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Chitosan: Emergence as potent candidate for green adhesive market

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ABSTRACT

Chitosan has gained significant attention during last decades as a potent natural adhesive. Its lower concentrations (<10% w/v) offer competitive strength as synthetic adhesives which would reduce economic constrains of adhesive production. There is increasing commercial interest on chitosan as it possesses biodegradability, biocompatibility, non-toxicity and anti-microbial properties which are of high interest for industries and consumers. Moreover, it has reactive amino side groups, which offer possibilities of chemical modification, increased ionic interactions and graft-reactions etc. Degree of deacetylation (DD) and molecular weight (Mw) is important in bonding mechanism. Most of the synthetic adhesives are comprised of petrochemicals that leave toxic residues such as formaldehyde and volatile organic compounds (VOCs), which are injurious to health and environment. Therefore, development of cost-effective, environmental and health-friendly green adhesives, based on renewable resources is main interest of adhesive industries these days. Rising oil prices are another driving force in research for development of bioadhesives as substitute of synthetic adhesives. This review is focused on current developments of chitosan adhesives for structural and general bonding applications during last decades as well as its current market potential worldwide.

1. Introduction

The majority of commercial adhesives such as poly (vinyl acetate), epoxy, phenol-formaldehyde and polyurethane are based on non-renewable and depleting petrochemical resources. Furthermore, numerous adhesives consist of residual toxic chemicals and volatile organic compounds (VOCs). These are costly, harmful for the health of living beings as well as are pollutants of environments. Environmental Protection Agencies from various countries aims to diminish the use of these materials and encourage the development of adhesives from bioresources. Compared to synthetic adhesives, biopolymer based adhesives are expected to offer reduced price, a lesser degree of price volatility and a more favourable environmental footprint. Currently none of the bioadhesives offer very good strength as synthetic adhesive without containing VOCs. Hence research in this area is in great scope today. The effective bioadhesives are still under investigation and their bonding properties are actually an industrial challenge and an important research area [1].

Carbohydrates were well explored as food additives and as potent adhesive candidate for many decades viz. gums, polysaccharides, oligomers and monomers. For carrying adhesive properties, the fundamental structural feature of polysaccharides mainly comprises of high molecular weights and polar-functional groups [2,3]. Polymer based adhesives must have many physical, chemical and mechanical properties to promote adhesion. The most explored polysaccharides for adhesive development have been the starch, pullulan, levan, dextrin, Gum arabic, chitosan etc. [4–6]. Among various polysaccharides the most attractive polysaccharide for adhesive development appeared to be chitosan. It is a polymer of β-(1,4)-linked 2-acetamido-2-deoxy-D-glucopyranose (*N*-acetyl glucosamine) and 2-amino-2-deoxy-D-glucopyranose (glucosamine). Chitosan is a heteropolymer obtained by alkaline deacetylation of chitin at C-2 position (Fig. 1). Chitin is the second most abundant natural polymer in nature after cellulose. It is the main structural element of a large number of invertebrates such as crustaceans (exoskeleton) insects (cuticles) and the cell walls of fungi [7–11]. In contrast, chitosan only occurs naturally in some Mucoraceae fungi [12]. Production of chitosan is economical and environment-friendly [13]. Chitin is highly hydrophobic and is insoluble in water and majority of organic solvents whereas chitosan is water soluble due to amino groups present in it. The amino group has a pK_a value of ~6.5, which leads to a protonation

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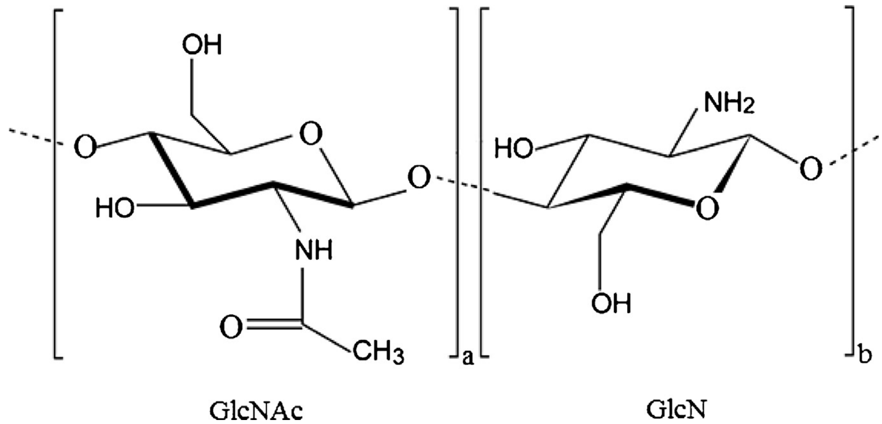

Fig. 1. Chemical structure of chitosan showing β-(1,4)-glycosidic linkage between (a) 2-acetamido-2-deoxy-D-glucopyranose (GlcNAc) and (b) 2-amino-2-deoxy-D-glucopyranose (GlcN) units.

in acidic to neutral solution with a charge density dependent on pH and the % deacetylation value.

Chitosan is an expensive polysaccharide approx. 10 USD/kg, but it is used in aqueous solutions less than 10% (w/v), bringing the cost down to less than 1 USD/L of solution, which is acceptable. Chitosan solutions are prepared in 1–2% (v/v) of acetic acid in water which forms viscous solution. These solutions are converted to solid adhesive bonds by the loss of water and solvent or by a chemical setting mechanism. Loss of water takes place either by evaporation or by absorption from porous adherend materials. Additives or plasticizers (citrate, glycerol, glucose) are often used to improve properties of the final adhesive film such as early strength development, moisture resistance and ultimate bond strength [5,6,14].

This review focuses on exploration of different molecular interactions between the components of chitosan adhesives and adherends for obtaining maximum bonding strength. The first part reviews the background information relative to adhesion theories, ideal properties of adhesives and the different tools available to evaluate adhesive performance. The second part focuses on exploration of chitosan adhesives on various bonding applications based on their properties. The last part highlights the bioadhesive advances, bottleneck of chitosan research and current market potential. Bonding strength discussed in this review is actually shear strength of the adhesive formulation.

2. Background information of adhesion

Adhesion is a process of attachment between surface of two substances that can be similar or dissimilar in structures. Adhesion requires energy that may come from chemical or physical linkages. These linkages can be reversible when reasonably more energy is applied. The bond strength of an adhesive to an adherend is the sum of various mechanical, physical and chemical forces that overlap and influence one another. The strength of adhesion depends on many factors. There are different adhesion theories proposed viz. *Mechanical adhesion*: adhesion occurs by the penetration of adhesive in irregular surface, pores or micro-cavities [15]. *Adsorption adhesion:* adhesion occurs due to inter-atomic or inter-molecular forces between adhesive and adherend molecules, based on associated energy (in kJ/mol) covalent (150–950), ionic (400–800), H-bond (40) and van der Walls (2–15) forces are respectably considered to be strong in above order [16]. *Electrostatic adhesion*: adhesion occurs due to electrostatic forces at interface having difference in electrical charges, this adhesion is applicable between non-compatible materials such as polymeric and metallic substances [16]. *Diffusion adhesion*: adhesion particularly effective with polymer chains where one end of the molecule diffuses into the other material (atoms diffuse from one particle to another). This adhesion can be applied in mutually miscible and compatible polymer [17]. This theory is relevant when temperature would be lower than the 'Glass transition temperature' (Tg) [18]. Tg is defined as transition of polymer material between solid and viscous phases [19]. Wetting phenomenon was introduced then thermodynamic theory of adhesion was proposed, in which inter-atomic and intermolecular force was the measurement of contact angle between adhesive and adherends at thermodynamic equilibrium [20].

There are several influencing factors determined which governs the degree of adhesion. Temperature was most governing factor in diffusion adhesion, likewise, pH in electrostatic adhesion, wettability and roughness are important factors in mechanical and diffusion adhesions [21] and void (air bubble) formation in mechanical adhesions [22]. To characterize the adhesion, different types of mechanical tests were used in order to evaluate the strength of adhesives. These test methods were based on load-dependent stresses on adhesive joints viz. tension, compression, cleavage, shear and peel stresses [21]. Likewise, different types of adhesive joints pattern have been discussed for carrying shear loads in which joints were employed for an overlapping adherend's arrangement. Shear loaded joints are the most popular because most of the bonded configurations induce shear type of failure in the bonded joints [23]. Double-lap joints configuration (Fig 2) has been largely used because it offers low peeling effect and more reliable strength measurement. Moreover, types of failure in the adhesive (cohesive failure) or interface of adherends and adhesive (adhesive failure) or in the adherend (structural failure) must be characterized, which has described in our previous article in details [21].

3. Salient features of chitosan for adhesion

Three properties must be present in a polymer to become an ideal adhesive, *Surface tension*: Lesser or equal on adherend's surface to achieve better molecular interaction, *viscosity:* more viscous to avoid fluidity and *penetration ability:* higher upon adherend's surface. Hence the lower the surface tension of an adhesive solution, the easier it will form an adequate wet film over adherend's surface. If the surface tension of the adhesive is greater than the surface energy of the substrate, it will not spread out and form a film. Metals possess higher surface tension than polymers [24,25]. Surface tension of viscoelastic thermal compressed wood ranged between 28.6 and 35.5 mN/m and 0.5% (w/v) chitosan shows 64 mN/m surface tension initially and decreased with time [26]. Chitosan surface tension decreases with increasing chitosan concentration. A 2% (w/v) chitosan in 1% (v/v) acetate