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The Use of Strain Energy Density to Identify Self-Healing Behavior in Chitosan Hydrogels

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ABSTRACT

Self-healing materials operate based on trigger mechanisms, release of healing agents, healing reactions and self-assembly. They are used in infrastructure, aerospace, electronics and biomedical applications. The efficiency of the healing process is crucial, as it must be fast and effective, with the repaired area being as strong as the original material. Experimental identification involves techniques to evaluate mechanical properties, structural integrity and healing efficiency. Chitosan-based hydrogels are promising due to their biocompatibility, biodegradability and excellent mechanical properties. The deformation energy density directly influences the mechanical properties, self-healing capabilities, cellular behavior and drug release.

Introduction

Self-healing materials are a fascinating field of research, and they operate on several key principles such as: Trigger Mechanism (Mashkoor, et al. [1]), Healing Agent Release (An, et al. [2]), Healing Reaction (Brochu, et al. [3]), Self-Assembly (Ghosh [4]). Trigger mechanism includes external and internal stimulus, since some materials require an external trigger, like heat, light, or pressure, and others rely on internal cues, such as the presence of a crack or damage, to activate the healing mechanism or to initiate the healing process (Mashkoor, et al. [1]). On the other hand, healing agent release involves microcapsules that containing a healing agent embedded within the material (An, et al. [2]) and when the material cracks, the capsules rupture, releasing the agent (Brochu, et al. [3]); vascular networks, since some materials have built-in networks of channels or veins that transport the healing agent to the damaged area (Ghosh [4]). The healing reactions may be chemical or physical. In the first, the released healing agent undergoes a chemical reaction, often polymerization or cross-linking, to form new bonds and repair the damage (Brochu, et al. [3]). In the second one, the healing agent simply fills the crack or void, restoring the material's structural integrity. The more important principle is the self-assembly. Some materials have molecules that can self-assemble into new structures, filling the gap left by the damage, and this makes them a strong candidate for use in self-healing processes (Zhang [5]).

Self-healing materials are used in infrastructure in which self-healing concrete and asphalt can extend the lifespan of roads and bridges (Jiang, et al. [6]); in aerospace industry, since self-healing coatings can protect aircraft from damage and corrosion (Guadagno, et al. [7]); in electronics, self-healing electronic materials can improve the reliability of devices (Liu, et al. [8]); in biomedical applications from implants to hemostatic powders being able to reduce the risk of infection and failure (Beserra Junior, et al. [9]). The healing process should be efficient, repairing the damage quickly and effectively (Pollock [10]). The repaired area should be as strong and durable as the original material (Mitchell [11]) and the material should be able to heal multiple times without significant degradation, even though the process should not only be environmentally friendly but not produce harmful byproducts (Dallaev [12]). By understanding these principles, researchers are developing innovative materials with the potential to revolutionize various industries.

Identifying Self-Healing Behavior Experimentally

To experimentally identify the self-healing behavior of a material, should typically be employed a combination of techniques to assess its mechanical properties, structural integrity, and healing efficiency before and after damage. The main information regarding the mechanical properties of self-healing materials is related to measure of the material's strength and elongation before and after damage and healing (Abend, et al. [13]); the material's bending strength and stiffness (Didem, et al. [14]); the material's resistance to sudden impact loads (Smith [15]); Structural analysis is performed using data obtained through scanning electron microscopy (SEM), obtaining the visualization of the microstructure of the material, including the damage and the healed region (Ural [16]); transmission electron microscopy (TEM) that examines the material at the atomic level to understand the healing mechanism (Song, et al. [17]). Others property measurements such as thermal analysis that measures changes in thermal properties, such as glass transition temperature or melting point are important to assess the impact of healing (Kalista SJ Jr [18]); and electrical conductivity that measures changes in electrical conductivity to evaluate the restoration of material properties. It was very important also knows the healing kinetics specially by time-lapse imaging and real-time monitoring. The first one monitors the healing process over time using techniques like optical microscopy or SEM; the second one uses techniques like infrared spectroscopy or Raman spectroscopy to track the chemical changes during healing.

Properties that Identify Self-Healing Behavior in Materials

The principal properties that identify self-healing behavior in materials are: autonomous healing, recovery of mechanical properties, durability of the healed region, repeatability of healing, efficiency of the healing process, and environmental compatibility. Autonomous healing refers to the material's ability to initiate and complete the healing process without external intervention, including automatic damage detection and the release of healing agents (Hobbs, et al. [19,20]). Recovery of mechanical properties means the material regains its original or near-original mechanical properties, such as strength, stiffness, toughness, and other relevant properties, after healing (Ganesan [21]). Durability of the healed region ensures that the repaired area is as durable as the undamaged material, capable of withstanding further loading and environmental conditions without re-rupturing (Osada, et al. [22]). Repeatability of healing allows the material to undergo multiple cycles of damage and healing without significant degradation, ensuring long-term performance and durability (Vishe, et al. [23]). Efficiency of the healing process is crucial, as it requires a rapid and efficient repair to minimize downtime and maintenance costs, especially in applications demanding quick fixes (Choi, et al., [24]). Finally, environmental compatibility is essential, as the healing process and materials used should be environmentally friendly, avoiding the release of harmful substances or negative impacts on the environment (Dallaev [12]).

The Relationship between Self-Healing Behavior and Strain Energy Density

The relationship between self-healing behavior and strain energy density is complex. Strain Energy Release Rate (SERR) plays a crucial role in triggering self-healing. When a crack propagates, it releases strain energy (Broek [25]). If this energy is sufficient to activate the healing mechanism, the material can initiate the repair process. The efficiency of the healing process can be influenced by the amount of strain energy released, with more energy potentially leading to faster and more complete healing. Additionally, the material's inherent properties, such as elasticity, plasticity, and toughness, can affect how strain energy is stored and released, impacting the self-healing process. Specific self-healing mechanisms include capsule-based systems, vascular networks, and intrinsic self-healing. In capsule-based systems, high strain energy ruptures capsules, releasing healing agents (Reda, et al. [26]). The amount of healing agent released and its ability to react and fill the crack depend on the energy available. Vascular networks utilize strain energy to induce pressure gradients, driving the flow of healing agents to the damaged area. The healing rate is influenced by the fluid flow rate, which is related to the strain energy input. Intrinsic self-healing involves molecular rearrangement facilitated by strain energy, allowing the material to reorganize itself and heal. The extent of healing depends on the material's ability to dissipate and utilize the strain energy for bond reformation.

Optimal self-healing requires a balance of strain energy, careful material design, appropriate healing agent selection, and consideration of environmental factors (Jiang, et al., [27]). The Strain Energy Release Rate (SERR) is a critical parameter in fracture mechanics that quantifies the energy released as a crack propagates through a material (Broek [25]). When a crack extends, the material releases stored elastic strain energy (Long, et al. [28]). This energy is balanced by the energy required to create new crack surfaces and dissipate energy through other mechanisms like plastic deformation or heat. The critical SERR (Gc) is the minimum SERR required to propagate a crack. By understanding the SERR, engineers and scientists can design materials with enhanced fracture toughness and self-healing properties, leading to more durable and sustainable structures.

Chitosan-Based Hydrogels as Self-Healing Material

Chitosan-based hydrogels have emerged as promising materials for self-healing applications due to their biocompatibility, biodegradability, and excellent mechanical properties (Manasi, et al. [29]). Their self-healing mechanisms primarily involve dynamic covalent bonds (imine and disulfide bonds) (Cui, et al. [30-32]) and physical crosslinking (hydrogen bonding and ionic crosslinking) (Ahmadi, et al. [33]). Additionally, self-assembly of chitosan molecules into ordered structures contributes to their self-healing ability (Ganesan, et al. [21,32,34]). Self-healing chitosan hydrogels possess several key properties: mechanical strength, self-healing ability, biocompatibility,

biodegradability, and tailorability. These properties make them suitable for various applications, including tissue engineering (Manasi, et al. [29]), drug delivery (Manasi, et al. [29]), wound dressing (Rajinikanth, et al. [35]), and sensor applications (Wu, et al. [36]).

Importance of Strain Energy Density for Chitosan Hydrogels in Biomedical Applications

Strain energy density is a crucial factor influencing the performance of chitosan hydrogels in biomedical applications. It directly impacts their mechanical properties, self-healing capabilities, cell behavior, and drug delivery. Higher strain energy density allows hydrogels to withstand greater deformation, support heavier loads, and trigger more efficient self-healing mechanisms (Tianyi, et al. [37]). Additionally, it influences cell adhesion, proliferation, migration, and drug release kinetics. To enhance strain energy density, strategies such as physical and chemical crosslinking, incorporation of nanoparticles or fibers, and the design of intrinsic self-healing mechanisms can be employed (Wu, et al. [38,39]). By carefully controlling strain energy density, researchers can develop chitosan hydrogels with tailored properties for various biomedical applications. Strain energy density plays a critical role in the self-healing behavior of chitosan hydrogels, influencing their ability to absorb energy, dissipate stress, and initiate the healing process. High strain energy can trigger self-healing mechanisms such as capsule rupture and dynamic bond breaking and reforming. It also enhances healing efficiency by providing the necessary energy for bond formation and reorganization, accelerating the healing rate. Additionally, a high strain energy density capacity allows the hydrogel to redistribute stress around the damaged area, preventing further crack propagation and maintaining mechanical integrity post-healing.

The mechanical properties of the hydrogel, influenced by its strain energy, can affect cell behavior, promoting cell adhesion, proliferation, and tissue integration. To optimize strain energy density, strategies such as crosslinking, incorporation of nanoparticles or fibers, and the design of intrinsic self-healing mechanisms can be employed. By carefully controlling strain energy density, researchers can develop chitosan hydrogels with enhanced self-healing abilities, improved mechanical properties, and optimized biological performance for a wide range of biomedical applications. Generally, more strain energy density can lead to more effective self-healing. Higher strain energy can rupture microcapsules embedded in the material, releasing healing agents (Nik Md Noordin Kahar, et al. [40]), and facilitate the breaking and reforming of dynamic covalent bonds, a key mechanism for self-healing. Increased strain energy provides the necessary energy for bond formation and molecular rearrangement, accelerating the healing process. Additionally, self-healing can help redistribute stress around the damaged area, preventing further crack propagation and maintaining the overall mechanical integrity of the material (Wu, et al. [41]). However, excessive strain energy can lead to irreversible damage, hindering the self-healing process. The optimal strain energy level depends on the specific material, its self-healing mechanism, and the desired level of healing. To maximize self-healing, researchers focus on designing materials with appropriate mechanical properties, optimizing the healing agent release mechanism, and developing effective self-healing mechanisms that can respond to different levels of strain energy. By carefully considering these factors, it's possible to design self-healing materials that can effectively repair damage and maintain their performance under various conditions.

Materials and Methods

Four types of chitosan, supplied by CERTBIO/CCT/UFCG, were used, whose main properties are shown in Table 1. The preparation methods for all samples were described elsewhere (Navarro, et al. [42]). All samples of hydrogel used is this work were rheologically characterized using a HAAKE™ MARS™ rheometer (Thermo Fisher Scientific), equipped with a PP35TiL rotor with plate-plate geometry and a gap of 0.5mm, frequency sweep of 0.1 to 74 Hz, at 22 °C, 23 °C or 37 °C, depending on the application, whether internal or external, that the hydrogel would have.

Table 1: Properties of chitosan samples used.

Chitosan	MM (KDa)	AD (%)	pH	M
A	270	12	7	-
B	400	20	6	-
C	639	4	2.8-4.8	3
D	639	4	2.7-5.3	10

Results and Discussion

From the statistical treatment based on factorial design, the data were grouped and the effects calculated as if they were all linearly independent of each other. The factors were obtained using the Matrix Calculator® software, using the linear least squares method. For two factors varying under a constant third factor, W = W (i, j). For 4 factors varying simultaneously, W = W (i, j, k, l). As shown in Figure 1, under constant chitosan concentration, around 5.265% (w/v), the deformation energy density will be greater the higher the molarity and pH of the hydrogel. At constant acidic pH (pH = 4.0), W is more dependent on the molarity than on the chitosan concentration. The lowest values for W were found for 3.0 < pH < 4.5, for a wide range of concentrations. The highest values, as shown in Figure 2, are for the highest molarities (M > 9.5) for any value of chitosan concentration. Regardless of the molarity analyzed, whether 3M or 10M, the maximum values for the deformation energy density are found in a small range located in the upper left part of the variation W (pH, Ch. C.). The values vary diagonally along the pH x Ch. C. plane, with the lowest values for W being calculated for higher pH and lower chitosan concentration (Ch. C.) (see Figures 3a & 3b). Figure 4 shows that the lower the degree of deacetylation and, therefore, the higher the degree of acetylation, and the higher the molar mass of chitosan used in the production of the hydrogel, the higher the deformation energy density of the gel. When

the combined effects of molar mass, acetylation degree, pH and molarity are analyzed, it is observed that, the lowest value for W refers to the combination of lower molar mass, degree of acetylation and molarity and higher pH.

The highest value for W is related to higher molar mass, degree of acetylation and molarity and lower pH. For the purpose of self-healing behavior, it is desirable that the hydrogel has a pH close to neutral, low molar mass, low molarity regardless of the degree of acetylation, which implies W < 2,000.

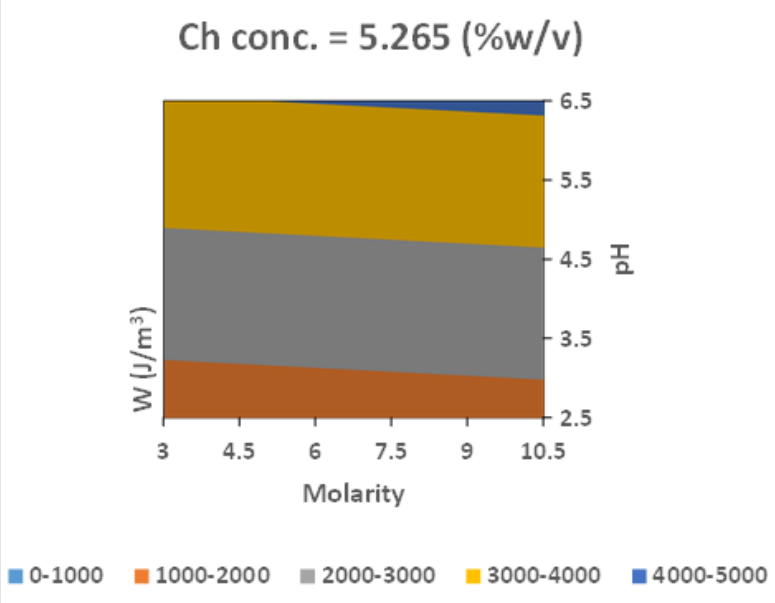

Figure 1: Effect of Molarity and pH under Constant Chitosan Concentration.

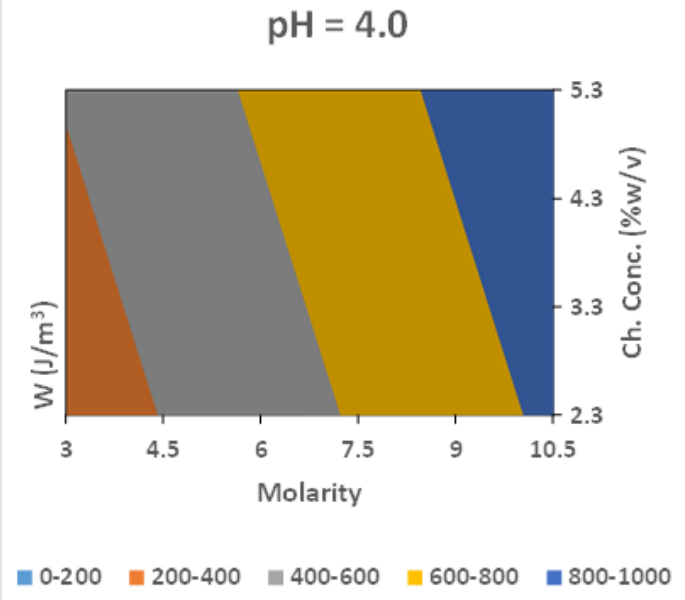

Figure 2: Effect of Molarity and Concentration of Chitosan under Constant pH.

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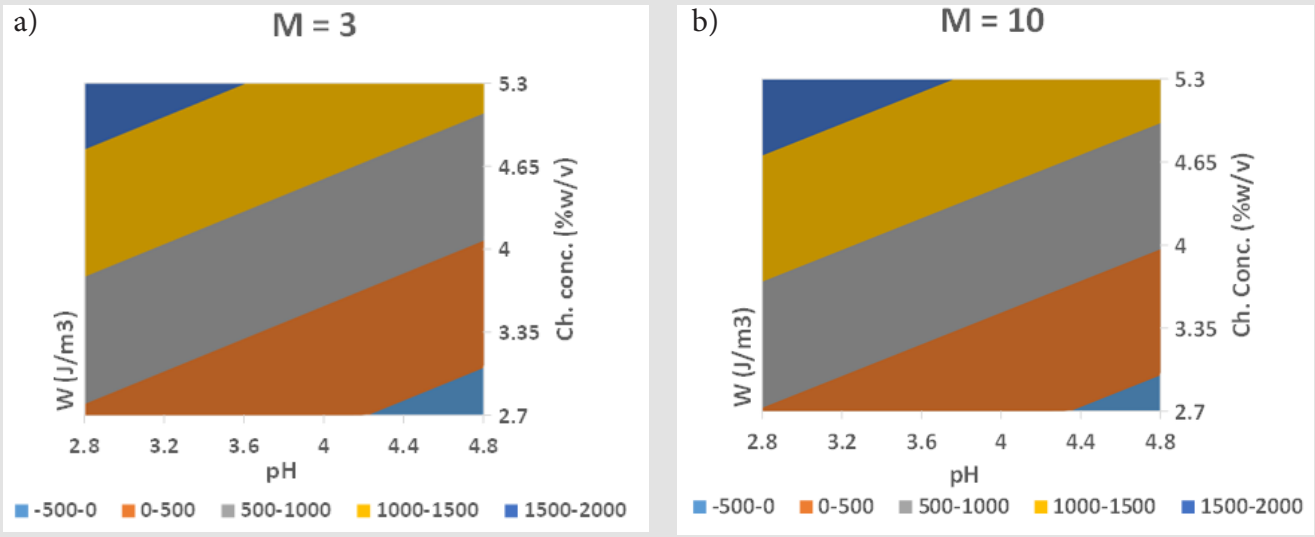

Figure 3: Effect of Chitosan Concentration and pH under Constant Molarity a) 3M and b) 10M.

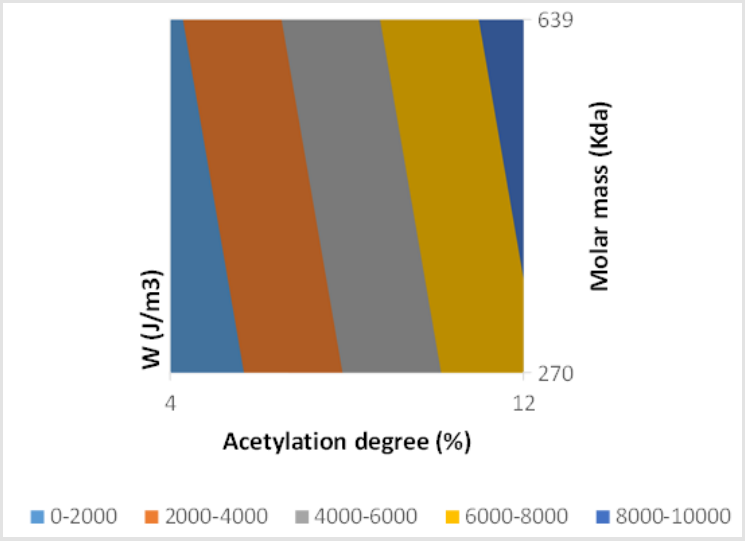

Figure 4: Combined Effect of Molar Mass and Acetylation Degree under Constant pH.

Conclusion

From the statistical treatment based on factorial design, the data were grouped and the effects calculated as if they were all linearly independent of each other. Under constant chitosan concentration, the deformation energy density will be greater the higher the molarity and pH of the hydrogel. At constant acidic pH (pH = 4.0), W is more dependent on the molarity than on the chitosan concentration. The lowest values for W were found for 3.0 < pH < 4.5, for a wide range of concentrations. the lower the degree of deacetylation and, therefore, the higher the degree of acetylation, and the higher the molar mass of chitosan used in the production of the hydrogel, the higher the deformation energy density of the gel. When the combined effects of molar mass, acetylation degree, pH and molarity are analyzed, it is observed that, the lowest value for W refers to the combination of lower molar mass, degree of acetylation and molarity and higher pH. The highest value for W is related to higher molar mass, degree of acetylation and molarity and lower pH.

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