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The Effect of PVP on The Molecular Interaction, Crystallinity, and Morphology of Biopolymer Film: A Review

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Abstract. *Blending of biopolymers with other polymers i.e. PVP (polyvinylpyrrolidone) is expected to improve the processability and properties of biopolymer-based films. This blending leads to the new molecular structures due to interactions between the polymers, which affect the crystallinity and morphology of the films, as results, enhance the mechanical, optical, and thermal properties of the biopolymer/PVP films. This review aims to provide an overview of the effect of PVP on the molecular interactions, crystallinity, and morphology of biopolymer films. such as chitosan, ethyl cellulose (EC), hydroxyethyl cellulose (HEC), and hydroxypropyl methylcellulose (HPMC). PVP can form hydrogen bonds with chitosan, HEC, and HPMC. Incorporating PVP with HPMC and HEC results in a uniform film morphology, whereas higher PVP ratios in chitosan/PVP blends can cause cracks, indicating the necessity for an optimal ratio to achieve a homogeneous matrix. The addition of PVP to EC results in discoidal features within the film matrix, signifying separate phases and immiscibility between PVP and EC. PVP also able to disrupts the semicrystalline structure of HEC and HPMC, making the film more amorphous.*

Keywords: *poly(vinyl)pyrrolidone; biopolymers; morphology; molecular interaction; crystallinity.*

Type of the Paper: Review.

1. Introduction

Biopolymer derived natural sources have emerged as promising materials for developing sustainable and eco-friendly material [1]. These biopolymers are biodegradable, offering a potential pathway for developing novel biodegradable polymer-based materials to mitigate environmental pollution typically associated with petrochemical-based polymers. Biopolymer films can be used in many areas, such as wound dressings [2], drug delivery systems [3], implants [4], packaging [5], mulch films [6], water filtration membranes [7], electronins, and disposable items like cutlery, and personal care products [8]. However, biopolymer films often have limitations, such as brittleness, poor heat resistance, and poor optical properties, which hinder their widespread application [9]. To overcome these challenges, biopolymers are often blended with other polymers through physical or chemical methods [10]. Physical polymer blending is a particularly convenient method, as it allows for a wide array of desirable physical and chemical properties without the need to modify the individual structures of the constituent polymers [11]. This method enables the creation of novel biopolymer-based films that utilize the advantageous

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properties of each polymer [12]. Additionally, polymer blends are favored for their reproducibility, simplicity, and cost-effectiveness [13].

Polyvinylpyrrolidone (PVP) is one of promising polymer blend materials for the manufacture of biocompatible and biodegradable materials [14,15]. Of note, PVP is a synthetic, non-toxic, and FDA-approved polymer so it has been used in various medical and pharmaceutical material [16]. In polymer blends, PVP is typically used to increase the thermal stability due to its high degradation temperature up to 430°C [17]. PVP has excellent film-forming abilities and creates high transparent film [18]. PVP also known for its excellent adhesive properties due to the abundance of carbonyl groups, which can form hydrogen bonds with biological surfaces, making it ideal for bio adhesive delivery systems [19]. PVP also help in dispersing fillers, further demonstrating its potential as polymer matrix in bio-composite films [20].

Blending biopolymers with PVP creates new molecular arrangements due to interactions between the molecules. This process affects how the polymers arrange themselves in the film, resulting in different crystallinity and morphology than the constituent polymer film. By understanding these structural properties, the physical and chemical properties of the biopolymer/PVP films can be designed and controlled for the suitable and targeted application. In particular, the stronger intermolecular forces and increased crystallinity can significantly enhance the mechanical strength and thermal stability of films [21,22]. A more homogeneous blend can reduce defects and prevents porous structures, offering better barriers to moisture and gases qualities highly desirable in packaging films [23,24]. In term of sustainability perspective, tailoring properties is also important key on developing biodegradable films with meticulous degradation rates, contributing to environmental sustainability, as high crystallinity plastic results in slower degradation rate [25]. Additionally, the degree of crystallinity influences the film's opacity where higher crystallinity results in a more translucent film [26]. The well-designed mechanical, thermal, barrier, degradation, and optical properties of the films are essential for optimizing its performance in packaging, electronic, and sensor applications.

Therefore, investigating such effect on molecular interactions, crystalline structure, and morphology, is crucial on developing polymer blend films. This review aims to outline the effect of PVP on the molecular interactions, crystallinity, and morphology of biopolymer/PVP films. Several studies reporting on PVP blends with biopolymers i.e. chitosan, ethyl cellulose (EC), hydroxyethyl cellulose (HEC), and hydroxypropyl methyl cellulose (HPMC) were included in this report. This review discusses findings on the physicochemical properties (molecular interaction, crystallinity, and morphology) of biopolymer/PVP films using FTIR, XRD, and SEM techniques.

2. Synthesis of Biopolymer/PVP Films

Fig. 1 illustrates the chemical structure of PVP, chitosan, HPMC, and HEC. PVP also known povidone, is a synthetic polymer created through radical polymerization of N-vinylpyrrolidone [27]. It is non-toxic, non-ionic, inert, resistant to temperature and pH changes, biocompatible, and exhibits complex interactions with both hydrophilic and hydrophobic substances [28,29]. PVP polymer contains functional groups such as C=O, C-N, and CH_2, with a hydrophilic pyrrolidone ring and a hydrophobic alkyl group [30]. PVP is high soluble in both water and organic solvents (methanol, chloroform, acids, and amine)s due to the polar amide group in the pyrrolidone ring, along with the non-polar methylene and methine groups in the ring [31,33,34]. On the other hand, the hydrophobic carbon chains in PVP polymer backbone can create steric hindrance effect [32]. .

Chitosan, on the other hand, is the second most abundant biopolymer after cellulose and is typically derived from chitin through alkaline hydrolysis (deacetylation). Chitin occurs in nature as ordered macrofibrils in the exoskeleton crustaceans and mollusks, as well as in fungi and insect cuticles. Over 1000 tons of chitin are produced annually, with approximately 70% comes from marine species [35]. Chitosan is a cationic linear polysaccharide composed of repeating β-(1–4)-linked units of 2-acetamido-2-deoxy-D-glucopyranose [36]. Chitosan monomer contains functional groups such as primary amine (NH) as well as primary and secondary hydroxyl group (OH) [37]. Chitosan dissolves in acidic aqueous media, such as acetic acid, through the protonation of its primary amine groups [38]

Moreover, cellulose is the most abundant natural polymer on earth, consisting of a linear polysaccharide made up of β-(1→4)-linked D-glucopyranosyl units [39]. Hydroxypropyl methylcellulose (HPMC) or hypromellose is a cellulose mixed ether, produced by substituting cellulose's hydroxyl groups with methyl and hydroxypropyl groups [40,41]. This is achieved by first treating cellulose with NaOH solution to activate its hydroxyl groups, followed by the addition of methyl chloride and propylene oxide [42]. The degree of substitution (DS) refers to the number of methyl groups per unit, while the molar substitution (MS) measures hydroxypropyl groups [42,43]. HPMC is soluble in cold water as well as certain organic solvents such as ethanol and methanol, and the solution remains stable across a broad pH range from 2 to 12 [40]

Hydroxyethylcellulose (HEC), in advance, is a derivative of cellulose, produced by substituting the hydroxyl group with hydroxyethyl group (CH_2CH_2OH). On industrial scale, HEC is produced by first treating starch with sodium hydroxide with pristine starch to form reactive alkali cellulose [44]. It is then reacted with gaseous ethylene oxide in an etherification process, replacing hydrogen atoms in the cellulose with hydroxyethyl groups which make this polymer soluble in water. HEC is a tasteless and colorless to light yellowish powder that has no odor [45].

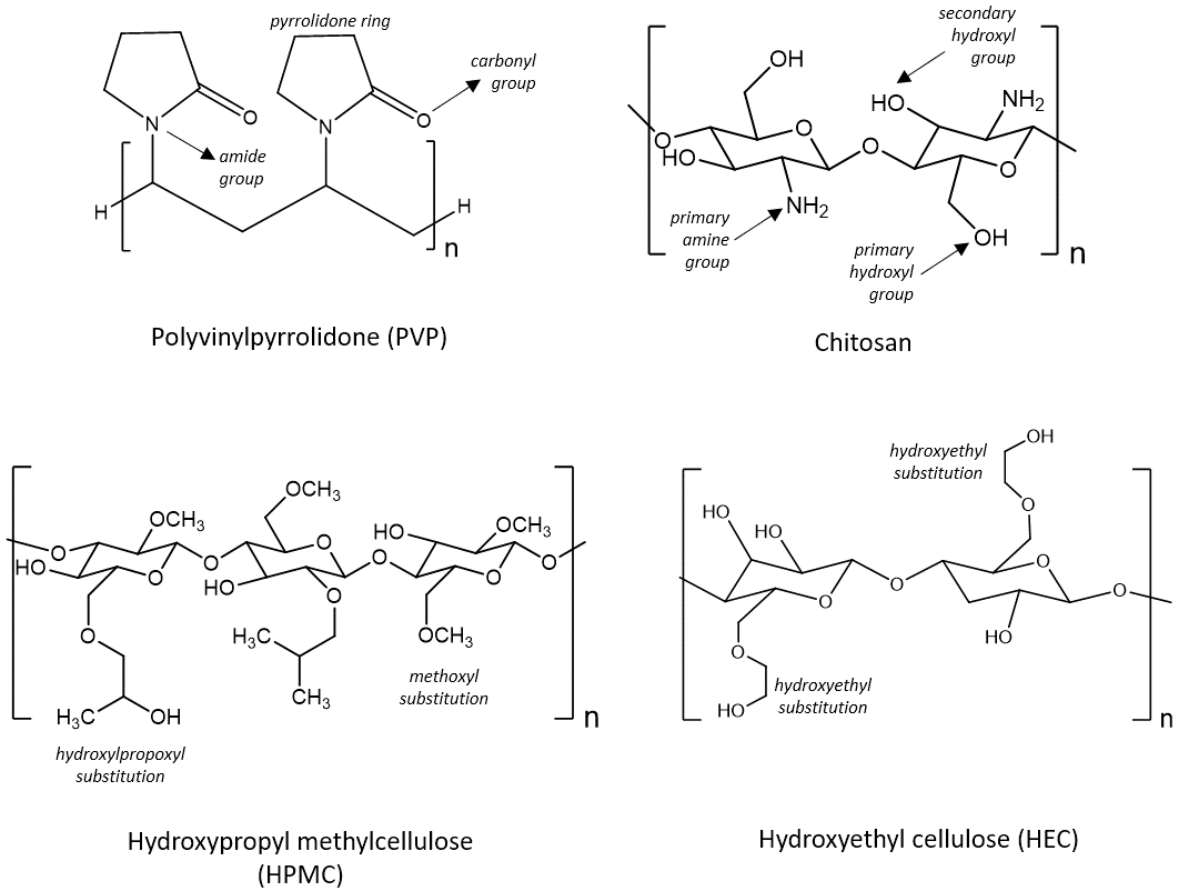

Fig. 1. Chemical structures of PVP, chitosan, HPMC, and HEC.

Table 1 presents a series of studies on biopolymer/PVP films produced using solution casting method (Fig. 1). In this method, the biopolymer and PVP are firstly dissolved in appropriate solvent. PVP has a carbonyl group with hydrophilic properties and high polarity and a methylene group which is non-polar and hydrophobic on the pyrrolidone ring [31]. These two groups contribute to the ability of PVP to dissolve in water and organic solvents.

A plasticizer, like glycerol, can be added to the polymer blend solution to enhance the flexibility, compatibility, and processability of the produced film [46]. The polymer blend solution and plasticizer are mixed together to form a homogeneous blend, which is then degassed to remove bubbles, typically using vacuum or ultrasonication. After degassing, the solution is cast into a petri dish or spread into a substrate and dried using a vacuum oven or at room temperature. As the solvent evaporates, the polymer chains form an intercalated structure, resulting in tightly packed polymer blend film.

Currently, solution casting is the only method has reported for producing biopolymer/PVP films. Table 2 shows several other film synthesis methods such as extrusion, spin coating, doctor blade (knife coating), and electrospinning with their advantages and disadvantages in comparation

to solution casting method. Compared to extrusion method, solution casting produces films that are more transparent, smoother, homogeneous, and have fewer pores/voids [47]. Solution casting is not ideal for large-scale production due to challenges in controlling film thickness. In contrast, extrusion is better suited for mass production, providing consistent thickness and quality. However, before using extrusion, it's crucial to understand the film's thermal properties, such as melting and degradation temperatures, since extrusion involves melting. In particular, for small-scale production, methods like spin coating, doctor blade coating, and electrospinning can be used to achieve precise film thicknesses. In case of electrospinning, it is important to consider the potential risk of biopolymer denaturation caused by the electric field.

Table 1. Synthesis of biopolymer/PVP blend films fabricated using solution casting method

No	Blends	Solvent type	Plasticizer	Optimum composition of biopolymer/PVP ratio (w/w)	Ref
1	Chitosan/PVP Chitosan with low M_W PVP K30 (M_W 40 kDa)	Acetic acid	None	3:1	[48]
2	HEC/PVP HEC technical grade PVP K30	Water	Glycerol	5:3	[49]
3	HPMC/PVP HPMC (Mw 370 kDa) PVP (Mw 1300 kDa)	Water	None	7:3	[50]
4	EC/PVP PVP (Mw 360 kDa)	Ethanol	None	1:8	[51]

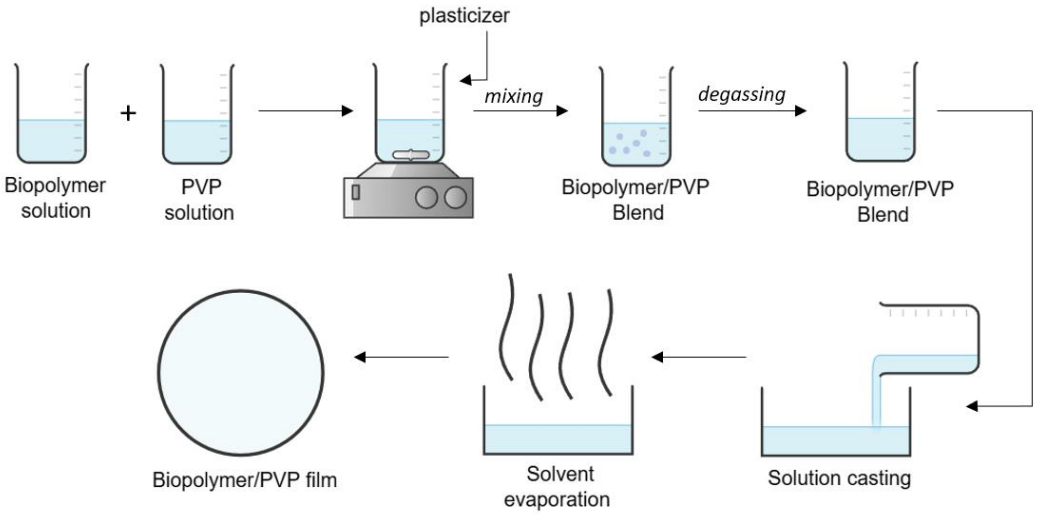

Fig. 2. Synthesis of biopolymer/PVP blend film using solution casting method

Table 2. Overview of film synthesis methods: description, advantages, and disadvantages

Film synthesis method	Description	Advantages	Disadvantages	Ref
Solution casting	A polymer solution is cast onto a flat surface, spread evenly, and then allowed to dry, forming a film	- Simple and easy to implement - Suitable for lab-scale experiments and producing small batches	- Slower process, not ideal for large scale production - Thickness control can be challenging - Requires solvent removal	[52,53]
Extrusion	Polymer material is melted and forced through a die to form a continuous film, which is then cooled and solidified	- High production speed - Suitable for mass production - Solvent is not necessary - Consistent film thickness and quality - Cost effective for large-scale application	- Limited control over very thin films - High initial setup cost for equipment - Requires specific conditions and temperature for certain polymers	[54,55]
Spin coating	A polymer solution is dropped into a substrate, which is then rotated at high speed to spread the solution into a thin, uniform film	- Produces highly uniform thin films - Ideal for application requiring precise film thickness - Fast process	- Suitable for small-area films - Material loss during the spin process (almost 95-98% got discarded) - Not suitable for large-scale production	[56,57]
Doctor blade coating (knife coating)	A polymer solution is spread onto a substrate using a blade set a fixed height to control film thickness	- Simple, scalable method for creating thin films - Good control over film thickness - Not suitable for large-scale production	- Prone to defects like streaks or bubbles - Thickness uniformity may be challenging to maintain - Limited specific application and substrates	[58]
Electrospinning	A polymer solution is subjected to an electric field, causing the polymer to form fine fibers that collect on a surface as a film	- Produces highly porous, nanoscale films - Can be used with a range of polymers	- Requires specialized equipment - Not suitable for dense or thick films - Can cause partial denaturation problem of some natural polymers	[59,60]

3. Molecular Interaction of Biopolymer/PVP Films

Polymer blends are typically described as physical mixtures of two or more different polymers without any covalent bonds between them [61]. The interactions that occur are usually van der Waals forces, dipole interactions between polymer backbones, or hydrogen bonding between the functional moieties of polymers. FTIR can be used to investigate the molecular interaction between polymer in blends. In principle, the oscillating dipole moments of molecules will alter when two different polymers are mixed together at the molecular level [62]. Interactions between these two polymers will result on band shift or peak widening in FTIR spectra compared to the spectra of the individual polymers [63].

Fig. 3 shows the FTIR spectra of PVP blend with chitosan, HPMC, and HEC and their pure biopolymers. Both characteristic peaks from PVP and biopolymer were found in the biopolymer/PVP FTIR spectra. PVP may form hydrogen bonds through the carbonyl group on the pyrrolidone ring as well as the nitrogen atom [32]. However, since the steric hindrance prevents the nitrogen atom from participating in the intermolecular interactions, the carbonyl group is more advantageous for hydrogen bonding [51]. Fig. 4 shows the functional groups involved in hydrogen bonding between the biopolymer and PVP.

FTIR spectra indicate hydrogen bonding in chitosan/PVP films through the observed shifts of the -OH and carbonyl peaks to lower wavenumbers, resulting from interactions between chitosan's amino and hydroxyl groups and PVP's carbonyl groups [48]. In HPMC/PVP films, the shift of the -OH band to a lower wavenumber and the C=O and C-O bands to higher wavenumbers suggesting the hydrogen bonding between HPMC's hydroxyl side groups and PVP's carbonyl groups [50]. Likewise, the shift of the -OH group absorption band to a lower wavenumber in HEC/PVP films signifies hydrogen bonding, as evidenced by increased hydrogen bond energy and decreased hydrogen bond distances [64–66].

The FTIR spectra can also reveal the immiscibility of polymer blends. In case of EC/PVP films, the FTIR spectra showed no significant shift in the carbonyl group peak (1650 cm^{-1}), indicating a lack of polymer interactions and confirming the immiscibility between EC and PVP [51]. Table 3 shows the peak shifts reported in FTIR spectra as an evidence of hydrogen bonding between biopolymer and PVP.

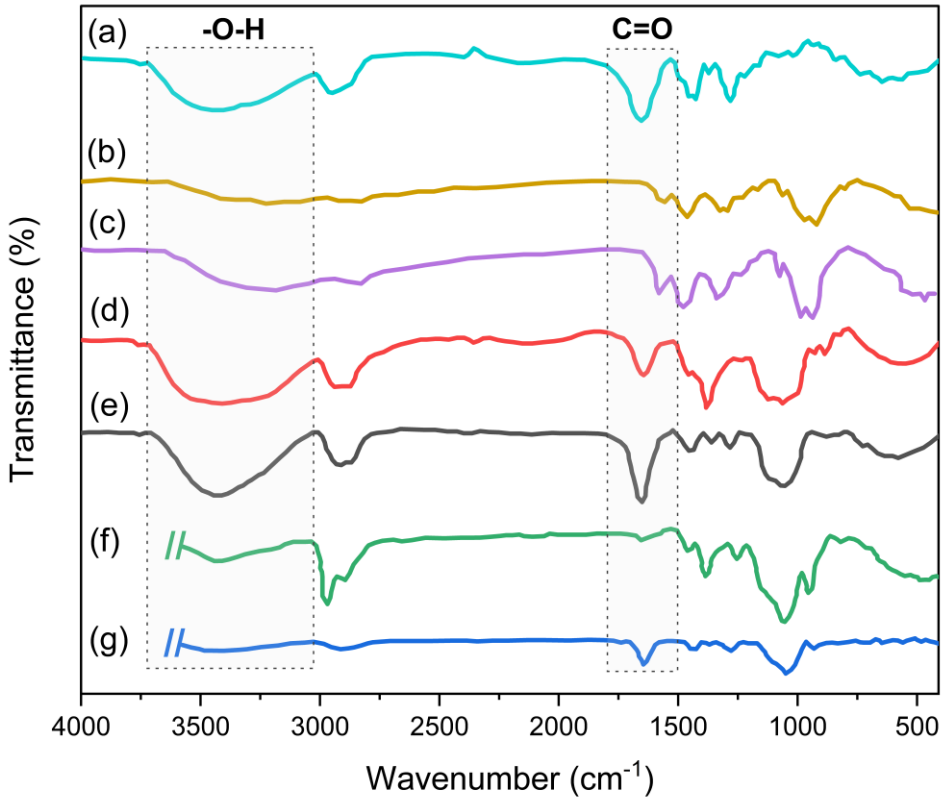

Fig. 3. FTIR spectra of (a) PVP [49], (b) chitosan [48], (c) chitosan/PVP [48], (d) HEC [49], (e) HEC/PVP [49], (f) HPMC [50], and (g) HPMC/PVP [50]

Table 3. Peak shifts in FTIR spectra as a result of intermolecular forces via hydrogen bonding between biopolymer and PVP

Blends	Functional group band (cm^{-1})		Ref.
	Before addition of PVP	After addition of PVP	
Chitosan/PVP	-OH:3424	-OH: around 3422	[48]
	C=O:1646	C=O around 1644	
HPMC/PVP	O-H: 3428	O-H: 3421	[50]
	C=O: 1643	C=O: 1646	
	C-O: 1056	C-O: 1064	
HEC/PVP	-OH: 3429	-OH: 3424	[49]

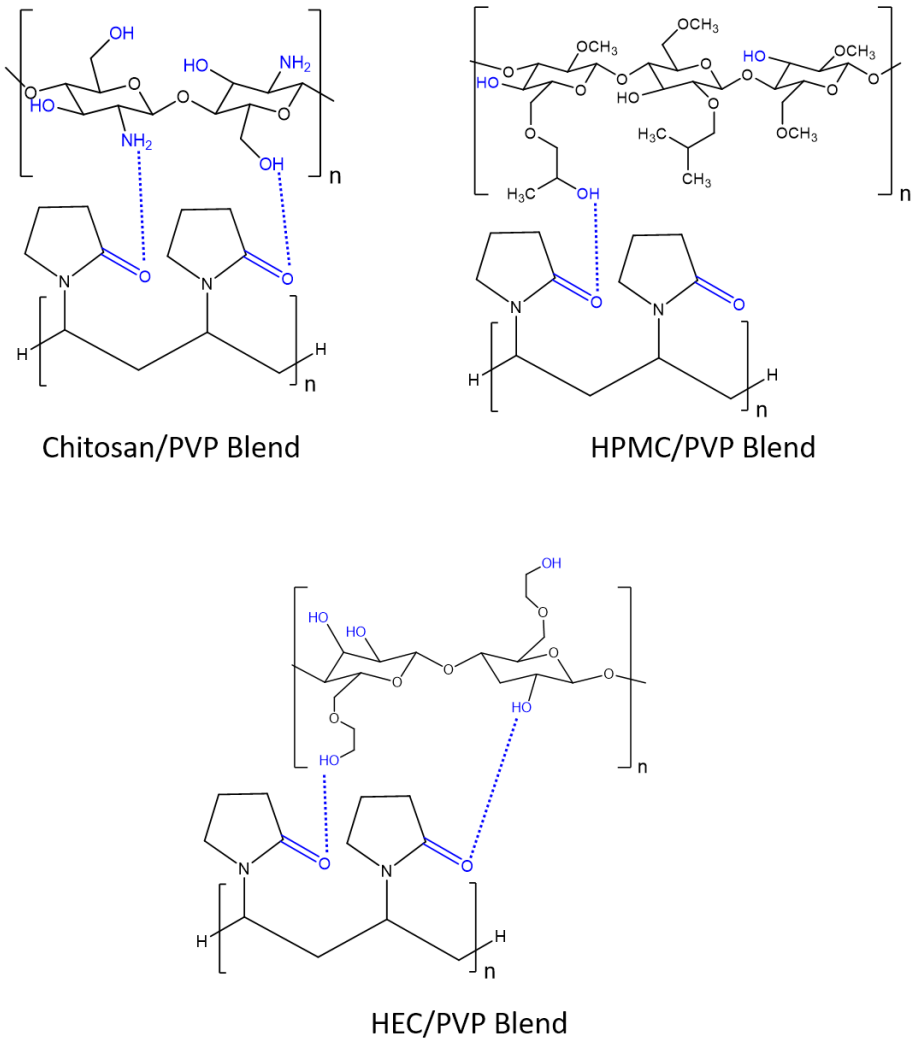

Fig. 4. Hydrogen bonds in chitosan/PVP, HPMC/PVP, and HEC/PVP blends. The groups involved in these hydrogen bonds are highlighted in blue, and the hydrogen bonds themselves are indicated by dashed blue lines.

4. Crystallinity of Biopolymer/PVP Films

Binary polymer blends can show varied supramolecular structures and phase morphologies based on the miscibility and crystallization abilities of their components. [67]. When PVP is blended with biopolymers, it can create different crystalline structures and polymer chain arrangements. Crystallinity changes can be observed through X-ray diffraction (XRD) by examining variations in peak broadening and intensity in the diffraction patterns [68]. Broadening of peaks in an X-ray diffraction (XRD) pattern generally indicates that the material has lower crystallinity, meaning the crystalline structure is less ordered. Conversely, narrower peaks suggest that the material has larger and more ordered crystalline domains. Additionally, a decrease in peak intensity typically means reduced crystallinity, while an increase in peak intensity indicates greater crystallinity.

A more quantitative approach for assessing the modification in the film crystallinity can be

carried out using Debye-Scherrer equation and calculation of the crystallinity index (CI) [49]. The Scherrer equation estimates the average size of crystalline domains (crystallites) using the formula shown by Eq. (1) where K is the Scherrer constant (0.94), λ is the X-ray wavelength (0.154 nm), H is the peak's FWHM in radian unit, and θ is the Bragg degree. A reduction in crystallite size generally indicates lower crystallinity, whereas an increase in peak intensity signifies larger and more ordered crystalline domains.

$$D = \frac{K\,\lambda}{H \times \cos\theta} \tag{1}$$

The crystallinity index (CI) is a quantitative measure of the degree of crystallinity within a sample. It is calculated by comparing the area of the crystalline peaks (A_c) to the total area of the diffraction peaks (Eq. (2)). A higher CI value indicates greater crystallinity in the film.

$$CI\ (\%) = \frac{A_c}{Total\ peak\ area} \times 100 \tag{2}$$

In the case of HEC/PVP films (Fig. 5(a-b)), the crystallinity decreased with higher PVP content as indicated by decrease in peak intensity. This indicates that PVP can disrupt the original semi-crystalline structure of HEC, leading to an amorphous structure. As the PVP content increases, the peak shifts to a lower 2θ value. This shift means that the d-spacing in the crystal structure increases, indicating more distant packing between HEC and PVP polymer chains.

The ability of PVP to integrate into the biopolymer crystalline network and form a more amorphous structure was also observed with chitosan/PVP film (Fig. 5(c-d)). At a chitosan/PVP ratio of 50:50, the film remains semicrystalline. However, at a higher concentration of PVP (chitosan/PVP 25:75), the blend becomes more amorphous, as indicated by the disappearance of sharp crystalline peaks and the formation of broad peaks. The intensity of the peak also decreases with higher PVP concentrations. Besides, due to the miscibility of chitosan/PVP and HEC/PVP, PVP has a linear structure and a smaller molecular weight than HEC and chitosan, making it easier to slip into the biopolymer network [69].

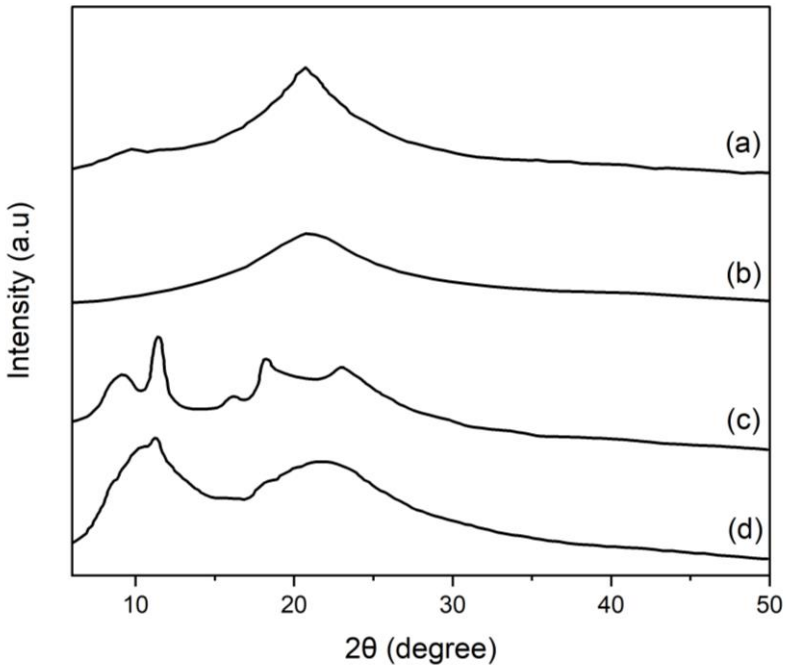

Fig. 5. XRD diffractogram of (a) HEC [49], (b) HEC/PVP [49], (c) chitosan [48], and (d) chitosan/PVP film [48].

5. Morphology of Biopolymer/PVP Films

The morphology of polymer blend films can be investigated using Scanning Electron Microscopy (SEM), which can provide high-resolution images of the surface and cross-sectional views of the films. SEM analysis allows for an in-depth examination of the film's topology, phase separation, and the presence of defects or voids [70]. Fig. 6 shows SEM images of HEC/PVP, HPMC/PVP, EC/PVP, and chitosan/PVP films. The addition of PVP to HEC results in a smoother surface compared to pure HEC films [49], while incorporating PVP into HPMC produces films without pores and bubbles [50]. These observations indicate that HEC/PVP and HPMC/PVP blends have good mixing and compatibility, as evidenced by their uniform film structures.

Although PVP is compatible with HPMC and HEC, it is immiscible with EC, as shown by distinct discoidal features in the EC/PVP film's cross-section [51]. Furthermore. Energy Dispersive X-ray (EDX) analysis confirmed that EC forms part of the EC/PVP film matrix, while PVP appears in discoidal structures. For chitosan/PVP films, the morphology varies with different ratios; uniform, defect-free matrices are observed at chitosan/PVP ratios of 3:1 and 1:1, whereas a 1:3 ratio results in surface cracks [48]. These findings highlight the influence of the biopolymer-to-PVP ratio on film morphology.

Incorporating polyvinylpyrrolidone (PVP) into biopolymer films significantly influences their molecular interactions, crystallinity, and morphology. These changes, in turn, impact the mechanical, thermal, and optical properties of the biopolymer/PVP blend films. The hydrogen

bonding potential of PVP enhances these interactions, capitalizing on the abundant hydrogen bonds in biopolymers. Due to the biodegradable and biocompatible characteristics of the biopolymers and PVP, this combination holds significant potential for use in biomedical applications, drug delivery, and food packaging. The biopolymer/PVP blend material emerges as a sustainable alternative, potentially matching the performance of traditional petroleum-based films.

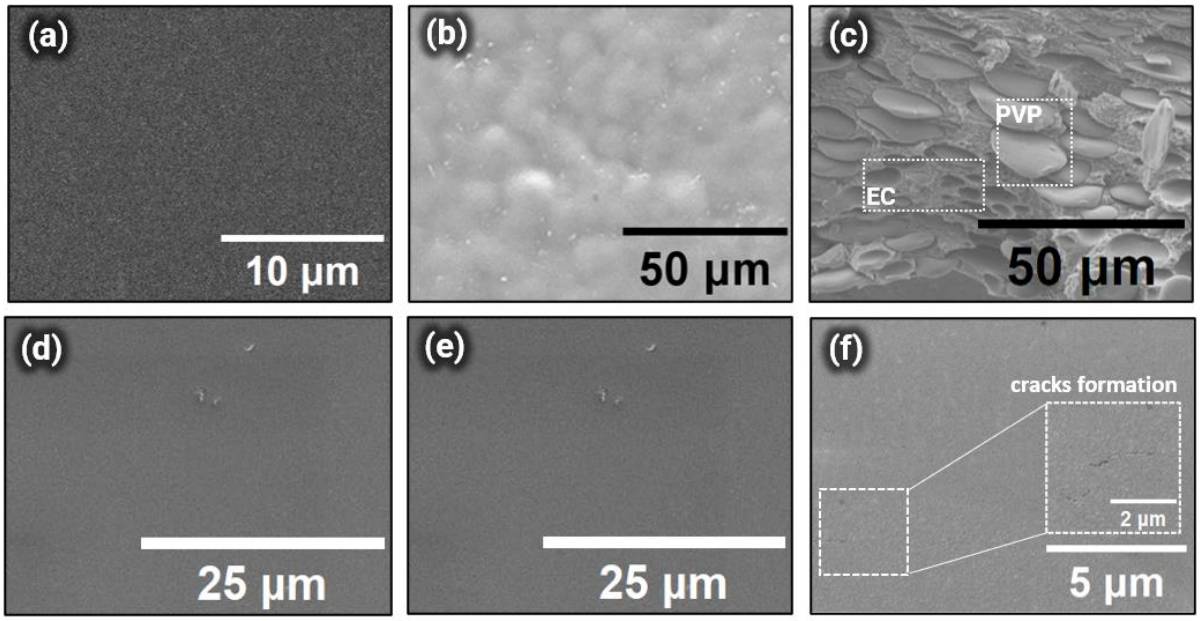

Fig. 6. Morphology PVP with (a) HEC [49], (b) HPMC [50], (c) EC [51], and (d-f) chitosan blend films [48].

The future research on PVP in biopolymer blends should explore the compatibility and performance of emerging biopolymer when combined with PVP. Investigating new types of biopolymers, such as polysaccharides and protein-based polymers, that exhibit enhanced compatibility with PVP could lead to development of advanced and multifunctional blends. Blending PVP with biopolymers can create innovative green materials that are both biocompatible and biodegradable, making them highly suitable for applications in packaging, sensors, biomedical fields, and drug delivery systems. It could also focus on alternative blending strategies to optimize the properties of these combinations, including the use of novel compatibilizers or processing techniques. The forthcoming works should consider industrial-scale film synthesis methods, such as extrusion, to achieve better control over film thickness and facilitate mass production. It is also important to investigate various physicochemical properties of the film, such as optical, mechanical, and thermal characteristics, to better understand how its structure affects overall performances.

6. Conclusions

Film blends of chitosan, ethyl cellulose (EC), hydroxyethyl cellulose (HEC), and hydroxypropyl methyl cellulose (HPMC) with PVP were synthesized using the solution casting method. PVP incorporation remarkably affected the physicochemical properties of biopolymer, in particular, the molecular interaction between polymer chains, crystallinity, and morphology. PVP can interact with biopolymers through hydrogen bonding via the carbonyl group in the pyrrolidone ring. The hydrogen bond between PVP and biopolymers is observable through FTIR peak shifts of the C=O and -O-H groups in chitosan/PVP, HEC/PVP, and HPMC/PVP films. PVP disrupts the semicrystalline structure of biopolymers, resulting in more amorphous films. PVP also forms a uniform film matrix with HEC and HPMC. In the case of chitosan/PVP films, the ratio of PVP is crucial in controlling the morphology, as higher concentrations of PVP can cause cracks in the film. Phase separation is evident in the cross-sectional view of EC/PVP films, indicating immiscibility between EC and PVP.

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