Tech Science Press

# No-Aldehydes Glucose/Sucrose-Triacetin-Diamine Wood Adhesives for Particleboard

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**Abstract:** A three reagents adhesive system for wood particleboards not containing any aldehyde was developed by the reaction of glucose or sucrose with triacetin (glycerin triacetate) and with hexamethylene diamine. The system was found to be based on the mix of three reactions, namely the reaction of (i) glucose with triacetin, (ii) of the diamine with triacetin, and (iii) of glucose with the diamine. The chemical species formed were identified by Matrix Assisted Laser Desorption Ionization Time of Flight (MALDI-ToF) mass spectrometry. Wood particleboard panels were prepared with this adhesive system and gave good internal bond (IB) strength results suitable for interior grade panels and with extremely low formaldehyde emission.

**Keywords:** No-formaldehyde adhesive; no-aldehyde adhesive; monosaccharide-triacetin-hexamethylene diamine; glucose; sucrose; wood adhesive; particleboard; MALDI

## 1 Introduction

In the search for alternative adhesives for wood panels not using formaldehyde a large number of different approaches have been taken by a considerable number of research groups. These span from substituting formaldehyde by non- or less toxic non-volatile aldehydes in traditional synthetic adhesives [1,2] to a variety of bio-based adhesives of many different types, from traditional to even rather unconventional approaches [3–9].

The use of unconventional approaches to wood adhesives is slowly mounting in interest, by use of different polymeric materials or unusual reactions. In this paper a totally new approach, never tried before, partially bio-based, but compounded by non-toxic synthetic materials and their unusual reactions is presented. The adhesive resin is based on the reaction of simple carbohydrates such as glucose and sucrose with triacetin (glycerine triacetate, also a biosourced material) and hexamethylene diamine.

The reason this adhesive was chosen for experiments was by serendipity. In the research of non-isocyanate polyurethanes (NIPU) for adhesives [3,10] and other applications the work was centered on glucose a sucrose reacted with dimethyl carbonate and hexamethylene diamine. Starting from this combination the question arose if other materials could react with monosaccharides and hexamethylene diamine to obtain a useable resins while increasing the bio-sourced content of the resin itself. It is for this

reason that triacetin, an inexpensive chemical, was chosen as it presented characteristics rendering it capable to react with both glucose and a diamine. The systems was tried and the bonding results obtained were sufficiently encouraging to decide to explore what really happened at the molecular level for such an adhesive to work.

The approach can be extended to other diamines or multiamines even biosourced or of natural origin, diamine having been chosen only for the simplicity of demonstrating the concept of this new adhesive. The internal bond (IB) strength results of particleboard bonded with this new approach and the distribution and structure of the complex oligomers formed leading to the final, hardened cross-linked network have also been investigated.

Since its introduction by Karas et al. [11], Matrix-Assisted Laser Desorption/Ionization (MALDI) mass spectrometry (MS) has greatly expanded the use of mass spectrometry towards large molecules and has revealed itself to be a powerful method for the characterization of both synthetic and natural polymers [12–17]. Fragmentation of analyte molecules upon laser irradiation can be substantially reduced by embedding them in a light absorbing matrix. As a result intact analyte molecules are desorbed and ionized along with the matrix and can be analysed in a mass spectrometer. The technique is then particularly useful to separate and identify a sequence of oligomers of progressive molecular mass issued from a reaction, without the need of mixture separation. It has been used successfully for such a type of application on wood adhesive resins of several different types [2–4,9,10,18–21]. This soft ionization technique is mostly combined with time-of-flight (TOF) mass analysers. This is so as TOF + MS present the advantage of being capable to provide a complete mass spectrum per event, for its virtually unlimited mass range, for the small amount of analyte necessary.

## 2 Experimental

### 2.1 Reaction of Glucose with Triacetin and Hexamethylene Diamine

The adhesive system was prepared as follows: 100 g of glucose were mixed with 81 g of triacetin and 100.02 g of water, and heated to 60°C for 60 min in a glass vessel equipped of reflux condenser and mechanical stirring. 162.96 g hexamethylene diamine were then added to the mixture and heated to 90°C for 60 min, then cooled to room temperature. The glucose-triacetin-diamine resin obtained had a pH of 8.9, a viscosity at 25°C of 205 mPa.s and a density of 1.032 g/ml. The sucrose-triacetin-resin obtained had a pH of 9.1, a viscosity of 148 mPa.s and a density of 1.025 g/ml.

### 2.2 Matrix Assisted Laser Desorption Ionization (MALDI-TOF) Mass Spectrometry

All samples for matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) analysis were prepared by first dissolving 5 mg of samples in 1 mL of a 50:50 v/v acetone/water solution. Then 10 mg of this solution is added to 10 µL of a 2,5-dihydroxy benzoic acid (DHB) matrix. The locations dedicated to the samples on the analysis plaque were first covered with 2 µL of a NaCl solution 0.1 M in 2:1 v/v methanol/water, as enhancer of the spectra, and pre-dried. Then 1 µL of the sample solution was placed on its dedicated location and the plaque is dried again. MALDI-TOF spectra were obtained using an Axima-Performance mass spectrometer from Shimadzu Biotech (Kratos Analytical Shimadzu Europe Ltd., Manchester, UK) using a linear polarity-positive tuning mode. The measurements were carried out making 1000 profiles per sample with 2 shots accumulated per profile. The spectrum precision is of +1D.

### 2.3 Wood Particleboard Preparation and Testing

Duplicate one layer particleboard panels of 350 × 350 × 14 mm dimensions were prepared by adding 10% of the resin solids mixture on dry wood particles, for a percentage wood moisture content of the resinated particles of 13% and pressed at a maximum pressure of 28 kg.cm$^2$ followed by a pressure-decreasing pressing cycle, at 220°C for a 10 minutes pressing cycle. The target density of the panels was

of 0.75 g/cm$^3$ .The panels, after light surface sanding, were tested for dry internal bond (IB) strength (EN 312) [22], 24 h cold water swelling and for formaldehyde emission (EN 120) [23].

## 3  Results and Discussion

The possibility of a mixed complex reaction between different materials was originally due to the search for monosaccharides-based non-polyurethane (NIPU) for adhesives, coatings and foams [3,4,10,24]. During such a work awareness arose that, even without producing NIPUs, alternative reactions occurred to reach a hardened network that can be used as an adhesive. One of these reactions, leading to a type of polyamides, was first explored as a binder for wood particleboard with more than encouraging results [9]. The second set of reactions discovered for the formation of alternative types of adhesives is the one described here. It is based on three concomitant reactions, namely (i) the reaction of glucose or sucrose with triacetin (glycerine triacetate), and (ii) the reaction of a diamine with triacetin, and (iii) the reaction of a diamine with monosaccharides, and their interactions leading to system cross-linking. These three reactions can be schematically represented as follows:

**Reaction (1)**
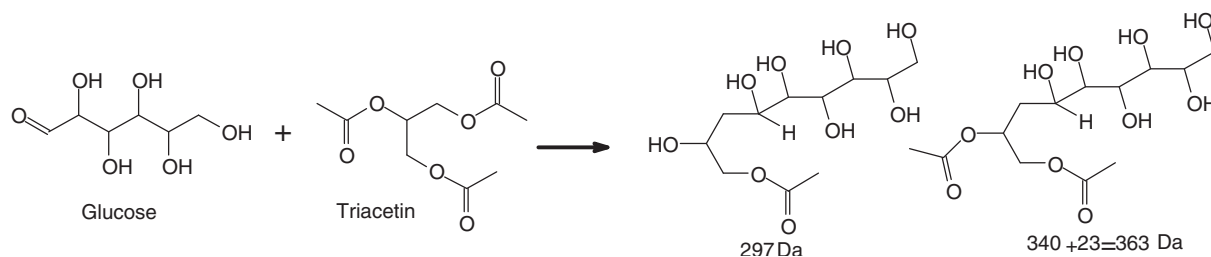


Leading to the two products shown indicated and to other compounds too.
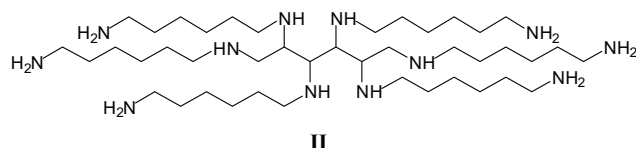
**Reaction (2)**
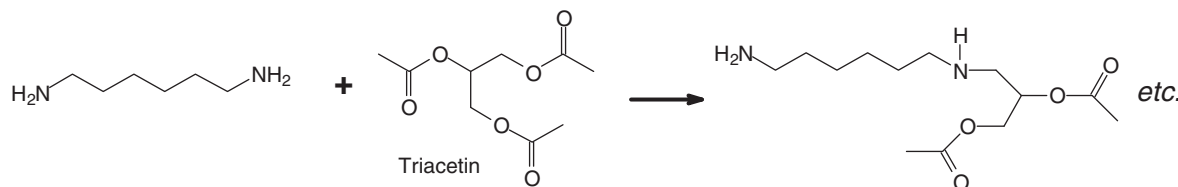


**Reaction (3)**
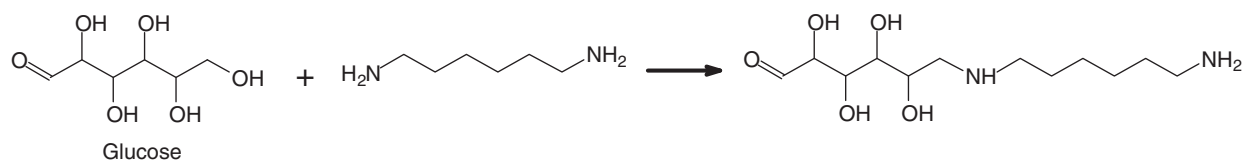


To show this, the MALDI ToF mass spectrometry gives a good insight in the compounds formed. The assignment for the peaks in Fig. 1 are listed in Tab. 1.

Among these three categories of products are noticed according to the three reactions given above. Thus the peaks at 279 Da, 442 Da and 643 Da represents the progressive substitution of the acetate ion by glucose on the glicerine structure of the triacetin as described in reaction (1) above. The peaks at 297 Da, 351 Da and 407 Da are the first products of the progressive substitution of the acetate ion by the diamine as per reaction (2) above. Furthermore, reaction 2 leads to diamine-triacetin oligomers such as 430 Da and 456 Da, 570 Da, 702 Da and 726 Da the 702 Da and 726 Da peaks being represented by structure (**I**):
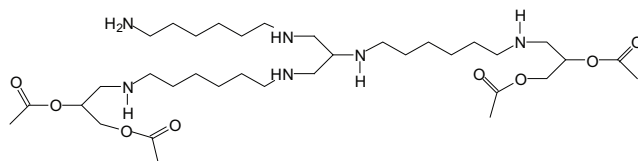
Without and with Na+, connecting three triacetin molecules in which the acetate ion is partially or totally substituted by three diamines.

Equally, structures obtained by reaction of the diamine with glucose according to reaction (3) above correspond to the peaks at 278 Da, 378 Da, 499 Da, 595–597 Da, 697 Da and 793 Da. Two conclusions can be drawn from these peaks. First of all that all the –OH group of glucose can react and be substituted with a NH group of the diamine giving even species up to structures as the 378 Da peak such as structure (II):



II

This reaction appearing to be fairly easy to occur. Second observation is that compounds having a structure of two glucoses linked by a diamine do not occur whatsoever. This means that polymerization to higher oligomers and cross-linking cannot occur through this reaction alone, contrary to reactions (1) and (2) where the reaction can proceed to higher oligomers at suitable molar ratios of the reagents.

More interesting are the oligomers formed by the crossing of the three reactions listed above and leading to cross-linked polymer networks suitable as wood panel adhesives. The peaks of mixed structures glucose-triacetin-diamine are represented by the peaks at 393 Da (and 416 Da), 492–495 Da, 552 Da, 608 Da (and 632 Da), 751–753 Da, 854 Da, 947 Da, 1027 Da and 1185 Da. The type of structures leading to cross-linking of the system can be evaluated by observing structure (III) at 1185 Da:



III
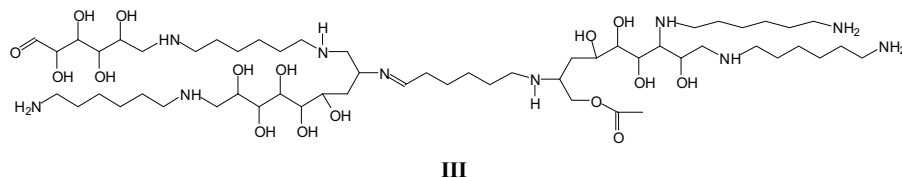
As the system proceeds further to higher structures in which more glucose hydroxyls have reacted with the diamine, and both glucose and diamine have reacted with triacetin, the point of gelling and hardening is reached.

Having thus defined the chemical reactions occurring in this three reagents mixture, one has to check if the system can be used as a wood panel adhesive. Laboratory single layer particleboards were prepared and then tested according to EN 312 [10] for internal bond (IB) strength, 24 hours thickness swelling and formaldehyde emission (EN 120) [11]. The results show in Tab. 2 indicate that for the adhesive system the IB strength satisfies well the requirements for interior grade panels of relevant standards, and moreover that the formaldehyde emission is extremely low, being limited to just the level of what is emitted by the heated wood furnish as no aldehydes are present in the adhesive system itself.
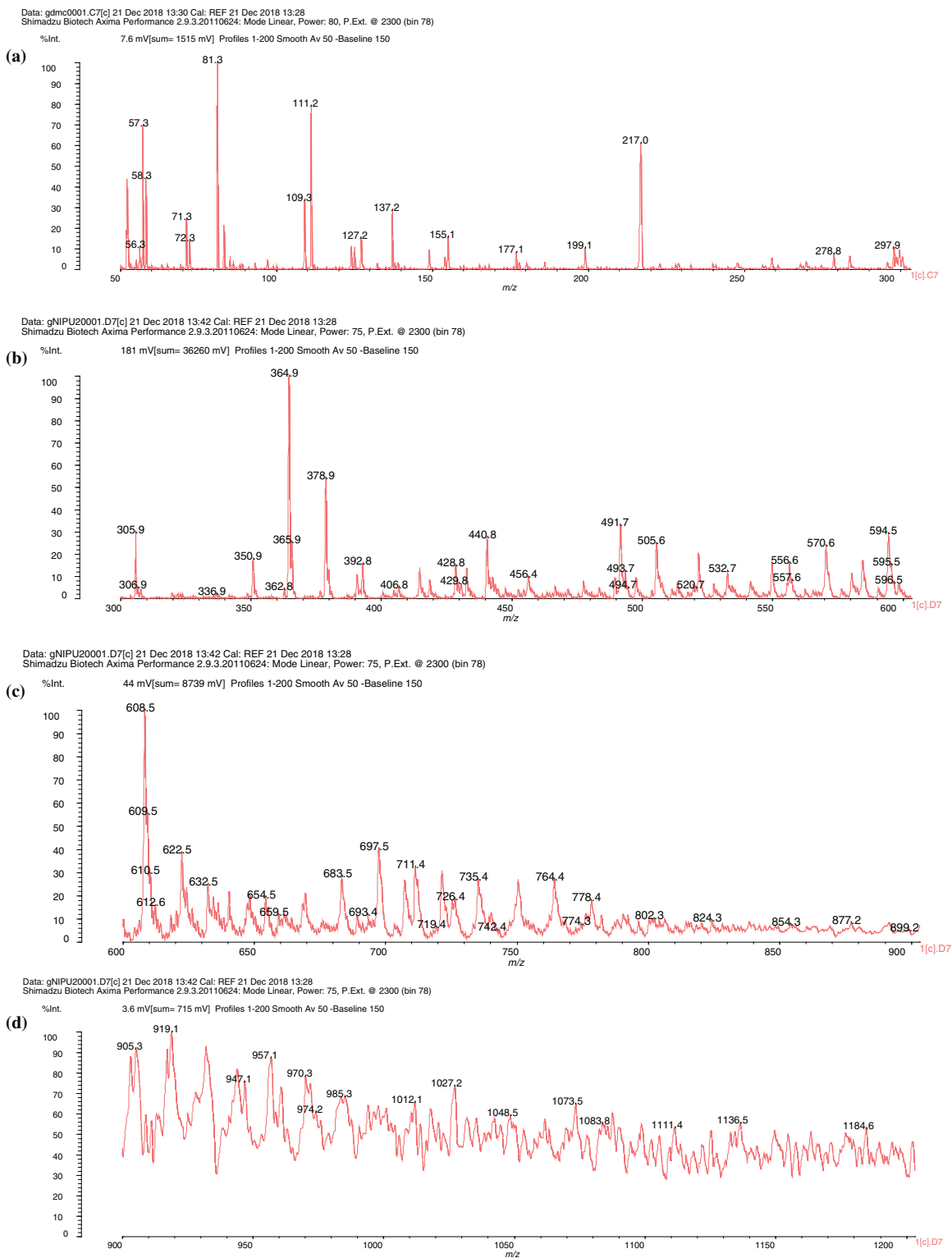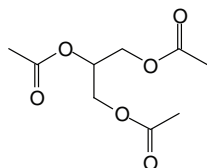
**Figure 1:** MALDI ToF spectra of glucose-triacetin-hexamethylene diamine reaction. (a) 50 Da–300 Da range; (b) 300 Da–600 Da range; (c) 600 Da–900 Da range; (d) 900 Da–1200 Da range
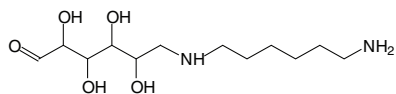
**Table 1:** Peak assignements of MALDI ToF spectra
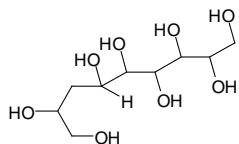
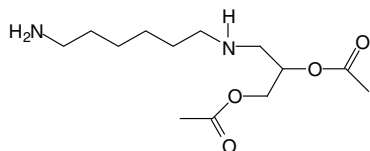177 Da (no Na+) glucose deprotonated

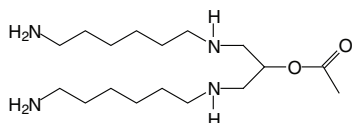217 Da (no Na+) triacetin

278 Da (no Na+)
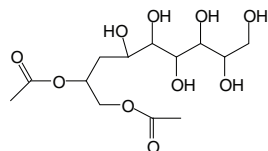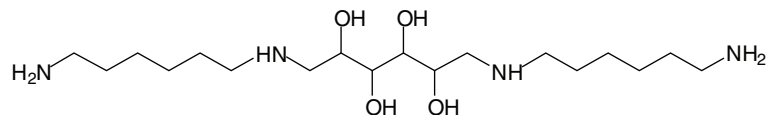
279 Da (with 23 Da Na+)

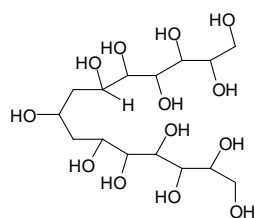297 Da (with 23 Da Na+)

351 Da (with 23 Da Na+)

363 Da – 365Da

378 Da (no Na+)

**Table 1  (continued ).**

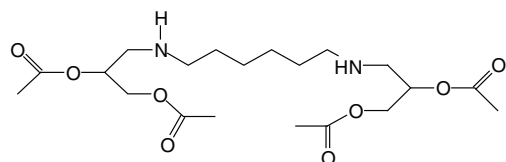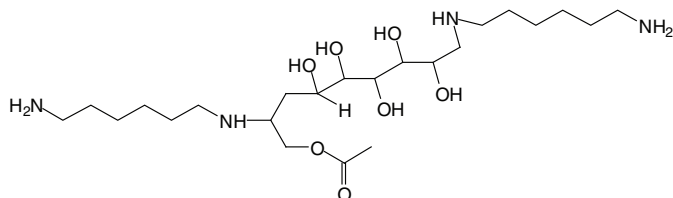393 Da (no Na+) and 416 Da (with 23 Da Na+)
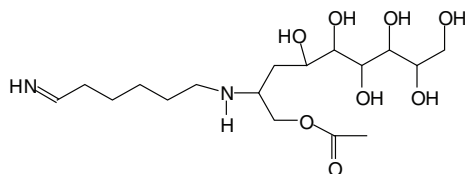
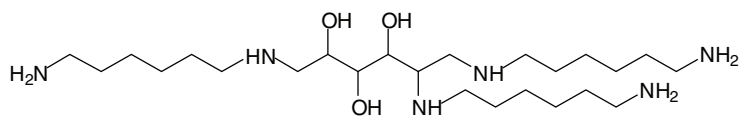407 Da (with 23 Da Na+)
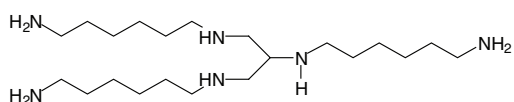
442 Da (with 23 Da Na+)

456 Da (with 23 Da Na+) and 430 Da (no Na+)

492-495 Da (no Na+)

499 Da (with Na+)

552 Da (no Na+)
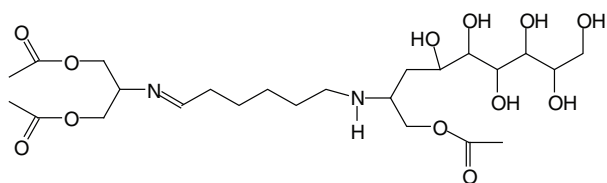
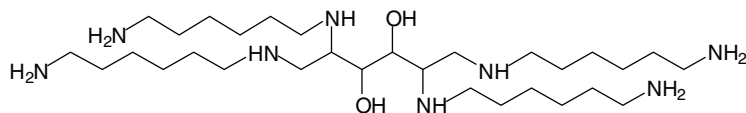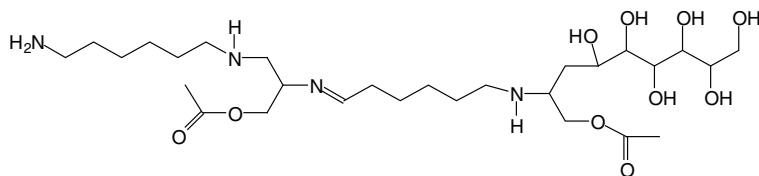**Table 1  (continued).**

570 Da (with 23 Da Na+)
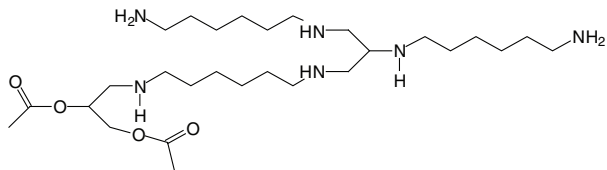


595 Da-597 Da (with Na+)



608 Da (no Na+) and 632 Da (with 23 Na+)



623 Da (with 23 Da Na+)
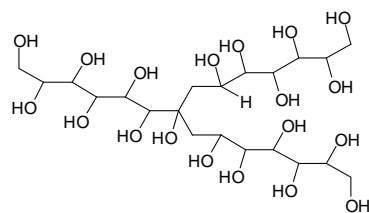


697 Da (with Na+)
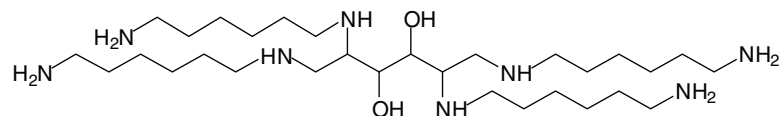


702 Da (no Na+) and 726 Da (with 23 Da Na+)
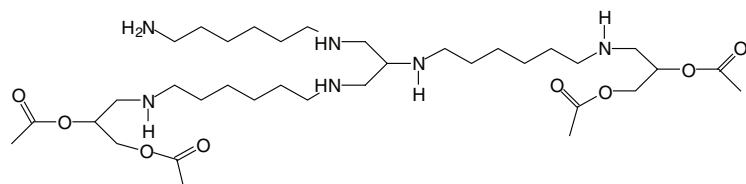


751-753 Da (with Na+)
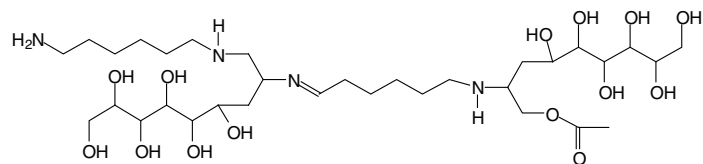
**Table 1 (continued).**

793 Da (with Na+)
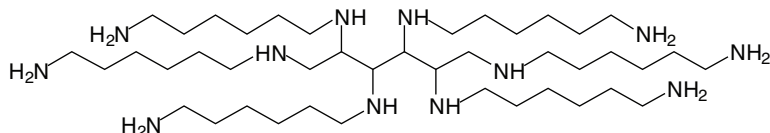
854 Da (with Na+)
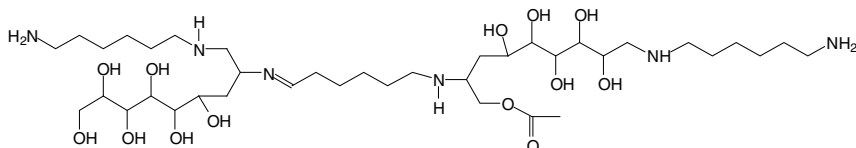
947 Da (with Na+)

1027 Da (no Na+) and 1049 Da (with Na+)

1185 Da (no Na+)
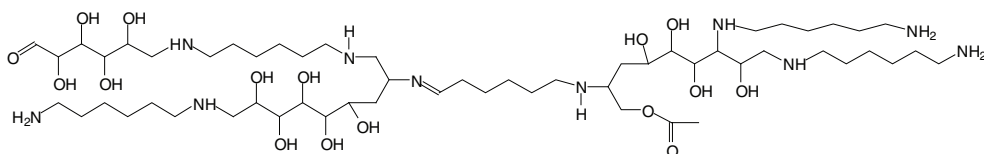
**Table 2:** One layer, no wax emulsion, laboratory particleboard results pressed at 220°C for 10 minutes

| Adhesive type | Board density (g/cm$^3$) | IB strength (MPa) | 24 h cold water thickness swelling (%) | Formaldehyde emission (mg/100 g panel) |
|---|---|---|---|---|
| Sucrose-based | 0.74 | 0.69 +/− 0.04 | 23 | 0.3 |
| Glucose-based | 0.75 | 0.87 +/− 0.11 | 15 | 0.3 |
| EN312 and EN120 | – | >0.35 | – | <6.5 |

## 4 Conclusions

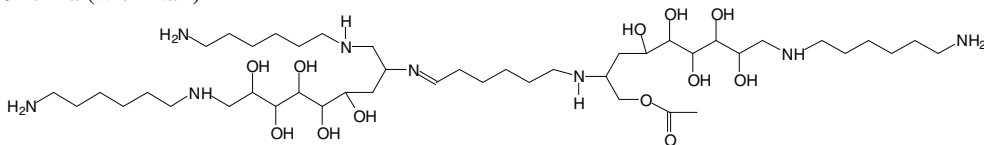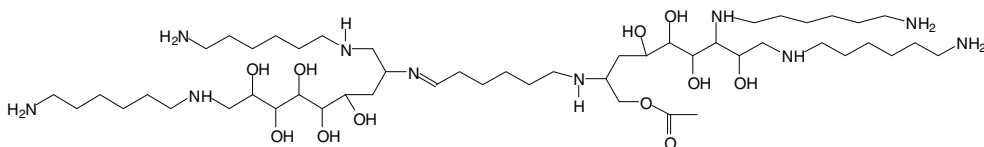The adhesive system based on the unusual set of concomitant reactions between a monoasaccharide (such as glucose or sucrose ) with triacetin and with a diamine yielded mixed product species based on the reaction of glucose with triacetin, of glucose with hexamethylene diamine ad of the diamine with triacetin. It led to polymerization and cross-linking through the formation of chemical species comprising all the three reagents linked together through the three different reactions. Confirmation of the capacity of this novel, no-aldehyde, wood adhesive system to bond particleboard panels was

obtained by the good IB strength results suitable for interior grade particleboard and the extremely low formaldehyde emission obtained.

**Conflicts of Interest:** The authors declare that they have no conflicts of interest to report regarding the present study.

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