods. A hypothetical plant xylan structure showing different substituent groups as shown in Figure 1.

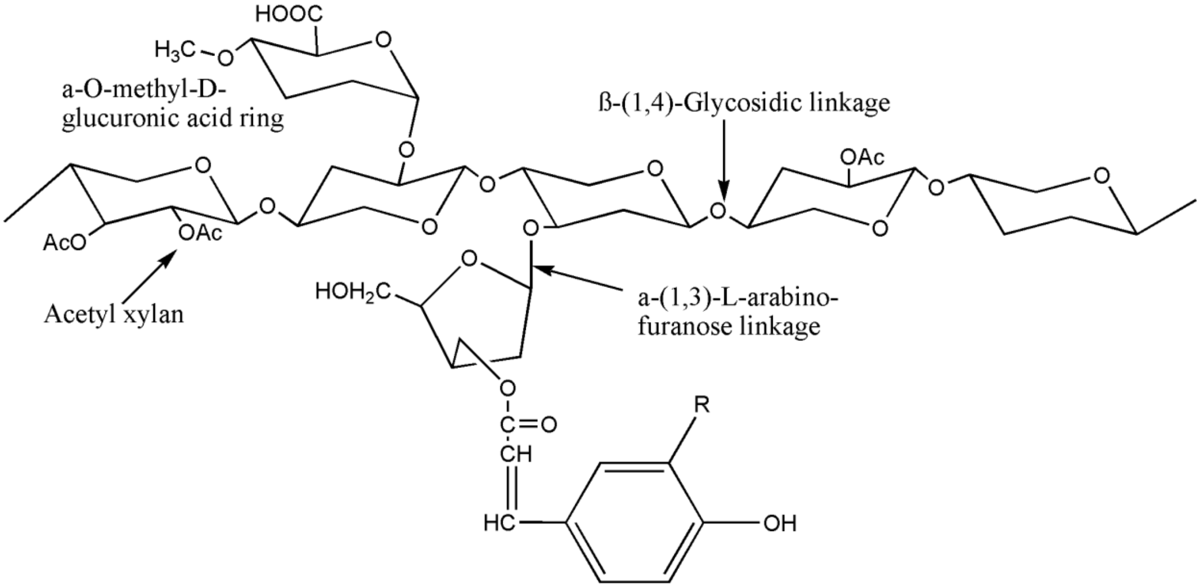

Figure 1. A hypothetical plant xylan structure showing different substituent groups

The xylan substituents exhibit a significant susceptibility to alkaline treatment. Consequently, during the extraction process, the substituents that are connected by the xylose monomeric units' main linear chain are eliminated. According to Kumar et al (2014) [21], FTIR spectroscopy has also verified the elimination of sidechains or substituents. Thus, the probable structure of xylan is shown in Figure 2.

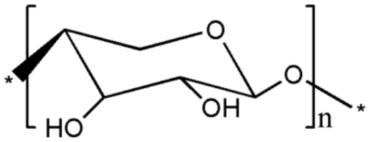

Figure 2. Linear chain of xylose monomeric unit of xylan

3. Modification of xylan

3.1. Oleoylation of xylan

Oleoylation of xylan was carried out by Sun et al (2004) [12] in the following manners. A fixed amount of xylan-rich hemicelluloses was dissolved in distilled water by heating and stirring process followed by addition of DMF with continuing stirring for another 5 min. The water present in the reaction mixture was removed from the swollen gel by repeated distillation under reduced pressure at 50 ℃ and followed by the addition of LiCl/DMF and the required amount of catalyst. Then varying ratios of carboxyl functionality such as oleoyl chloride in DMF was added dropwise and the homogeneous reaction mixture was stirred for different time intervals at different temperature. Upon completion of the reaction the homogeneous reaction mixture was slowly poured into ethanol with stirring. The white product that separated from the solution was filtered off and collected. Schematic representation of chemical reaction of oleoylation is shown in Figure 3.

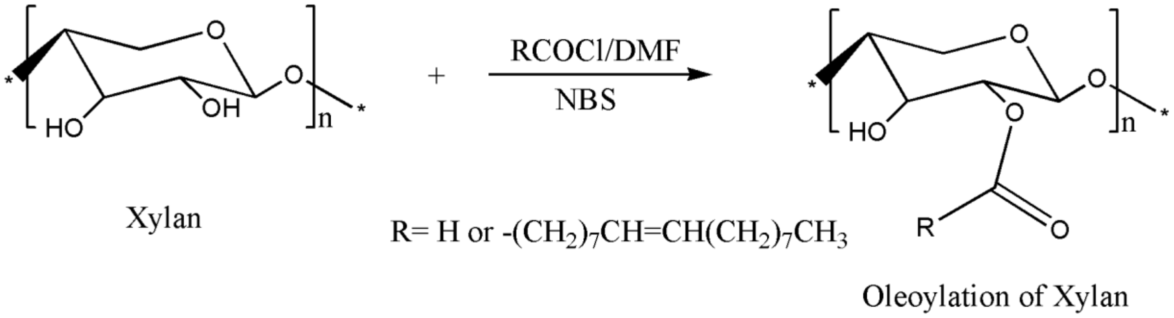

Figure 3. Schematic representation of oleoylation of xylan

3.2. Synthesis of carboxymethyl xylan (CMX)

Ren and his coworkers synthesized carboxymethyl xylan (Figure 4) after extracting the xylan from sugarcane bagasse by using sodium monochloroacetate and sodium hydroxide in ethanol/water medium via etherification reaction [3]. They obtained the product with the maximum degree of substitution (DS) of 0.56. It was found that a significant degradation of the polymers occurred during carboxymethylation. The thermal stability of carboxymethyl xylan was higher than that of the native xylan [3]. Arabinoxylans were also derived with sodium monochloroacetate in a 2-propanol alkaline medium to carboxymethylation [24].

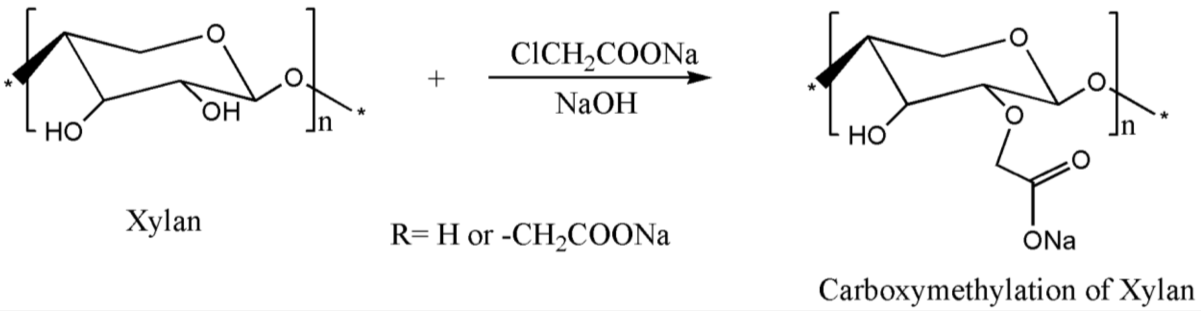

Figure 4. Schematic representation of carboxymethylation of xylan

Table 1. Alteration of xylan to carboxymethyl xylan (CMX)

Substrate	Solvents	Acetylating agents	References
Anhydrous xylan (AXU)	2-propanol + NaOH solution	Sodium monochloroacetate (SMCA)	[24]
Xylan	2-propanol + NaOH solution	sodium monochloroacetate (SMCA)	[25]
Xylan	Ethanol + NaOH solution	sodium monochloroacetate (SMCA)	[15]
	Ethanol/toluene + NaOh	sodium monochloroacetate (SMCA)	
	2-Propanaol + NaOH	sodium monochloroacetate (SMCA)	
Xylan	NaOH+ 2-Propanol	sodium monochloroacetate (SMCA)	[26]
Beechwood xylan	NaOH solution	sodium chloroacetate solution (SMCA)	[2]

4. Technique for determining the degree of substitution of carboxymethyl xylan

4.1. Degree of substitution (DS)

The degree of substitution (DS) for a xylan ester is defined as the number of substituents of hydroxyl groups per D-xylopyranosyl structural unit of the xylan polymer. The average values of the degree of substitution (DS) were ascertained by using acidometric titration as follows [3].

4.1.1. Calculation of purity parameter of carboxymethyl xylan derivatives

Using a gravimetric technique, carboxymethyl xylan's purity was assessed. The precise weight of the carboxymethylated product (0.5 g) was dissolved using 10 ml of distilled water. After adding 10ml of 1M HCl, the mixture was stirred to ensure full dissolution. Following the addition of five drops of phenolphthalein indicator to the liquid, 1M sodium hydroxide was added dropwise while stirring until the solution took on a red color. Stirring constantly, 100ml of 95% ethanol was gradually added to the mixture and the liquid was left for 15 minutes to settle. Following the solution's settling, the liquid supernatant was filtered using a glass cullender of the G3 type and disposed of. The precipitate was washed with 80% ethanol. Next, 50ml of 95% ethanol were used to wash the precipitate one more. The precipitate, which was dried for four hours at 105°C in an oven, is regarded as pure carboxymethyl xylan. The purity of carboxymethyl xylan was calculated as equation 1

$$a = \frac{m\prime}{m} \quad ....(1)$$

where a is the purity of carboxymethyl xylan, m' and m are the carboxymethylated products purified after and before.

4.1.2. Calculation of consumption in mmol/g of sulfuric acid per gram of carboxymethylated xylan (β)

A 250 ml flask containing precisely 0.2 g of carboxymethyl xylan was taken with 50 ml of distilled water and swirled for ten minutes. The solution's pH was raised to 8 with the use of alkali. After that, the solution was titrated with 0.05 M H_2SO_4 until an acidometer read 3.74 for the pH of the mixture. Therefore, mmol/g of H_2SO_4 consumed per gram of carboxymethylated compounds (β) was calculated as per equation …………………2

$$\beta = \frac{2 \, x \, M \, x \, V}{a \, x \, m} \quad ....(2)$$

4.1.3. Calculation of degree of substitution

After calculating the β, the degree of substitution was calculated based on the equations 3

$$DS = \frac{0.132 \, x \, \beta}{1-0.08 \, x \, \beta} \quad ....(3)$$

M is the molarity of H_2SO_4 used, V is the ml of H_2SO_4 used to titrate sample, B is the mmol/g of H_2SO_4 consumed per gram of carboxymethylated products.

4.2. Effect of sodium hydroxide concentration on DS

According to observations made by Ren and colleagues (2008) [3], the DS of carboxymethyl xylan rose as the sodium hydroxide concentration increased and reached a maximum DS of 0.56. Beyond this concentration, the DS began to decrease. The observation can be clarified by examining the carboxymethylation process, which involves the simultaneous occurrence of two competing processes.

In the first, as described in chemical reaction in section 3.2, the hydroxyl groups of xylan reacted with sodium monochloroacetate (SMCA) in the presence of sodium hydroxide to produce carboxymethyl xylan (CMX).

The second process, represented by chemical reaction (Figure 5) of sodium hydroxide with sodium monochloroacetate to produce sodium glycolate.

Figure 5. Chemical equation of formation of sodium glycolate

Up to the ideal concentration of alkali, it seemed that the first reaction won out over the second. Over this point, the production of glycolate predominated, which meant that monochloroacetate was inactivated and consumed by this side reaction [3]. Similar observations had been reported for the etherification of sugarcane bagasse hemicelluloses [27].

4.3. Effect of solvent on percentage yield and degree of substitution

The LiCl/DMF combination is widely utilized as a solvent for dissolution and derivatization of xylan-rich hemicelluloses. This strong aproptic solvent may prevent hemicelluloses from aggregating while also improving the interactions between the reagents and the substrate. As a result,the molar ratio of oleoyl chloride to anhydroxylose units in hemicelluloses, along with the concentration of NBS, reaction temperature, and reaction duration, all regulated the degree of substitution. Raising the molar ratio of oleoyl chloride obviously improved the efficiency of the oleoylation reaction. This could imply that more oleoyl chloride molecules are accessible near the hemicellulosic molecules at greater esterifying agent concentrations [12]. Ren et al (2007) [14] esterifyning xylan using acetic anhydride and iodine as a new catalyst in an environmentally friendly ionic liquid (IL) solvent such as 1-butyl-3-methylimidzolium chloride [C4mim]Cl. The results demonstrated that by varying the various parameters, acetylation reaches a maximum with a degree of substitution of 1.53 using 15% iodine catalyst.

5. Thermal stability of carboxymethyl xylan (CMX)

Thermogravimetric analysis showed that the unmodified hemicelluloses were more stable than oleoylated polymer having DS 0.29. The lower thermal stability of the oleoylated polymers *(*DS < 0.29*)* was probably due to the disintegration of intramolecular interactions of hydrogen bonds between polymer chains. Following chemical alteration, the products' thermal stability dropped somewhat, but for DS ≥ 0.29, no discernible additional decline in thermal stability was seen. Such low-DS polymers require more research since they have potential uses in both food and non-food applications [12]. For instance, the thermal stability of CMX films were considerably enhanced with the use of linoleic acid and crosslinking agents. The composite films of CMX-linoleic acid displayed less yellowing and greater tensile strength at break, elastic modulus, and hydrophobicity. The addition of linoleic acid and crosslinking agents improved the CMX film's thermal stability as well. Linoleic acid was added to CMX film, which resulted in decreased Water vapor permeability (WVP), Oxygen permeability (OP) and antibacterial efficacy against Gram-positive bacteria. These findings revealed that linoleic acid and crosslinking agents enhanced the characteristics of CMX films, suggesting that CMX films are a potential material for food packaging [26].

6. Applications of carboxymethylation of xylan

Carboxymethyl xylan (CMX) is used in many different industries due to its special properties. A few peculiar uses for carboxymethyl xylan are as follows:

6.1. Used as adhesive materials

The carboxymethyl xylan-dopamine nanocomposite hydrogels were produced by using polyacrylamide crosslinker and 2D bentonite nanoparticles as nanofillers. The research outcomes demonstrated that bentonite, when used as a nanofiller, may increase the mechanical strength of nanocomposite hydrogels in terms of compressive strength, tensile strength, and elongation at break. Moreover, catechol of dopamine gave nanocomposite hydrogels adhesion qualities; these hydrogels could stick to polytetrafluoroethylene (PTFE), glass, plastic, and metal [28].

6.2. Used as packaging materials

Polyacrylamide-g-carboxymethyl xylan (PAM-g-CMX) composite hydrogels were created with the employment of varaying range of 0D nanoparticles (MgO, ZnO, Al_2O_3, Fe_2O_3, SiO_2, and TiO_2) as nanofillers by Liu and colleagues. The findings demonstrate that the hydroxyl groups on the nanoparticle surface create hydrogen bonds with the carboxyl and amino groups in the PAM-g-CMX cross-linked network, enhancing the mechanical strength of the nanocomposite hydrogels. The results also showed that, because of the spherical form and tiny size of MnO, the hydrogel containing 20nm MgO has the longest elongation, the maximum compressive strength, and the maximum tensile strength. The hydrogels containing nanoparticles will provide fresh perspectives on the use of xylan derivatives [29].

6.3. Used as paper additive materials

CMX is used as a paper additive by the paper industry to enhance the strength, printability, and absorbency of paper products. It can also improve the retention of color and filler during the paper-making process. One of the authors, [30], increases the paper's dry strength by adding polyelectrolyte complexes, which are created by adducting cationic xylan derivatives, like quaternary ammonium-adducted xylan (QAX), in almost all proportion to anionic xylan derivatives, like carboxymethyl xylan (CMX). Therefore, polyelectrolyte complex might be advantageous to the paper sector.

6.4. Used as food preservative materials

CMX is a food additive that is mostly used in sauces, dressings, and baked goods as an emulsifier, thickening agent, or stabilizer. It can extend shelf life, enhance texture, and retain moisture. A novel polysaccharide-based preservative namely carboxymethyl hemicellulose p-hydroxybenzoate (P-CMHC) was synthesized by esterification of carboxymethyl hemicellulose (CMHC) with p-hydroxybenzoic acid (Figure 6) [31]. At ideal esterification conditions, the resultant product (P-CMHC) was produced with 0.232 degree of substitution. Results also demonstrated that the prepared P-CMHC exhibits excellent antioxidant activity and hydroxyl radical scavenging activities, negligible cytotoxicity and attractive hygroscopic and moisturizing qualities, making it a safe, healthy, and promising preservative. P-CMHC is therefore a novel substance with potential uses in the food, cosmetics, and biomedical industries [31].

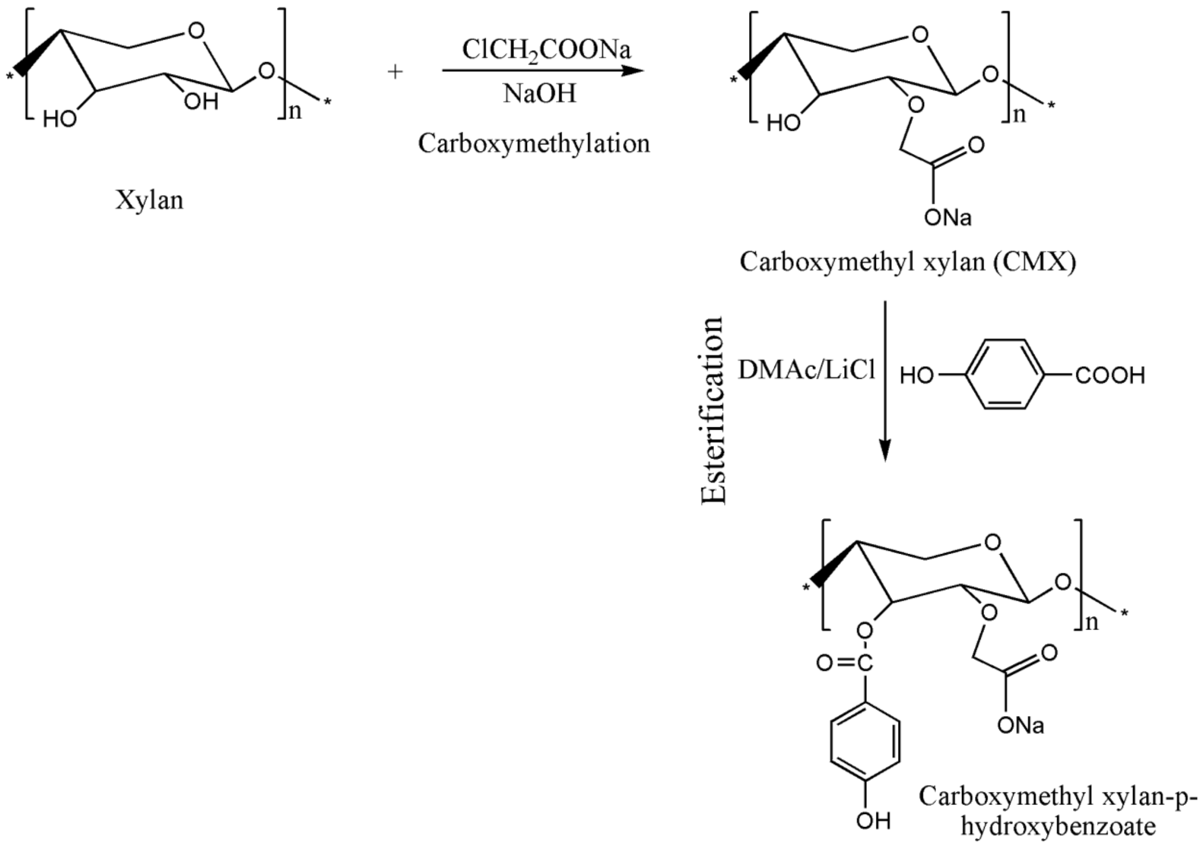

Figure 6. Chemical equation for the preparation of carboxymethyl xylan-p-hydroxybenzoate

6.5. Used as food packaging materials

Xylan isolated from rice straw was altered by Kapil et al (2023) [32] to produce acetylated xylan (AX) and carboxymethylated xylan (CMX). Following this, xylan/modified xylan (1% and 2%) was reacted with polyvinyl alcohol utilizing glycerol as a plasticizer and citric acid as an inexpensive, environmentally acceptable cross-linker to create biofilms. The maximal antibacterial efficacy of 2% CMX biofilms against Bacillus subtilis and Pseudomonas sp. was demonstrated by zones of inhibition measuring 33.5 and 30.5 mm, respectively. Additionally, the biodegradation of 2% CMX biofilms was also the highest (86.5%), which may be explained by the creation of ether and ester linkages, which accelerated the destruction of the biofilms. Thus, it is possible to draw the conclusion that the produced biofilms have superior bioactive qualities, making them a suitable material to use in food packaging instead of synthetic polymers [32].

6.6. Used as emulsifying materials

Liu et al (2024) [33] used extracted arabinoxylan for alteration to carboxymethylated arabinoxylans (CMAX). Ababinoxylan's carboxymethylation would significantly increase its ability to emulsify and stabilize emulsions. Emulsions could be efficiently stabilized by CMAX with reduced DS when stored at a concentration of 0.5% and pH between 6 and 7. Conversely, because of the delicate interface created by an excess of intermolecular ionic force, higher DS resulted in increased flocculation and lower emulsion stability. The study discovered that CMAX has promise for further food processing uses and emulsion stabilization.

6.7. Used as a biodegradable composite materials

Biodegradable composite film were created using wheat straw holocellulose which underwent a catalytic transformation into carboxymethylated holocellulose (CMHCS). High degree of substitution upto 2.46 was attained by using a cocatalyst consisting of cetyltrimethylammonium bromide and polyethylene glycol 2.46 was attained. The mechanical characteristics of the composite film were much better and increased with increasing DS as compared to pristine holocellulose. Additionally, the CMHCS-derived composite film was showed considerable biodegradation of upto 71.5% after 45 days when tested under soil burial biodisintegration conditions. Thus, research outcome revealed that the crated composite film maight be used in the production of biodegradable composite materials [34].

6.8. Used as wound dressing materials

Hydrogels were created by reacting carboxymethyl xylan with acrylamide (AM) in the presence of N, N′-methylenebis(acrylamide) (MBA) as a cross-linking agent and ε-poly-(L-lysine) carbon dot (PL-CD) as an antibacterial agent. The study's findings showed that PL-CD also functionsed as a nano-reinforcing agent to enhance the hydrogels' mechanical qualities. These hydrogels could be applied as a wound dressing with prolonged medication release [35].

7. Conclusions

Chemical modification of xylan to carboxymethyl xylan, which causes the polymeric chain to become insoluble. The activation circumstances might conveniently govern the distribution of function and the process of change. The degree of substitution (DS) and distribution of substitutes in altered xylan (or xylan derivatives) caused variations in their characteristics. Thus, xylan derivatives have an intriguing range of potential uses based on structure–property interactions. They can be utilized as antibacterial agents, emulsifiers, food packaging, food additives, paper additives, flocculation aids, and hydrogel-based drug delivery systems. They could function as polymeric tensides similar to methyl xylan and be employed as drug carriers (xylan esters nanoparticles).

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Disclosure statement

The authors declare no conflict of interest.

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