



Title	Studies on Preparation of Naturals-Based Cryogels via the Inverse Leidenfrost Effect and Their Modifications with Phospholipid
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Abstract of Thesis

Name (Endang Ciptawati)	
Title	Studies on Preparation of Naturals-Based Cryogels via the Inverse Leidenfrost Effect and Their Modifications with Phospholipid (逆ライデンフロスト効果を利用した天然物由来クライオゲルの調製およびリン脂質による修飾に関する研究)
Abstract of Thesis Cryogels have gained significant attention over the past two decades for their distinctive mechanical strength and porous structure, making them ideal for biomedical and environmental applications. These materials are macroporous polymeric networks generated via cryotropic gelation, a process that typically occurs under subzero temperatures. Many existing cryogels are synthesized predominantly from synthetic, petroleum-derived polymers. The escalating waste from synthetic materials, which are predominantly non-biodegradable, presents a grave environmental concern. Coupled with the dwindling fossil-based energy sources, there is an urgent call for green alternatives sourced from renewable materials. Chitosan, a natural polymer derived from crustacean shells via the deacetylation process, stands out as a potential answer. This prevalent biopolymer is versatile, non-toxic, cost-effective, and biodegradable. Moreover, chitosan can be adapted into a stable three-dimensional (3D) cryogel network. Specifically, chitosan cryogel offers a sustainable substitute to petroleum-based products. In chapter II, the preparation of biodegradable sponge-like cryogel particles of chitosan, utilizing the inverse Leidenfrost (iLF) effect and glutaraldehyde as the cross-linker was conducted. The resulting cryogels exhibited a sponge-like morphology with micrometer-scale interconnected pores and maintained their structural integrity through three compression-release cycles. To gain insight into the structure-property relationships between the polymer and solvent, as well as to optimize cryogel production, the influence of the acetic acid concentration on the characteristics of the produced cryogels was investigated. Variations in acetic acid concentration affected their properties, with particle sizes ranging from 1300 to 2900 μm. With increasing acetic acid concentration, the swelling degree decreased and stabilized at approximately six at 0.03 mol. Moreover, the FTIR peak shift of the OH and amino groups from 3261 to 3404 cm^{-1} confirmed the formation of cross-links between chitosan and glutaraldehyde. In chapter III, the co-gelation of chitosan and gelatin (CH-G) under inverse Leidenfrost (iLF) conditions to generate composite cryogel particles with interconnected porous networks, a critical step toward more functional natural macromolecules was introduced. Incorporation of gelatin into the chitosan matrix, crosslinked with glutaraldehyde, yielded cryogel particles exhibiting an optimal combination of mechanical elasticity and interconnected porosity. Relative to other systems, the CH-G cryogels showed superior performance in elasticity and structural integrity, with a specific surface area of 2.03 m^2/g. This enhanced mechanical resilience is attributed to synergistic interactions between the rigid chitosan backbone and the flexible gelatin polypeptide chains, which improve compressive recovery and pore uniformity. SEM analysis revealed a well-distributed, interconnected fibrous network, while nitrogen adsorption-desorption measurements confirmed the mesoporous character of the CH-G cryogels. These findings highlight the critical role of polymer hybridization and cross-linking strategies in modulating cryogel microarchitecture and mechanical properties. In chapter IV, two methods for coating chitosan cryogel employing lipid membrane made of dipalmitoylphosphatidylcholine (DPPC) were presented. Phospholipid-coated chitosan cryogel particles exhibit enhanced mechanical properties, with improved elasticity and durability under compression and release cycles. Among the two coating methods studied, the direct incubation in the liposome solution method resulted in a more effective and higher phospholipid distribution than the solvent evaporation method. Scanning electron microscopy (SEM) revealed that the phospholipid coating effectively smooths both the surface and cross-sectional pores of the cryogels, while energy-dispersive X-ray (EDX) analysis confirmed an increased phosphorus content in chitosan cryogels coated via incubation. The DPPC (dipalmitoylphosphatidylcholine) membranes promote strong interactions with the chitosan matrix, as evidenced by a shift in the transition temperature (T_m) observed in differential scanning calorimetry (DSC) measurements, resulting in enhanced mechanical resilience. Notably, the coated cryogels retained their structural integrity after five compression-release cycles, whereas uncoated chitosan cryogels withstood only three cycles. In chapter V, the evaluation of chitosan-based cryogels for Cu^{2+} adsorption was performed. According to the adsorption pH study, the optimum pH for Cu^{2+} adsorption is 5. In addition, the adsorption amount of Cu^{2+} by the original chitosan cryogel (without coating) decreased at higher pH values due to the precipitation of Cu^{2+} into $\text{Cu}(\text{OH})_2$. The Langmuir binding constant (b) for the CuSO_4 adsorption of the original cryogel is 4.9, whereas for the coated one is 0.027. The Langmuir model is the best fit among the 3 adsorption isothermal models. This means that the adsorption occurs on a homogeneous monolayer surface with no interaction between adsorbed species. At a higher temperature (41$^{\circ}\text{C}$), the adsorption of CuSO_4 by coated chitosan cryogel is increased compared to 30 $^{\circ}\text{C}$. This happened because of the change in the self-assembly of the phospholipid layer into a more disordered phase at the transition temperature, which allows more interaction between Cu^{2+} and the functional group of chitosan. Therefore, by changing the temperature, the sensitivity of the adsorption performance of the coated chitosan cryogel can be adjusted. In chapter VI, the general conclusion of this study is summarized. It outlines future research directions aimed at advancing the understanding and application of chitosan cryogels as next-generation biomaterials, thereby extending the relevance and impact of this work beyond the scope of the current thesis.	

論文審査の結果の要旨及び担当者

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論文審査の結果の要旨 Cryogelは、氷点下で起こる氷晶化プロセスを活用して生成される連結型多孔構造を有する材料であり、機械的強度と多孔質構造など秀でた特長を保持するため、医療材料あるいは環境浄化材料としての利用が期待されている。既存のクライオゲルの多くは合成ポリマーを原料としており、天然資源から取得できる天然ポリマーを活用した再生可能材料を原料とする環境に優しい代替材料への転換する潜在的なニーズがある。また、天然資源の1つであるリン脂質は両親媒性分子に分類され、単分子膜や2分子膜といった自己組織化構造を有することが知られており、その秩序構造を活用した高度分離材料の設計開発も進んでいる。本学位論文では、多種多様な特長を示す天然高分子キトサンCryogelを基盤材料として調製し、さらには、リン脂質分子膜と融合させた新規な天然複合材料の設計開発指針を目的とする。第1章では、当該研究分野における背景を調査し、前述のResearch Proposalの妥当性が明らかにされている。第2章では、inverse-Leidenfrost効果とグルタルアルデヒド架橋剤を活用して、最適な条件でスポンジ状キトサンクライオゲル粒子を調製し、マクロ孔形成、孔の相互連結性、機械的弾性、構造可逆性など秀でた特性を示すことが示されている。第3章では、第2章と同様の条件において、キトサンを基盤に、異種天然高分子(ゼラチンほか)との融合材料を調製した結果、機械的弾性、孔の相互連結性、さらには、比表面積に秀でる複合クライオゲル粒子を調製することに成功している。第4章では、3章までに調製された複合ゲル(キトサン-ゼラチン)表層に、リン脂質(dipalmitoylphosphatidylcholine (DPPC))膜を表層固定化した材料の調製について検討されている。リン脂質膜を表層固定したクライオゲル粒子は、機械的弾性、構造可逆性が大幅に改善され、さらには、示差走査熱量測定(DSC)解析の結果、リン脂質膜の物性の特長も有することを明らかにされている。上記の知見に基づいて、天然資源から、高分子やリン脂質など、異質の分子を回収し、分子の秩序を考慮して化学的・物理的に配置する手法を選択し、表層固定した複合ゲル担体として再構築するための方法論を一般的なスキームとしてまとめられている。第5章では、ケーススタディとして、最適化Cryogelにおける銅(Cu)イオンの回収プロセスの可能性について検討されており、5章までに得られた材料の有効性が示されている。第6章では、本研究の結論をまとめた上で、次世代バイオマテリアルとしての展開を促進するための提案が述べられている。以上の記述のとおり、博士(工学)の学位論文として価値のあるものと認める。			