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Effect of chitosan loading on structural and physical properties of polyvinylpyrrolidone/chitosan composites using simple casting process

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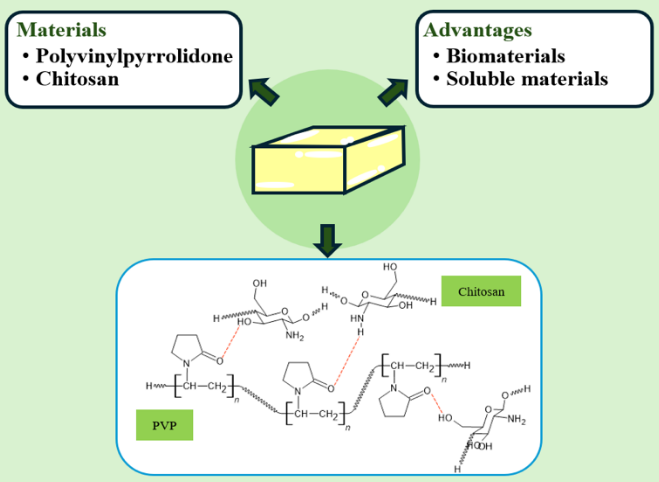
Abstract



This research focused on the development of polymer composite materials for dissolving needles applications. Polyvinylpyrrolidone (PVP) was selected as the matrix phase, with chitosan (CS) chosen as the reinforcement phase due to its unique ability to absorb various substances and maintain stability in a room-temperature environment. Acetic acid was used as a dissolving agent for the chitosan suspension. A 30% w/v PVP solution was prepared in deionized water under magnetic stirring. Subsequently, chitosan powder was dissolved in acetic acid (2 M) at a 1.00 : 1.75 mole ratio using an ultrasonic process. Different weight ratios of the chitosan suspension (0.0, 0.5, 1.0, 2.0, 5.0, and 10.0 wt%) were added to PVP matrix under continuous stirring at 200 rpm for 30 min. to achieve a homogenous suspension. Each PVP/CS suspension was then cast into a silicone mold and dried at 40 ºC in the oven. Examining the structural properties of the PVP/CS composite samples under an optical microscope revealed a well-dispersed arrangement of CS particles within the PVP matrix. In the chemical structure analysis using Fourier transform infrared (FTIR) spectroscopy, the spectra of the PVP composites with different CS ratios exhibited identical patterns for all the samples, indicating a correlation with the same phases in the precursor materials. Furthermore, the optimized ratio of 1 wt% chitosan loading in the PVP/CS composites achieved a balance between enhanced mechanical property and reduced solubility, influenced by the distribution of CS particles within the PVP structure. Moreover, the presence of hydrogen bonds between the NH_2 groups in chitosan and the C=O groups in PVP plays a key role in mechanical enhancement and soluble time.

Keyword: Polyvinylpyrrolidone; Chitosan; Polymer Composites

1. Introduction

Dissolving materials often undergo structural dissociation when exposed to solvents such as water, acids, organic compounds, and others. The dissolution mechanism often involves the breaking of bonds between the substance and the solvent, leading to the release of atoms, ions, or molecules. For instance, water-soluble polymers are organic materials that dissolve, disperse, or swell in water thereby modifying the properties of aqueous systems [1]. Water-soluble polymers are primarily used in pharmaceuticals, food processing, cosmetics, agriculture, and water treatment [2-6]. Polyvinylpyrrolidone (PVP), a water-soluble synthetic polymer with the chemical formula $(C_6H_9NO)_n$ and a molecular weight of 40,000 g/mol, features in a wide range of applications including cosmetics, hair sprays, pharmaceutical capsules, and microneedles owing to its non-toxicity, shape-ability, water solubility, film-forming agent, biocompatibility, and good adhesive properties [7-9]. Alternatively, acid-soluble polymers utilize the solvent's ions to cleave the polymer chains. These materials find extensive applications in various fields, including medicine (e.g., drug delivery) and construction (e.g., self-healing concrete). Chitosan (CS) is a biopolymer that is soluble in acidic solution with a pH below 6.5. It possesses a molecular formula of $(C_6H_{11}NO_4)_n$ and a molecular weight ranging from 50,000 to 190,000 DA. This natural polymer exhibits a melting point of 102.5°C and a boiling point of 115.5°C, with an elastic modulus of 1.5 GPa [10]. Chitosan is derived from chitin through a chemical process that modifies its molecular structure. Due to its natural origin, chitosan is biocompatible and widely employed in various applications, including encapsulation, drug patches, and microneedles [11]. Pakistani researchers utilized thiolated chitosan (TCS) and polyvinyl acetate (PVA) at the TCS:PVA ratios of 7:3, 8:2, and 9:1 for transdermal drug delivery by a casting process using a PDMS mold [12]. All conditions yielded composite films with desirable levels of both hardness and flexibility, demonstrating successful formability. Meanwhile, the successful development of a novel material for diabetic drug delivery systems that offered a sustained release profile comparable to traditional insulin injection was reported by Tay and research team [13]. The interesting materials were focused on a matrix phase of hyaluronic acid (HA) incorporated with a reinforcing phase of silica (SiO_2). The optimized results indicated that a composite comprising HA and 20 vol% of SiO_2 exhibited a significant hardness with desirable dissolution characteristics. While pure HA dissolved within 60 seconds, the HA-20% vol SiO_2 composite demonstrated a slightly extended dissolution time of over 90 seconds. This specific composition was identified as the most promising candidate for further development. Meanwhile, a polymer composite of PVP and cellulose nanocrystal (CNC) prepared by a freeze-drying process was reported by Voronova and research team [14]. After incorporating CNC into the PVP, it was observed that Young's modulus and hardness properties significantly increased; conversely, the elongation at break decreased as a result of the formation of the composite structure. The research on chitosan and PVP biocomposites for biomedical applications was conducted by R. Poonguzhali and the research group [15]. The optimal ratio of chitosan-to-PVP ratio was determined to be 1:1, corresponding to the highest swelling efficiency and mechanical property. The inherent rigidity and fragility of the PVP matrix could be improved by the incorporation of chitosan, which facilitated strong and extensive hydrogen bonding with the polymer backbone of the matrix.

Therefore, the influence of chitosan into polyvinylpyrrolidone to form a well-defined composite by mechanical process has been studied. The PVP/CS composite components are thought to be linked by external hydrogen bonds between the NH_2 groups in chitosan and the C=O groups in PVP, which contribute to the increased rigidity of the composite [16]. The PVP matrix exhibits excellent water solubility; however, some brittleness is observed in its structure. The fibrous nature of PVP and chitosan improves dispersion, leading to the enhancement of mechanical properties in the matrix [17]. Thus, the reinforcement phase with chitosan may offer superior strength encapsulation and a drug delivery system into the PVP matrix [18].

2. Materials and Methods

Materials

Polyvinylpyrrolidone (PVP K-30) in a cosmetic grade with a molecular weight of 40,000 g/mol was obtained from AK Scientific. Chitosan (CS) with a low molecular weight 50,000-190,000 Da and R&D grade was purchased from Sigma-Aldrich.

Synthesis of PVP/CS composite films

A 30 wt% PVP K-30 solution was prepared by dissolving 30 g of PVP K-30 in 70 mL of deionized (DI) water. The solution was stirred for 1 h at room temperature, yielding a clear and yellow liquid. For the CS suspension, 5 g of CS powder was dissolved in 27 mL of 2 M acetic acid. Subsequently, 68 mL of deionized (DI) water was added to the solution, followed by pulsed mode of sonication in 2 rounds; the first 8 hrs at temperature below 20℃ and second round 8 hrs in at temperature below 20℃ and keep it in the refrigerator. The resulting 5.0 wt% CS suspension exhibited a clear, yellow, and viscous appearance. To prepare the PVP/CS composite films, different weight ratios of CS in the PVP matrix (0, 0.5, 1.0, 2.0, 5.0 and 10 wt%) were prepared. The mixtures were stirred at ambient temperature for 45 min to ensure thorough mixing, which was followed by 5 min of sonication to eliminate entrapped air bubbles. The solutions were then cast into silicone molds and allowed to stand at room temperature for 24 h to facilitate solvent evaporation and reduce air bubbles. Finally, the PVP/CS composite films were dried in an oven at 40 °C for 24 h.

Characterization

All samples of the PVP/CS composite films appeared as thick flat films. The surface morphology and chemical bonding structure of the films were characterized using an optical microscope (Olympus, BX43 with 10x magnification) and Fourier transform infrared spectroscopy (FT-IR; PerkinElmer) over a wavenumber range of 400-4000 cm^{-1}. The thermal properties of the PVP/CS films were analyzed by thermogravimetry (Netzsch Model TG 209 F3 Tarsus) under a temperature range of 25-600 ºC, with a gas flow rate of 20 mL/min. The hardness of the PVP/CS composite films was measured using a Vickers microhardness tester (Shimadzu, HMV-2T). Additionally, the solubility of the composite films was evaluated by recording the time required for each sample to completely dissolve.

3. Results and Discussion

The morphologies of the PVP composite films with chitosan loadings of 0.0, 0.5, 1.0, 2.0, 5.0, and 10.0 wt.% by optical microscope images are depicted in Fig. 1. In the bare PVP film (Fig. 1(a)), some PVP aggregations inside the film were formed during the evaporation process owing to the excessive solubility of PVP's solubility at 20 wt% [19]. Meanwhile, the incorporation of CS at 0.5 wt% into the PVP matrix produced a similar morphology to that seen for the bare PVP film as seen in Fig. 1(b). The composite film with CS loading at 1.0 wt% in Fig. 1(c) exhibited a homogenous surface due to a high content of acid solvent addition into the system. Conversely, a progressively irregular surface morphology was observed in the composite films with a CS content of 2.0% or higher, as shown in Fig. 1(d) to 1(f). This was probably attributable to the increased viscosity and competition between the interactions of

CS–PVP phase and PVP phase–H_2O molecules during the preparation process followed by higher CS concentrations [20].

FTIR spectra of PVP/CS composite films with varying chitosan contents are illustrated in Fig. 2. The spectra of the composite films exhibited well-defined peaks corresponding to the characteristic functional groups of the PVP matrix. In pure PVP, the peaks at 571 cm^{-1}, 1075 cm^{-1}, and 1289 cm^{-1} related to C=O bending, C-O-C bending, and C-N stretching vibrations, respectively. Characteristic peaks were recorded at 1430 cm^{-1}, 1644 cm^{-1}, and 2957 cm^{-1} which corresponded to C-N bending, C=O stretching in the carboxyl group, and C-H stretching vibrations, respectively [21]. A broad stretching band observed between 3000 to 3750 cm^{-1} was assigned to O-H stretching and N-H stretching vibrations [22]. Notably, the intensity of the C-O-C stretching vibration at the peaks of 1028 cm^{-1} and 1075 cm^{-1} (arising from bare PVP) was increased with the addition of the chitosan reinforcement phase. Meanwhile, no significant shifts were observed at other wavenumbers, the data suggested a physical interaction rather than chemical bonding between PVP and CS. Therefore, it can be inferred that the PVP/CS composite materials do not undergo chemical reactions to form a new substance [23].

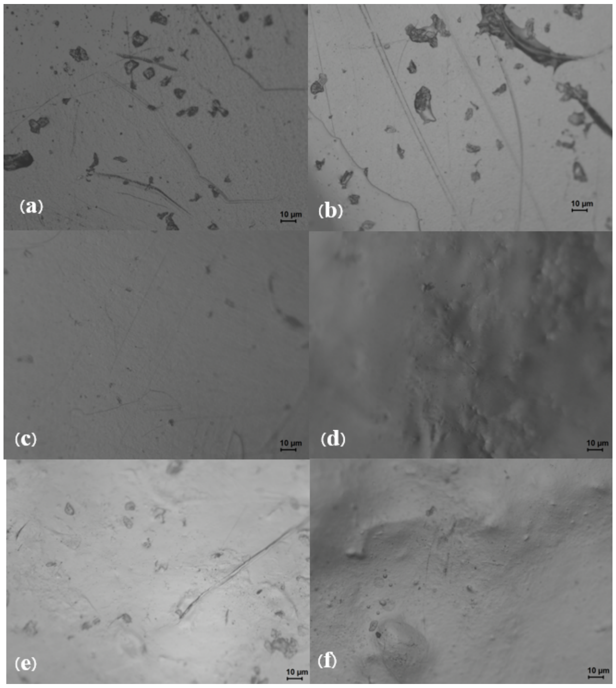


Fig. 1 Optical microscope images of PVP/CS composite films with increasing chitosan loadings (0.0%–10.0% by weight)

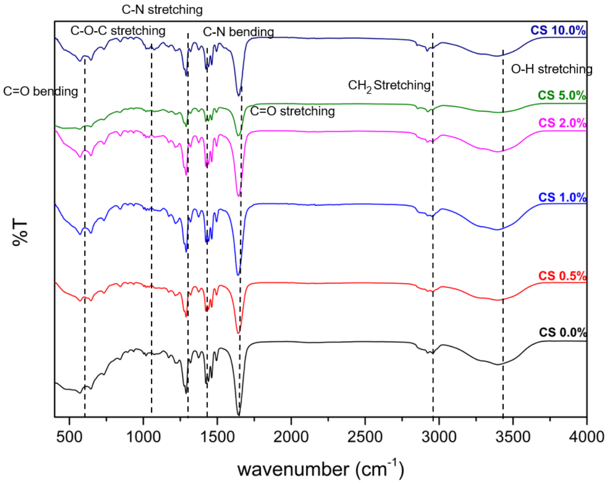


Fig. 2 FTIR spectra of PVP/CS composite films with various chitosan loading.

The thermal properties of the series of PVP-based composites containing varying chitosan contents investigated by thermos-gravimetric analysis is demonstrated in Fig. 3. The TGA profiles of all conditions exhibited similar trends and could be divided into four distinct regions. A significant mass loss was distinctly observed in the initial region (50-150°C) and could be attributed to the evaporation of residual moisture and acetic acid. The subsequent second region (250-400°C) was characterized by a further mass loss primarily due to the depolymerization of chitosan chains, and decomposition of pyranose rings in chitosan molecule [24-25], with the extent of mass loss directly correlated with the chitosan content. The sample with 10.0 wt% CS in the PVP matrix exhibited the highest weight loss in this region, depending on the high chitosan content in the composite film. The third region (400-450°C) in TGA analysis corresponded to the degradation of the PVP polymer backbone [26], which resulted in a significant mass loss. Finally, in the fourth region above 450°C, a thermally stable carbonaceous residue remained. This residue was composed of carbon-rich material that was resistant to further degradation. It was observed that in the TGA testing of the composites, the PVP and CS precursors exhibited decomposition characteristics that were consistent with those of their original forms. TGA analysis revealed distinct degradation stages: chitosan decomposed between 250-400°C, while PVP degradation was observed between 400-450°C. The composite materials exhibited a combination of these characteristics. Therefore, it can be concluded that the incorporation of CS into PVP formed a composite, and no production of new chemical products took place. In terms of TGA, no distinct changes were observed in the PVP/CS composite films.

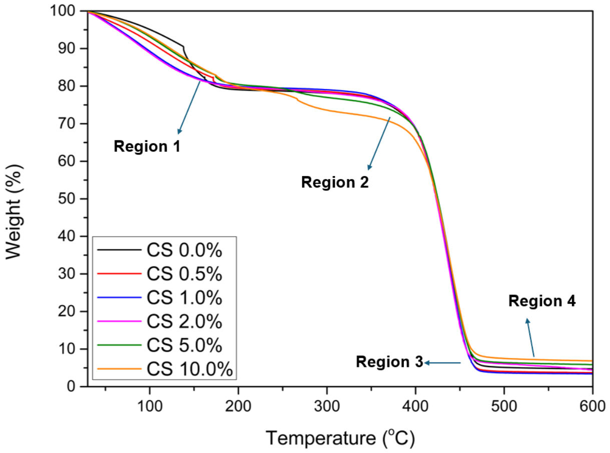


Fig. 3 Thermogravimetric analysis of PVP/CS composite films with various chitosan loading.

The Vickers hardness test was employed to assess the influence of chitosan content on the mechanical properties of the PVP/CS composite films, as shown in Fig. 4. A distinct trend of increase in the hardness value of the composite films was seen with the increase in CS loading. Notably, the PVP/CS film at 10.0 wt% CS loading exhibited the highest hardness among all tested samples.

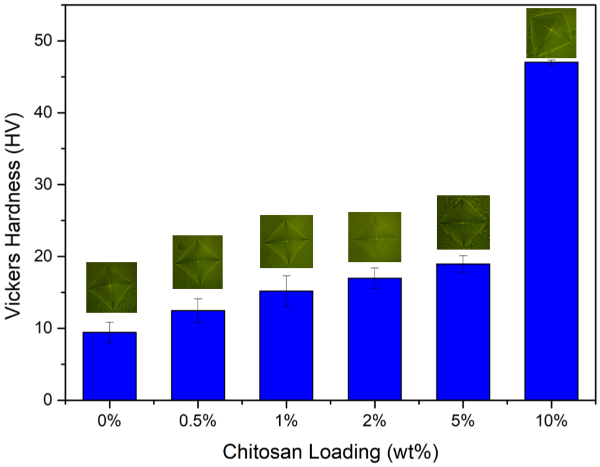


Fig. 4 Vickers hardness values of PVP/CS composite films with various chitosan loading.

The increase in hardness in the composite films was attributed to the addition of CS filler phase, which helped the load distribution in the PVP matrix, and followed higher chitosan content. The improvement in mechanical properties of the PVP/CS composite films was driven by the influence of external hydrogen bonds between the NH_2 groups in chitosan and the C=O groups in PVP, leading to increased hardness with higher chitosan content.

The investigation of different chitosan concentrations in the PVP matrix on its solubility behavior in water is summarized in Table 1. Bare PVP readily dissolved in a neutral aqueous environment (pH~7) within 18 min, whereas chitosan exhibited limited solubility under this condition. The addition of 0.5 wt% chitosan to the composite film resulted in a slower dissolution time of 23 min. Meanwhile, the composite film containing 1.0 wt% chitosan showed a further increase in dissolution time, with complete dissolution achieved in 28 min. A concentration-dependent trend was observed,

Table 1 Dissolving test of PVP/CS composites with various chitosan loading in water.

Condition	Dissolving time (min.)	S.D.
0.0%	17.17	1.71
0.5%	22.41	1.50
1.0%	27.53	4.02
2.0%	41.30	0.99
5.0%	82.73	4.96
10.0%	N/A*	-

N/A* means non-dissolving

with increasing chitosan concentration leading to progressively reduced dissolution rate. The 2.0 wt% chitosan in PVP film required 40 min. to dissolve completely, which was double the time needed for the 1.0 wt% sample. The 5.0 wt% chitosan film dissolved within 80 min, while the film containing 10.0 wt% chitosan remained undissolved, forming a gel-like material. This reduced solubility was attributed to the chitosan component. While PVP dissolved as expected in neutral conditions, chitosan required an acidic environment for dissolution, making it difficult to dissolve in water. As a result, the overall solubility efficiency of the material decreased with higher chitosan concentrations.

Fig. 5 presents a comparative analysis of hardness values and dissolving rates of the PVP/CS composite films with various chitosan loadings. It is evident that the incorporation of chitosan increased the hardness, as chitosan acted as a reinforcing material within the structure. This presence led to an enhancement of composite hardness as measured by the Vickers hardness test. Additionally, solubility testing revealed that the inability of chitosan to dissolve in water adversely affected the overall solubility efficiency of the material.

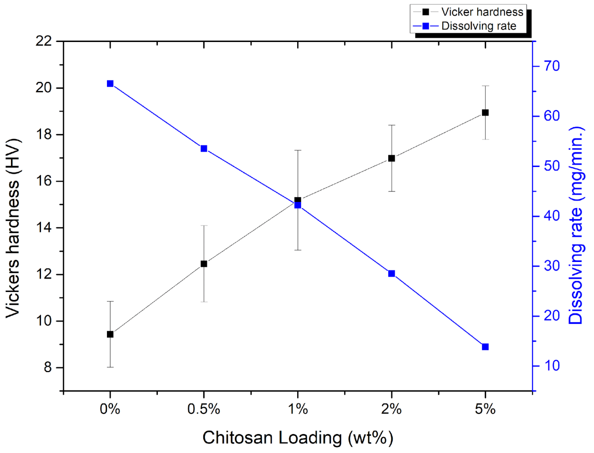


Fig. 5 The comparison of hardness values and dissolving rates of PVP/CS composite films at various chitosan loadings.

The improvement in hardness was accompanied by a marked decrease in dissolving rate. The intersection points of the curves suggested that the optimized chitosan loading in the PVP matrix was approximately 1.0 wt%, at which point a balance between enhanced hardness and lowered solubility was achieved.

4. Conclusion

In this work, the effects of chitosan loading in PVP composite films were studied. The results revealed that the chitosan loading produced homogenous film and did not involve chemical interaction, as indicated by the FTIR spectra of the composites being very similar to that of pure PVP. The Vickers hardness test further supported the addition of chitosan to increase the material's hardness, with chitosan acting as a reinforcing material within the structure. The hardness improved from 8 HV in pure PVP to 15 HV with the addition of 1.0 wt% chitosan. However, solubility tests also showed a decrease in the material's solubility, attributed to the non-water-soluble nature of chitosan. Therefore, when comparing the increase in hardness with the decrease in solubility, the data converged at the addition of 1.0 wt% chitosan, which represents the optimal balance in the PVP matrix where the material maintains its solubility while achieving maximum hardness.

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