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SYNTHESIS OF CARRAGEENAN-BASED BIOCOMPOSITE PLASTICIZED WITH DEEP EUTECTIC SOLVENT AND CHARACTERIZATION OF ITS MECHANICAL PROPERTIES

(Sintesis Biokomposit Berasaskan Karaginan Diplastikkan dengan Pelarut Eutektik Dalam dan Penyifatan Ciri-Ciri Mekanikal)

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Abstract

Carrageenan from seaweed tends to be brittle in the formation of hard capsules. In this study, a carrageenan-based biocomposite was synthesized to provide an alternative to gelatin hard capsules. This study aims to characterize the mechanical properties of carrageenan biocomposite plasticized with a deep eutectic solvent (DES) of choline chloride (ChCl) and glycerol. The carrageenan biocomposite was formulated at varying concentrations (0, 0.2, 0.4, 0.6, 0.8, and 1.0 v/v%) of DES to improve the strength and elasticity of carrageenan biocomposite films and hard capsules. The absence of the ChCl band at 1348 cm^{-1} and the reduced intensity of the C–O glycerol band at 1107 cm^{-1} in the ATR-FTIR spectra of DES were regarded as evidence for the formation of the eutectic mixture. This can be explained by the hydrogen bond donor and acceptor interaction between the DES constituents, which are chloride ions (Cl^-) of ChCl and the hydroxyl group (–OH) of glycerol ($Cl^-\cdots OH$). The highest viscosity of Carra-DES 0.2 at 504.9 mPa·s reflects the improved film tensile strength up to 60.1 MPa, which gives a positive effect after the addition of DES. The capsule loop strength reached its peak at 31.7 N for Carra-DES 0.4. A significant increase in the elongation at break of Carra-DES film was observed at DES concentrations of 0.2–0.6%. However, the concentration of DES should be controlled to achieve high tensile and loop strengths in hard capsule application. In conclusion, the incorporation of DES in carrageenan biocomposite can reduce its brittleness while improving its elasticity and strength in the production of hard capsules.

Keywords: Biocomposite, carrageenan, choline chloride, deep eutectic solvent, plasticizer

Abstrak

Karaginan daripada rumpai laut cenderung menjadi rapuh dalam pembentukan kapsul keras. Dalam kajian ini, biokomposit berasaskan karaginan telah disintesis sebagai alternatif kepada kapsul keras gelatin. Kajian ini bertujuan menyifatkan ciri-ciri mekanikal biokomposit karaginan yang ditambah pemplastik pelarut eutektik dalam (DES) yang diperbuat daripada kolina klorida

(ChCl) dan gliserol. Biokomposit karaginan telah dirumuskan dengan DES menggunakan kepekatan yang berbeza (0, 0.2, 0.4, 0.6, 0.8, dan 1.0 v/v%) untuk meningkatkan kekuatan dan keanjalan filem biokomposit karaginan dan kapsul keras. Ketiadaan jalur penyerapan ChCl pada 1348 cm^{-1} dalam analisis ATR-FTIR dan peralihan jalur getaran C–O dalam gliserol ke arah 1728 cm^{-1} dianggap sebagai bukti pembentukan campuran eutektik. Ini boleh dijelaskan oleh interaksi penderma dan penerima ikatan hidrogen antara konstituen DES, iaitu ion klorida (Cl^-) ChCl dan kumpulan hidroksil (–OH) gliserol ($Cl^{-}\cdots OH$). Kelikatan tertinggi Carra-DES 0.2 pada 504.9 mPa·s mencerminkan kekuatan tegangan filem yang lebih baik sehingga 60.1 MPa dan memberikan kesan positif selepas penambahan DES. Kekuatan gelung kapsul mencapai kemuncaknya pada 31.7 N untuk Carra-DES 0.4. Peningkatan ketara pemanjangan filem Carra-DES semasa putus berlaku pada kepekatan DES 0.2% hingga 0.6%. Walau bagaimanapun, kepekatan DES harus dikawal untuk mencapai kekuatan tegangan filem dan gelung kapsul yang tinggi dalam aplikasi kapsul keras. Kesimpulannya, penggabungan DES dalam biokomposit karaginan dapat mengurangkan kerapuhan di samping meningkatkan keanjalan dan kekuatan dalam menghasilkan kapsul keras.

Kata kunci: Biokomposit, karaginan, kolina klorida, pelarut eutektik dalam, pemplastik

Introduction

A high interest in sustainable polymers from plants has been shown to replace gelatin hard capsules from animal sources due to consumers' dietary restrictions. Carrageenan, a versatile natural polysaccharide, emerges as a promising alternative material for hard capsules with characteristics similar to gelatin, including thermal reversibility and film-forming properties. Derived from seaweed, this resource abounds in Malaysia, particularly in East Malaysia, Sabah [1]. Unveiling superior gelling and high viscosity properties, carrageenan is able to form a biopolymer film, finding widespread application in the pharmaceutical industry as a thickener, stabilizer, and emulsifier [2]. The distinctive attributes of this material have assured its market demand. Despite its film-forming ability, an inherent brittleness limits its application as a hard capsule, presenting an intriguing challenge for further exploration. In order to overcome the shortcomings of carrageenan, formulations of carrageenan biocomposite are thoroughly studied. A biocomposite is a blend of two or more naturally derived materials to develop a reinforced product with improved performance over individual constituent materials. The formulation of carrageenan biocomposite has been modified by incorporating isovanillin as the crosslinker [3] with cellulose nanocrystals (CNCs) and cellulose nanofibers as the reinforcing agents [4, 5]. Thickening agents have also been incorporated, such as gum Arabic [6, 7], hydroxypropyl methylcellulose [8], and carboxymethyl starch [9]. In the application of green bioplastics, *Chlorella vulgaris* microalgae have also been blended into the formulation to improve the hydrophobicity of the carrageenan film [10].

Plasticizer is an additive introduced in polymers to produce more flexible films, increase elasticity, and reduce friction during the manufacturing process. Deep eutectic solvent (DES) has properties that are suitable as a potential plasticizer to improve the mechanical properties of biocomposite films [11]. It is a novel solvent system that can be prepared from a range of anionic and/or cationic chemicals that are commonly available to form an eutectic mixture [12]. Deep eutectic solvent, an analog to ionic liquid (IL), is also utilized as a solvent, reagent, catalyst, and crosslinker in various applications [13]. Deep eutectic solvent is safe and non-toxic as opposed to IL based on its non-volatility and the alleged benign nature of its main constituents [14]. Studies on DES have begun with choline chloride (ChCl) as a hydrogen bond acceptor (HBA), and it is one of the most commonly used compounds in synthesizing DES [12]. Glycerol, the hydrogen bond donor (HBD) used in this study, is a simple natural polyol that is inexpensive, biodegradable, non-toxic, and extensively used in the food industry [15]. The simplicity of DES synthesis, achieved by the precise mixing of HBA and HBD components in specific molar ratios, as well as low toxicity, make it a more viable and safer choice for numerous applications, such as edible biocomposites [16].

In comparison to conventional plasticizers, DES (ChCl and glucose/glycerol/urea) are highly promising plasticizers for cellulose-based biocomposites, with an increase in elongation at break (EAB) up to 81%, while the tensile strength is comparable to that of a single component plasticizer [13]. Furthermore, DES (ChCl/urea) has also been proven to refine film

uniformity and smoothness with only 0.01% of DES, preserving the structural stability and optical properties of the CNC film while significantly reducing film brittleness [17]. The addition of DES (ChCl/lactic acid) with lignin also increased the tensile strength of the chitosan film to 31.6 MPa and effectively increased the plasticity, giving a maximum EAB of 62.6% [18]. The EAB of the gelatin/polyvinyl alcohol composite film reached up to 654% when the mass fraction of DES (sodium acetate trihydrate/urea) was 60% [19]. Most studies reported the advantages of DES for polysaccharides and better plasticizing ability than conventional plasticizers [20,21]. Currently, it is difficult to find research on the influence of DES as a plasticizer for carrageenan biocomposite and the plasticization effect on the carrageenan biocomposite film and hard capsules. This work aimed to synthesize carrageenan biocomposite plasticized with DES (ChCl/glycerol) at different concentrations and to characterize the mechanical properties of the resulting biocomposite films and hard capsules. It was hypothesized that the addition of DES as a plasticizer can reduce the brittleness and increase the carrageenan hard capsule strength when incorporated in an appropriate amount.

Materials and Methods

Materials

Refined carrageenan as the main material of the biocomposite was bought from CV Simpul Agro Globalindo, Indonesia. Hydroxypropyl methyl cellulose (84 kDa) as a thickening agent, 4-methoxybenzyl alcohol (98%) as a crosslinker, and calcium alginic acid (584.5 Da) as a toughening agent were obtained from Sigma-Aldrich (USA). Meanwhile, CNCs for reinforcement were prepared from the microcrystalline cellulose (Avicel PH-101) purchased from Sigma-Aldrich (St. Louis, MO, USA). The DES composed of ChCl (98%, 139.62 Da) and glycerol (99.5%, 104.06 Da) as a plasticizer were obtained from Merck (Darmstadt, Germany). All chemicals used are of analytical grade. Deionized water was used throughout the entire experiment.

Preparation of DES as a plasticizer

Pure ChCl was pretreated to remove any possible moisture by drying in a vacuum oven overnight at 80 °C and was stored in a dry place for further use [22]. Accordingly, ChCl and glycerol were mixed with gentle stirring at a molar ratio of 1:2 at 60 °C for 30 min until homogeneous with no evidence of solid particles [23, 24]. The eutectic mixture of ChCl and glycerol was designated as the DES solution.

Preparation of CNC as a reinforcement agent

The CNC solution was prepared according to Mohd. Amin et al., where 5.0g of microcrystalline cellulose was stirred overnight in 500 mL of deionized water using a hot plate [25]. A QSonica (Q700, USA) ultrasonicator was used to sonicate the cellulose dispersion for 20 min at a 20% amplitude. This process was carried out with 8 s pulsed on and 2 s pulsed off. After resting for 10 min, the bottom layer of the solution was removed, and the solution was left overnight. The top clear layer of the solution was removed to collect 300 mL of the concentrated portion, which was identified as the CNC solution.

Synthesis of carrageenan biocomposite

The biocomposite solution was prepared by dissolving 3.0g of refined carrageenan in 150 mL of deionized water. The solution was heated for 30 min at 60 °C under continuous stirring using a hot plate and a magnetic stirrer. Then, 4-methoxybenzyl alcohol (0.7 w/v%), CNCs (1.6 w/v%), hydroxypropyl methylcellulose (0.8 w/v%), and calcium alginic acid (0.07 w/v%) were added gradually to the biocomposite solution. These concentrations were incorporated into the carrageenan biocomposite following previous research from Hamdan et al. [4] and Ramli et al. [8]. The DES, which composed of ChCl and glycerol, was added to the biocomposite solution at varying concentrations from 0 to 1.0 v/v%, as shown in Table 1. The solution was poured on a round stainless-steel tray with a diameter of 20 cm after 3 h of mixing, while the remaining solution was dipped using the stainless-steel mold pins (size 1) to form the hard capsule. All samples of biocomposite films and hard capsules were dried overnight at room temperature.

Table 1. Sample formulation of carrageenan biocomposite plasticized with DES at various concentrations

Samples	Concentration of Carrageenan (w/v%)	Concentration of DES (v/v%)
Control	2.0	0
Carra-DES 0.2	2.0	0.2
Carra-DES 0.4	2.0	0.4
Carra-DES 0.6	2.0	0.6
Carra-DES 0.8	2.0	0.8
Carra-DES 1.0	2.0	1.0

Functional group determination

The presence of different functional groups in ChCl and glycerol was analyzed by conducting Fourier transform infrared (FTIR) spectroscopy to recognize any potential shifting of the chemical bonds in the formation of DES. The samples were subjected to an attenuated total reflection (ATR)-FTIR spectrometer (Perkin Elmer, Frontier, USA) equipped with OMNIC software within the range of 400-4000 cm^{-1}. Overall, 32 scans were collected with a spectral resolution of 8 cm^{-1} at a rate of 0.15 s/scan [26].

Rheological analysis

The viscosity is a crucial characteristic of a biocomposite as it will affect the mechanical properties of the carrageenan biocomposite. Higher viscosity relates to stronger intermolecular forces between the materials, where the molecules are strongly bonded together. The viscosity and shear stress of the biocomposite solution were measured using a rotational viscometer (Brookfield, Rheo 3000, USA) equipped with LCT 25 4000010 geometry. Approximately 16.5 mL of the biocomposite solution was poured into the cylindrical compartment of the viscometer for each measurement. The sample was evaluated in triplicate at a constant temperature of 40 °C using a preset speed of 300 rpm with 100 MPoints [27].

Mechanical strength evaluation

The mechanical evaluation was carried out to investigate the deformation of the produced films and hard capsules in response to a load or force applied. A texture analyzer (CT3, Brookfield, USA) was used to measure the tensile strength and EAB of the biocomposite films. The analyzer was outfitted with TexturePro CT V1-8 Build 3.1 software and a 5-kN load cell. The tensile strength was measured following the standard method of ASTM D882-12. The biocomposite films were cut into strips with a dimension of 20 × 60 mm^2. The film thickness was calculated as the average of three distinct positions of the film samples measured with Vernier calipers. The analysis was controlled by setting up the texture analyzer with a baseline grip width of 80 mm and a crosshead speed of 30 mm/min to a maximum distance of 15 mm [28]. The tensile strength and the EAB for each sample were calculated as in Equation 1 and Equation 2, respectively. The load at break and the elongation at rupture were collected from the results of the texture analyzer, and the initial gauge length was the set-up value for the crosshead speed used for the measurement.

$$\text{Tensile strength (MPa)} = \frac{\text{Load at break}}{\text{Initial width} \times \text{Initial thickness}} \quad (1)$$

$$\text{Elongation at break (\%)} = \frac{\text{Elongation at rupture}}{\text{Initial gauge length}} \times 100\% \quad (2)$$

The same texture analyzer (CT3, Brookfield, USA) was used to conduct the capsule loop test, but with a capsule loop fixture. A hard capsule was attached to a pair of separating rods, with the lower rod positioned on the stationary platform and centrally beneath the probe. The upper rod gradually went higher at a speed of 0.50 mm/s with a target value of 5.0 mm until the hard capsule was torn apart. [29]. The applied force (N) to break the hard capsule was reported as the capsule loop strength. The analysis was conducted with at least three measurements taken for each sample to calculate the average result.

Moisture content determination

Moisture content can affect the mechanical qualities of a sample. Accordingly, a moisture analyzer (MS70, A&D Japan) was used to measure the moisture content in the biocomposite film. About 0.1 g of the sample was placed on the heating pan of the moisture analyzer [30]. The moisture in the sample would evaporate after air-drying at 30–200 °C. The sample was heated by a halogen lamp for fast and uniform heating to give a quick measurement. When the mass of the sample reached a constant value, the analysis was automatically stopped. The electric balance weighed the sample before and after heating to determine the moisture content, as shown in Equation 3.

$$\text{Moisture content (\%)} = \frac{\text{Initial weight - Dried weight}}{\text{Initial weight}} \times 100\% \qquad (3)$$

Results and Discussion

Functional groups of DES

The formation of the eutectic mixture was analyzed by ATR-FTIR spectroscopy for DES and its pure constituents. The spectra of DES together with ChCl and glycerol are shown in Figure 1. Pure ChCl exhibited vibrational bands at 3223 cm^{-1} and 1200–880 cm^{-1}, corresponding to stretching vibrations of –OH or N–H bonds. The vibrational bands at 3024 cm^{-1} and 1479–1348 cm^{-1} corresponded to alkyl groups or N–H vibrations in quaternary ammonium groups. Other bands in the wavelength ranged from 1273 to 864 cm^{-1}, with the most intense band at 950 cm^{-1}, also showed the existence of hydroxyl and ammonium group characteristics of ChCl. The most prominent group of CH_2 bending was detected at 1479 cm^{-1}. This is comparable to the band at 1482 cm^{-1} from the study by Jakubowska et al. [31].

The most important band in the glycerol spectrum is the typical O–H stretching of the hydroxyl group, which was represented by the vibrational band at 3384 cm^{-1}. The vibrational bands at 2932 and 2878 cm^{-1} corresponded to C–H stretching and 1412 cm^{-1} to CH_2 bending of the alkyl group. The bands at 1107, 1028, and 849 cm^{-1} corresponded to different functional groups, namely C–O stretching, asymmetric C–C–O stretching, and symmetric C–C–O stretching, respectively. An additional band that appeared at 1208 cm^{-1} referred to C–O–H bending. These functional groups are absorbed at a wavelength similar to that reported by Delgado et al. [32].

A few peaks related to ChCl coexisted after the formation of DES. The absence of a ChCl band at 1348 cm^{-1} is consistent with previous results pertaining to the solvent systems of ChCl/malonic acid [33], ChCl/lactic acid [31], and ChCl/acrylic acid [34]. The reduced intensity around 1475 and 1107 cm^{-1}, which indicated CH_2 bending of ChCl and C–O stretching of glycerol, could be interpreted as evidence for the formation of the eutectic mixture of DES. This can be explained by the hydrogen bond donor-acceptor interaction between the constituents of DES, which are chloride ions of ChCl and the –OH group of glycerol ($Cl^{-}\cdots OH$). The absorption band of glycerol at 3293 cm^{-1} was discovered to shift down to 3287 cm^{-1} in the DES, indicating the formation of a hydrogen bond between ChCl and glycerol, such as $Cl^{-}\cdots OH$ and $CH_3\cdots OH$. A similar trend of shifted peaks between the DES constituents was also observed by Sun et al., who synthesized 25 types of ChCl-based DES for cellulose [35].

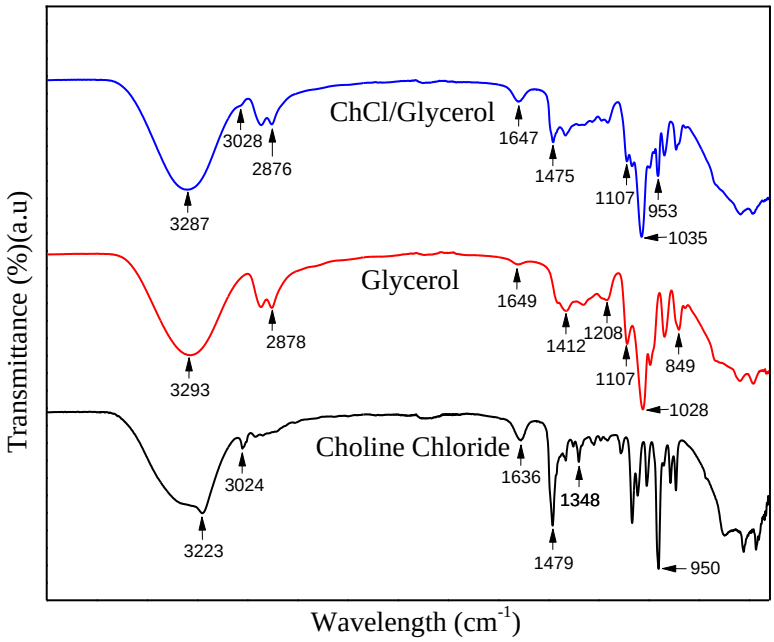

Figure 1. FTIR spectra of DES formation from ChCl and glycerol

Rheological analysis

Viscosity, a property of rheology, is defined as the measure of the resistance of a fluid to gradual deformation by shear stress. Figure 2 presents the relationship between shear stress and viscosity of the carrageenan biocomposite at different DES concentrations, ranging from 0 to 1.0 v/v%. The increase in shear stress between the layers of the biocomposite solution would also increase the viscosity of the solution [36]. The biocomposite without DES had a viscosity of 442.5 mPa·s and a shear stress of 171.2 Pa. The inclusion of 0.2 v/v% DES increased the viscosity and shear stress to their highest values of 504.9 mPa·s and 201.4 Pa, respectively. This increase is due to the rheological complexity of the carrageenan matrix when introduced with DES as a plasticizer. The trend for both plots of viscosity and shear stress fluctuated. It is worth noting that a significant reduction in the viscosity of Carra-DES 0.6 by 16.1% occurs because an excess amount of plasticizer enhances the molecular mobility of the biocomposite, reducing friction force or shear stress, thereby increasing the flowability of the biocomposite [37]. Defining the optimal concentration of a plasticizer in a formulation is crucial, as the viscosity of the biocomposite influences its mechanical properties.

Film tensile strength and EAB

The biocomposite materials used for hard capsules possess high mechanical properties to restrain the load applied, resulting in lower rejection rates during capsule filling. Although carrageenan has good film-forming properties, it is fragile and exhibits poor flexibility. The best concentration of DES as the plasticizer has to be quantified to produce hard capsules with low brittleness. In the mechanical evaluation, tensile strength and EAB were used as indicators for the biocomposite films, while loop strength was assessed for the hard capsules.

Figure 3 presents the tensile strength and EAB of carrageenan biocomposite at different DES concentrations. A significant peak in tensile strength was achieved by Carra-DES 0.2 with an increase of 67.1% from 19.8 to 60.1 MPa. This increase indicates that the addition of DES to the biocomposite film can effectively improve its flexibility and reduce the brittleness of the film. This enables its application as a plasticizer for hard capsules to be exploited. Moreover, the increase is directly related to the increase in viscosity of the biocomposite, as shown in Figure 2. The HBD and HBA of the DES were able to form hydrogen bonds with the hydroxyl groups on the glycosidic moiety of the polysaccharide chains of carrageenan. The increased

intermolecular interaction between DES and carrageenan strengthens the biocomposite film. This is applicable to the lower concentration of DES as the tensile strength gradually decreased with the increasing DES concentration from 0.4 to 0.8 v/v%. The newly formed hydrogen bonds were able to disrupt the intermolecular interactions between the polysaccharide chains, leading to an increase in chain movement and greater flexibility of the biocomposite [19].

In contrast, the EAB of the carrageenan biocomposite film depicted an opposite trend, which was consistent with previous studies [19, 38]. The EAB of the control film gradually increased from 6.1% and reached its maximum value of 45.5% with the addition of DES at a concentration of 1.0 v/v%. The directly proportional relationship between the EAB value and the DES concentration indicated that the DES had a significant plasticizing effect on the biocomposite films. The DES made from ChCl and glycerol was a viable plasticizer as it could significantly increase the percentage of EAB, even at a low volume. At a concentration of 0.6 v/v%, the EAB almost reached a constant value because the excess DES concentration disrupted the intermolecular hydrogen bonding between the polymer chains of carrageenan. This trend was comparable to the study by Zhao et al. in which a high concentration of natural DES was added to the chitosan/zein films [38]. In general, there is an inverse correlation between tensile strength and elongation. The best and most desirable biocomposite films for hard capsule application are those that exhibit both strength and flexibility in an optimal balance. These films would be able to withstand external forces while still being flexible enough to undergo deformation without breaking. Therefore, the amount of DES used in the formulation should be controlled to achieve high physical strength in hard capsule application.

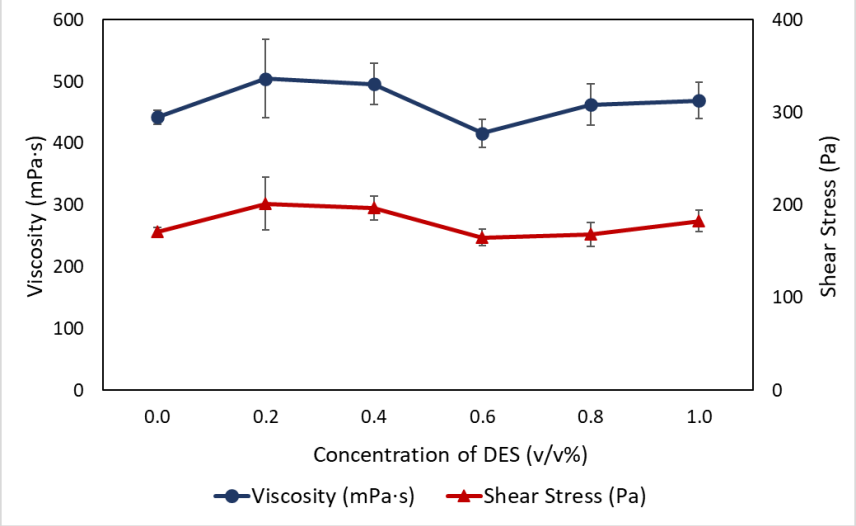

Figure 2. Viscosity and shear stress of carrageenan biocomposite at various DES concentrations

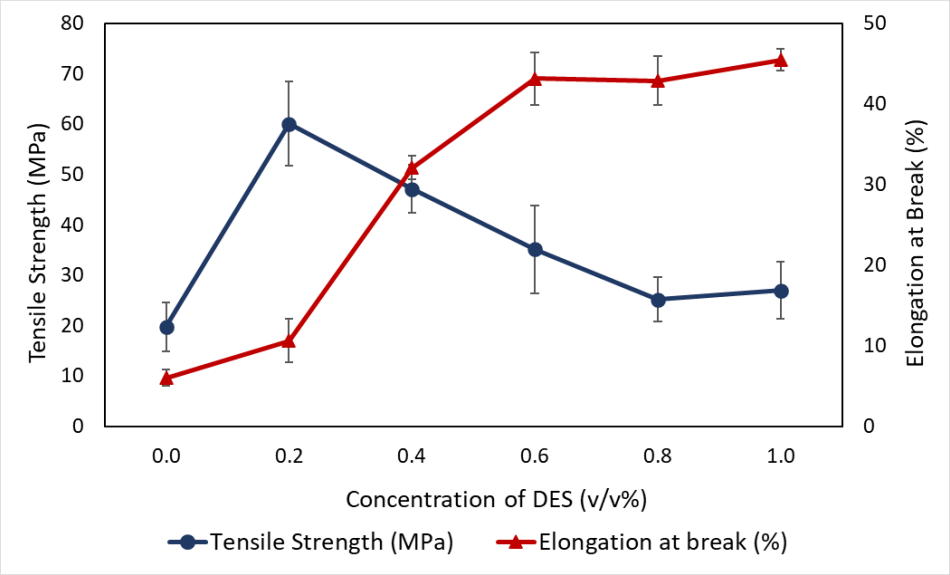

Figure 3. Tensile strength and EAB of carrageenan biocomposite films at various DES concentrations

Capsule loop strength

The loop strength for each carrageenan hard capsule sample at different DES concentrations is shown in Figure 4. The capsule loop strength increased significantly after the addition of DES, up to 35.4% for Carra-DES 0.4. The strength increased to 31.6 N as opposed to the control sample with 20.4 N. As discussed in the tensile strength result, the new hydrogen bond formed between the DES constituents and the carrageenan matrix improved the strength of the capsule loop due to the increased intermolecular interaction. The trend of the graph abruptly declined after the addition of DES at concentrations higher than 0.4 v/v%. The capsule loop strength decreased to 12.8 N in the sample of Carra-DES 1.0. The polar groups of DES made it easy to form hydrogen bonds with carrageenan. However, excessive plasticization weakened the carrageenan hard capsule as it could destroy the existing intermolecular hydrogen bonds between the carrageenan molecules [18]. Therefore, upon adding a higher concentration of DES, the capsule loop strength began to decrease.

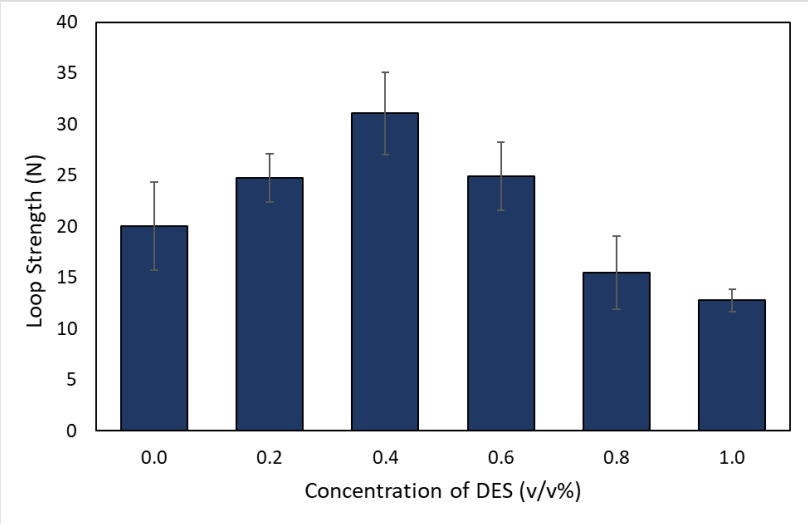

Figure 4. Loop strength of carrageenan hard capsules at various DES concentrations

Film thickness and moisture content

Table 2 presents the film thickness and moisture content of Carra-DES samples at varied concentrations. The control sample without DES was reported to be the thickest film compared to other samples with 0.23 mm. The addition of plasticizer increased the molecular mobility of the carrageenan matrix, which promoted the flowability of the biocomposite solution during film casting and thus reduced the film thickness. The thickness of the biocomposite films with the addition of DES from 0.2 to 1.0 v/v% presented a slight discrepancy, which was around 0.11–0.15 mm.

Table 2. Film thickness and moisture content of carrageenan biocomposite films at various DES concentrations

Samples	Film Thickness (mm)	Moisture Content (%)
Control	0.23 ± 0.02	14.5 ± 0.3
Carra-DES 0.2	0.12 ± 0.02	13.5 ± 0.5
Carra-DES 0.4	0.14 ± 0.01	15.4 ± 0.6
Carra-DES 0.6	0.11 ± 0.04	15.8 ± 0.6
Carra-DES 0.8	0.15 ± 0.01	15.9 ± 0.7
Carra-DES 1.0	0.12 ± 0.03	14.8 ± 0.1

Water can also act as a plasticizer for a biocomposite film, which in excess impairs its mechanical properties. Consequently, the moisture content of the carrageenan biocomposite film should be considered for the development of hard capsules. As shown in Table 2, the moisture content of all tested samples was around 13-15%, indicating that the influence of DES concentration was insignificant in this study. Moreover, these values were comparable to those of commercial gelatin capsules with a moisture content of 13% [39]. Similar results were also found by Hamdan et al., who reported that the moisture content of Carra-CNC biocomposites ranged from 15.5% to 17.5% [4]. However, it is noteworthy that high concentrations of DES at 0.4-0.8 v/v% had the highest moisture content, surpassing 15%. The hygroscopic characteristics of DES likely affect the ability of the film to absorb moisture from the surroundings when a high DES concentration is introduced into the formulation [40].

Physical appearances of films

Figure 5 presents the images of carrageenan biocomposite films at different DES concentrations with a black panel as the background. Based on the observation under natural light, the control sample appears transparent and has a rough surface due to the insoluble solid crystals of CNCs. The addition of the DES to the formulation improved the poor uniformity observed in the control sample. The transparency gradually decreased with increasing DES concentrations. Under the same conditions, Carra-DES 0.8 and Carra-DES 1.0 were observed to be almost opaque. These two samples have a relatively smooth surface compared to the control sample. Higher DES concentrations can improve the appearance of the carrageenan biocomposite film, where the smoothness increases differently. Nevertheless, a higher DES concentration would decrease the mechanical properties of the carrageenan biocomposite film, as discussed in Figure 3 and Figure 4. Wei et al. speculated that a higher DES concentration directly destroys the structure of CNCs, resulting in a loss of optical and mechanical properties of CNC/DES films [17].

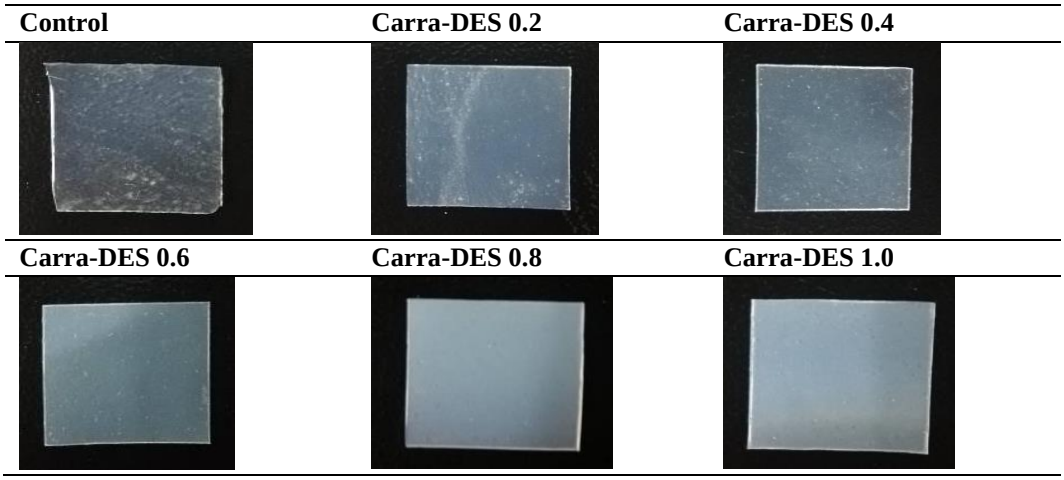

Figure 5. Images of carrageenan biocomposite films at various DES concentrations

Conclusions

In summary, DES has been successfully applied as a new type of plasticizer in the synthesis of carrageenan biocomposite films and hard capsules. The DES, which consists of ChCl and glycerol, is a good and feasible plasticizer because it can significantly increase the flexibility of carrageenan biocomposites even at low concentrations. The EAB of the carrageenan film greatly increased from 6.1% to 45.5% when the DES concentration increased to 1.0 v/v%. Meanwhile, Carra-DES at 0.2 v/v% gave the highest tensile strength of 60.1 MPa, which was the best concentration of Carra-DES biocomposite with a capsule loop strength of 24.8 N. The formation of hydrogen bonds between DES and carrageenan improves the mechanical strength of the biocomposite films. Despite that, an excess concentration of DES could have a detrimental effect on the film tensile and capsule loop strengths of the carrageenan biocomposite. In addition, the hygroscopic characteristics of DES would lead to poor stability of the hard capsule with increased moisture content. For that reason, it should be controlled at an appropriate concentration to achieve high mechanical strength in hard capsule application.

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