

1 Mechanical Properties of Bacterial Exopolymeric Adhesives and their Commercial Development

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1.1 Introduction

In industry and society today, there is a need for products which provide environmentally friendly features, such as 1) reduced usage of toxic components and VOCs (volatile organic compounds), 2) reduced dependence on depleting petrochemical resources, 3) safer production processes, and 4) less environmental impact of products after their use (Gross and Kalra 2002). The motivation for exploring biopolymers for use in adhesive applications is to exploit their unique properties to address these needs. Additional incentive for development of biological materials is economics. As the world economy grows and more demand is placed on depleting petrochemical feedstocks, products derived from renewable, biological resources are becoming more cost competitive.

Biopolymers are utilized by all organisms for numerous functions in varied environments and thus have evolved into a diversity of chemical compositions. Biopolymers offer the material scientist a source of unique compositions which are unavailable by synthetic means with which to search for novel properties, such as adhesive strength. The discovery of new compositions and optimization of their production is also becoming easier with new, sophisticated biological methods. In the future, biologically derived materials will increasingly fill needs in commercially important applications.

In biofilms, a widespread form of bacterial existence, cells form highly hydrated cohesive masses that adhere to surfaces. Extracellular polymeric substances are largely responsible for the structure and properties of biofilms, including the adhesion of cells to surfaces and to each other. In addition to facilitating the growth of the bacterial colony, biofilms can be problematic and result in, for example, corrosion and fouling in industrial systems, and resistance to antibiotics on medical devices (Costerton and Stewart 2001; Flemming and Wingender 2001). The mechanical properties of biofilms have been described as those of a viscoelastic fluid in which the biofilm behaves elastically at low shear stress and viscously at higher shear stress (Klapper et al. 2002). Thus, extracellular polymeric substances impart substantial mechanical properties to biofilms in their natural environment.

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Extracellular polymeric substances in biofilms are composed of polysaccharides, proteins, and nucleic acids (Flemming and Wingender 2001). Protein components are generally attributed to the initial adhesion processes (formation of a conditioning layer) and polysaccharides, in addition to various other biological functions, are largely responsible for the subsequent adhesive interactions and provide cohesive strength. This review will focus primarily on exopolysaccharides which are often the predominant extracellular component in bacterial biofilms and most readily developed for commercialization.

Bacterial exopolysaccharides have found use in other applications such as thickening and gelling agents for aqueous mixtures and have undergone a significant amount of commercial development. Examples are xanthan gum (from *Xanthomonas campestris*), gellan (*Sphingomonas paucimobilis*), curdlan (*Agrobacterium radiobacter*), dextran (*Leuconostoc mesenteroides*), and levan (*Bacillus polymyxa*). Scleroglucan and pullulan, although of fungal origin, show similar behavior. Sodium alginate is produced commercially from algae but structurally similar materials are also produced by the bacteria *Azotobacter vinelandii* and *Pseudomonas aeruginosa*. Structures of some of the polysaccharides described in this chapter are shown in Fig. 1.1. General structural features of polysaccharides which are useful in adhesives include high molecular weight and polar functional groups. Mechanical properties generally improve with molecular weight (Lazaridou et al. 2003) and native bacterial polysaccharides often possess molecular weights greater than 10^6 Da. Lower molecular weights can be produced, if desired, by control of culture conditions or depolymerization of the native product followed by fractionation. The polar and hydrogen-bonding functional groups of polysaccharides, such as ethers, hydroxyls, and carboxylates, impart good adhesion to high energy surfaces such as wood and metal and also strong interchain interaction for cohesive strength. The hydroxyl and carboxylate groups of polysaccharides also offer potential sites for synthetic derivatization and crosslinking which can be utilized to modify the adhesive properties. Tertiary structures, such as helices, are formed by some bacterial polysaccharides and account for their notable mechanical properties. Other distinguishing properties of bacterial exopolysaccharides are hydrophilicity, ability to form hydrogels (structure dependent), biodegradability, production from renewable resources, and generally low toxicity.

Xanthan gum, gellan, and dextran are produced commercially at volumes greater than 1 million lb/year. Production of most bacterial exopolysaccharides is accomplished by batch-wise fermentation in stirred tanks equipped with efficient agitation for the resulting highly viscous mixtures. Glucose and sucrose are commonly used as the carbon and energy sources. Raw materials account for a significant fraction of the product cost so substitution of cheaper carbon sources, such as agricultural waste products is advantageous. In the production of xanthan gum, which is the most successful industrial biopolymer produced by fermentation, yields of 30 g/L and productivities of 0.7 g/l-h are reported (Born et al. 2002). After the fermentation operation, the mixture is sterilized, and the biopolymer is isolated by precipitation into

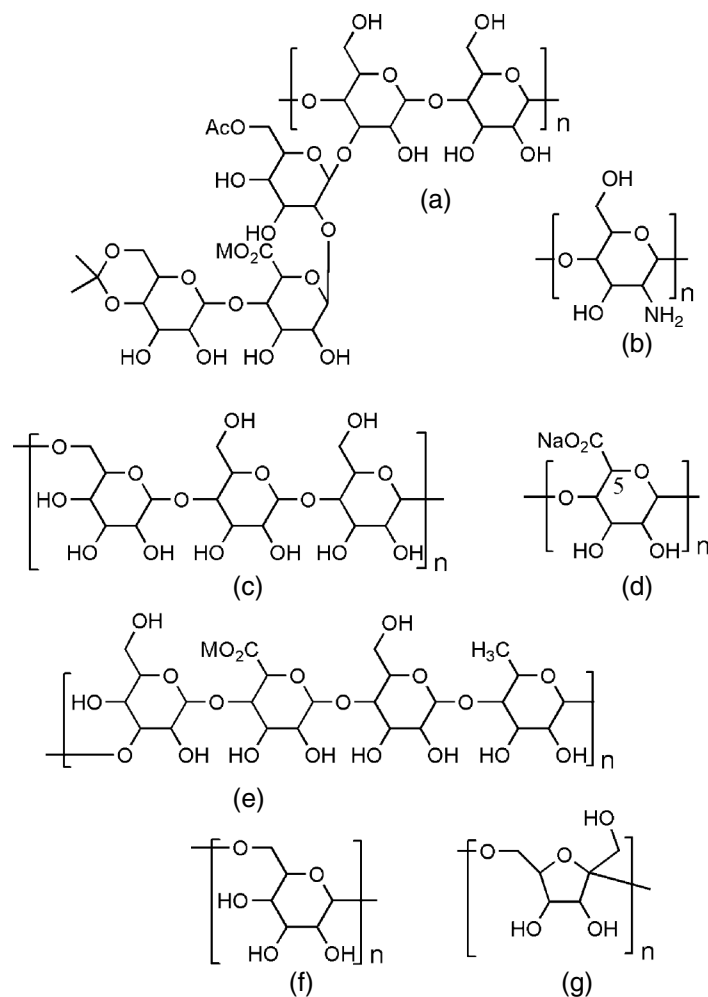


Fig. 1.1. Structures of some of the polysaccharides referred to in this chapter. (a) Xanthan gum (M=metal), (b) chitosan, (c) pullulan, (d) sodium alginate (note mixture of epimers at C-5), (e) gellan, (f) dextran, and (g) levan

isopropanol and then dried. Cell biomass is not separated for industrial grades of xanthan; higher purity grades are obtained by removal of the biomass by filtration or absorption. Xanthan gum is currently produced globally at a volume of 40 million lb/year (Sutherland 2002) and sells for \$4.5/lb (Chemical Market Reporter 2005).

Their performance in nature, unique chemical compositions, economics of production from renewable resources, and biodegradability make bacterial exopolysaccharides attractive candidates for development as adhesive materials. This review summarizes recent efforts to identify adhesive materials

derived from bacterial exopolysaccharides and evaluates their mechanical properties for adhesive applications. Comparisons include descriptions of adhesive composition and preparation, testing procedures, and testing results. In addition to the bacterial products, selected structurally related polysaccharides from plant and animal sources are briefly compared.

1.2 Adhesive Development

1.2.1 Mechanical Testing of Adhesive Bonds

The search for practical adhesives relies on evaluation of mechanical properties. Fundamental studies of the physical and mechanical properties of bacterial exopolysaccharides on the nanoscopic, molecular level in their native, aqueous environments have been accomplished with atomic force microscopy (AFM) (Dufrene 2002; Kawakami et al. 2004). In addition to the fact that mechanical properties measured on the molecular level are not directly related to adhesive strengths observed on the macroscopic level, the test conditions are also different than those in most industrial adhesive applications in which the adhesive is in a dry state and subject to varying levels of humidity and temperature. Thus, evaluation of new adhesives should employ conditions simulating expected uses. Standard methods have been developed by professional testing organizations such as the American Society for Testing and Materials (ASTM) for specific applications. The three forces to which adhesives are subjected are shear, peel, and cleavage (Fig. 1.2) (Pocius 1991). Shear strengths can be measured under tension or compression. Peel and cleavage tests measure similar forces, but the former is used with deformable substrates. Preliminary testing of adhesives for metal bonding applications generally employ single-lap shear test specimens with 3.2 cm² bond area (ASTM D 1002) or butt-joined bar specimens (ASTM D 2095). Preliminary testing of wood adhesives generally employ two methods: three-ply plywood specimens assembled from 1.6 mm-thick veneers with a 6.4 cm² bond area are sheared under tension (ASTM D 906); and two 19 mm-thick wood blocks with 19.4 cm² bond area are sheared under compression (ASTM D 905). Results are expressed in terms of stress or pressure, that is, the force required to break the bond divided by the bond area. Analysis of the bond failure mode is also commonly reported and indicates whether the bond failed at the adhesive-substrate interface (adhesive failure), within the adhesive itself (cohesive failure), or in the substrate (substrate failure).

Testing methods for bonding biological materials, such as tissue and skin, have been designed for these unique substrates, for example, ASTM F 2255-03 ("Test Method for Strength Properties of Tissue Adhesives in Lap-Shear by Tension Loading") (McDermott et al. 2004). In vivo testing of adhesive films on human skin has also been developed (Repka and McGinity 2001).

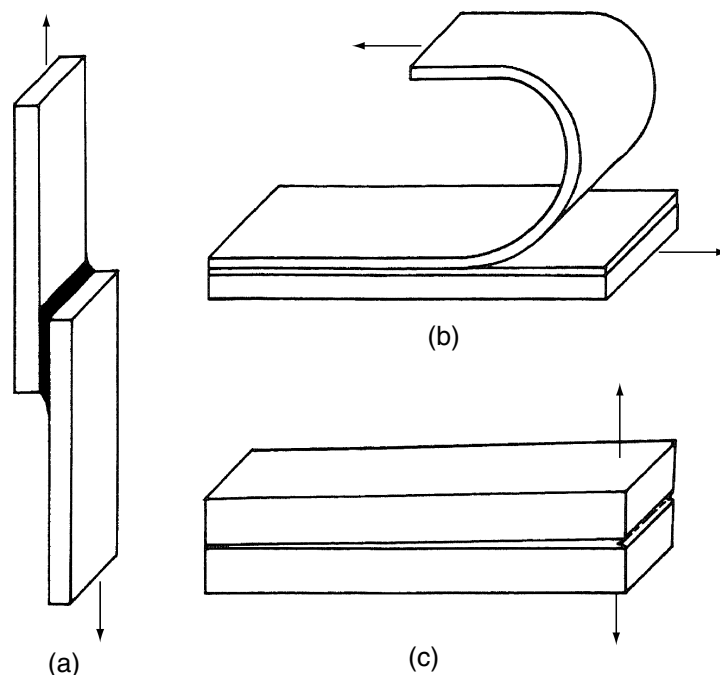


Fig. 1.2. Illustrations of forces to which adhesive bonds are subjected: (a) a standard lap shear specimen where the black area shows the adhesive. The adherends are usually 25 mm wide and the lap area is 312.5 mm². The *arrows* show the direction of the normal application of load; (b) a peel test where the loading configuration, shown by the *arrows*, is for a 180° peel test; (c) a double cantilever beam test specimen used in the evaluation of the resistance to crack propagation of an adhesive. The normal application of load is shown by the *arrows*. This load is applied by a tensile testing machine or other mechanical means of holding open the end of the specimen (Pocius 1991). Reprinted with permission of John Wiley & Sons, Inc., copyright ©1991

1.2.2 Bacterial Exopolymer Adhesives

1.2.2.1 Polysaccharide Adhesive Viscous Exopolymer

The marine bacterium *Alteromonas colwelliana* LST produces an exopolysaccharide which it uses to adhere strongly to surfaces under severe conditions in its natural environment. It also synthesizes tyrosinase, dihydroxyphenylalanine (DOPA), and related quinones which participate in water-resistant adhesive production in higher organisms (Yamada et al. 2000). Therefore, the mechanical properties of “polysaccharide adhesive viscous exopolysaccharide” (PAVE) isolated from several strains of this bacterium were evaluated on commercially relevant substrates (Labare et al. 1989). An efficient process for production of PAVE from one strain of bacteria was demonstrated (5–11 g/l). Depending on culture conditions, the carbohydrate/protein ratio in PAVE as

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