



# Nature as a blueprint for polymer material concepts: Protein fiber-reinforced composites as holdfasts of mussels



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## ABSTRACT

Today's demands for novel high-performance polymeric materials with precisely adjusted task-specific mechanics, durability and reliability require new concepts. This review introduces the byssus of blue mussels as a conceptual example of a natural functional proteinaceous material with gradual mechanical properties. The structure–function relationship of the involved proteins, as well as their arrangement and interplay are described in detail to gain insights into how nature deals with mechanical polymer gradients. The mussel byssus can serve as a blueprint which already led to bioinspired approaches for novel applications.

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**Abbreviations:** Å, Angström; DOPA, 3,4-dihydroxyphenylalanine; EGF, epidermal growth factor; EST, expressed sequence tag; His, histidine; MAP, mussel adhesive protein; Mfp, mussel foot protein; NMR, nuclear magnetic resonance; ORF, open reading frame; P4H, prollyl 4-hydroxylase; PCR, polymerase chain reaction; PTMP1, Proximal Thread Matrix Protein 1; SEM, scanning electron microscopy; TEM, transmission electron microscopy; TGA, thermogravimetric analysis; TMP, Thread Matrix Protein; w/w, weight percent.

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## 1. Introduction

Environmental conditions can exert huge impact on materials. Rain, snow, sea water and sun cause erosion and corrosion of a material, while biological processes like fouling additionally impair the materials quality and lifetime. Further, mechanical stress applied by wind, current or waves are a major challenge for materials. Therefore, in nature as well as in technical applications material design is the key prerequisite to compensate negative influences.

### 1.1. Environmentally exposed materials

Environmental impacts induce severe changes in exposed materials. Photolysis and photo-oxidation caused by UV radiation as well as hydrolysis can alter the mechanical properties of a material or lead to chemical weathering and shortens the material's lifetime. Physical processes like expansion and contraction due to changes in temperature or hydration can influence the material's integrity. Continuously changing mechanical forces caused by traction, compression, torsion and twisting require an effective dissipation of the applied loads to prevent material failure. Since one-component materials with a high tensile strength mostly show brittleness and elastic materials are often too soft, an optimal combination of both tensile strength and elasticity may result in a composite material with desired properties to withstand a whole range of environmental conditions.

The properties of composite materials are determined by the individual components, their geometry and arrangement in the material [1]. Depending on the filler they can be differentiated into particle-reinforced and fiber-reinforced composites. Flakes, beads or short filaments enclosed in a homogenous matrix (e.g. metal, ceramic or polymers)

can increase strength, lifetime and reliability of a material and are for instance suitable in light metal engineering, semiconductor technology or dentistry. In contrast, fiber-reinforced composites are often used as construction material in building industry, automobile manufacture or aircraft construction due to a high mechanical strength and stiffness, which is determined by the use of either randomly distributed or aligned fibers (e.g. carbon, glass, polymers, silicon carbide or metal) in a polymer or a resin matrix [2].

Combining materials with different mechanical properties, especially different stiffness, generates contact areas similar to bilayers which potentially are points of failure in the material. Under mechanical load these components deform differently leading to an increased radial stress at the interfaces causing cracks or micro-tears. Therefore, sharp and condensed contact areas have to be minimized to distribute local stress to a larger volume. Additionally, cross-linking (chemically or physically) between the components can sustain the composite [3]. However, a higher number of cross-links might decrease the material's flexibility. One approach for the minimization of contact sites is a gradual distribution of individual components [3,4].

### 1.2. Gradual materials

In a gradual distribution the contact areas of individual components and between distinct phases are enlarged. Consequently, sharp interfaces are reduced, which diminishes the appearance of exceeded local stress. Additionally, due to a larger interface, more cross-links between the individual components can be formed, which finally results in a high resistance against deformation, crack formation and rupture [3,4]. However, a tunable manufacturing of composites with a seamless gradual component distribution remains challenging.

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