CHAPTER-IX

Synthesis of cellulose / sb-cd composite membrane using \([\text{BMIM}]^{+}\text{BF}_4^{-}\) and \([\text{BMIM}]^{+}\text{PF}_6^{-}\) Ionic liquids

9.1. Introduction

Nowadays, the synthetic and non-biodegradable polymers have become a threat to the environment in our developing society. Therefore, an increasing attention has been paid on the development of environmentally benign natural bio-based materials, which is a solution not only to growing environmental threats and also for other electrochemical, pharmaceutical applications and water treatment process [1].

The bio-polymers such as β-cyclodextrin and cellulose have the potential advantages of such bio-based materials, apart from their environmental gains, low cost, available from natural resources and enabling to replace some synthetic polymers, etc. However, their inherent disadvantages such as relatively low mechanical strength and the poor solubility. Furthermore, all the polymers cannot melt and cannot be processed like thermoplastic polymers. This process is much different from the synthetic polymer. Traditionally, some bio-based polymers have been incorporated into other polymeric materials at lower cost and biodegradable fillers. Many systems based on these natural polymers have been investigated recently, such as poly(ε-caprolactone)/starch, poly(hydroxybutyrate)/lignin, poly(ε-caprolactone)/cellulose etc.[2-4]
Recently, many attentions had been paid on preparing the totally biodegradable blends with the natural polymers and their derivatives, such as cellulose diacetate/starch, starch acetate/native starch, cationic starch/cellulose and chitosan/cellulose acetate etc., [5,6]. These blends are present in good compatibility and retain biodegradability. The preparation of environmental friendly materials based on pure natural polymers, using their derivatives will increase the cost and complicacy.

The structural modified cellulosic polymers have some important behaviors. It is possible to structural change of cellulose using cyclodextrin. The β-cyclodextrin is a water soluble carbohydrate polymer, containing seven glucose units linked by glucosidic bonds. Like a shallow truncated cone, cyclodextrin has a hydrophobic cavity and a hydrophilic exterior. The hydroxyl group of β-cyclodextrin can be replaced by other groups such as sulfonic acid groups for increased reactivity [7,8]. The β-cyclodextrin polymer was covalently fixed on cellulose by a polycondensation reaction at controlled conditions. The β-cyclodextrin polymer solution is able to anchor on cotton cellulose in gelation process in order to impart new surface property of cotton. The introduction of sulfonic acid groups (-SO₃H) on polymer surfaces have found important for biomedical applications. It has been shown that the expansion on polymeric materials is improved if the surface of the polymer contains sulfonic acid groups [9]. Pharmaceutical applications of cyclodextrins have been mainly described [10,11].

The stiff and close packing molecules have solubility problems caused by the hydroxyl groups in the sugar residues due to the several inter- and intra- molecular hydrogen bonds. N-acrylchitosan-cellulose fiber, chitin/cellulose composite gels and membranes [12,13] are well-known as the solvents for these polysaccharides.
Range of room temperature Ionic liquids can be used for dissolve cellulose has been reported [14]. Some of the research groups reported the preparation of cellulose membranes by casting the solutions of cellulose in Ionic liquid [BMIM] Cl onto a glass plate [15]. The composite membrane preparation method is simple, very attractive and used Ionic liquids as a solvent. This product has a high thermal stability making them so Ionic liquids called “green solvents”. High molecular weight polymers such as cellulose, around 15–20% can be dissolved in room temperature Ionic liquids and to form various cellulose objects such as fibers, gels, membranes and composites [16,17].

The miscibility in polymer blend is assigned to specific interactions between polymeric components, which usually give rise to a negative free energy of mixing in spite of the high molecular weight of polymers. The most common interactions in the blends are hydrogen bonding, Ionic and dipole, π-electrons and charge-transfer complexes. Most polymer blends are immiscible with each other due to the absence of specific interactions [18]. It is expected that cellulose will be miscible with cyclodextrin and the introduction of sulfated β-cyclodextrin into cellulose will result interesting applications. On basis of the upstairs views and expected this type of composite membranes also have some functional behaviors. In this chapter to discussed the applications of Ionic liquids as solvent for synthesis of cellulose/sb-cd composite membranes.

9.2. Results and Discussion

9.2.1. Strength analysis of cellulose/sb-cd composite membranes

Tensile and elongation strength studies are important for mechanical properties of the prepared composite membranes. Figure 9.1 shows the tensile strength of 1:3 and 3:1 ratio cellulose/sb-cd composite membranes. The ratio effects do not exhibit major difference in the strength analysis. It was found that in dry and wet states the tensile strength values of
composite membranes obtained from [BMIM][BF$_4$] higher than [BMIM][PF$_6$]. The miscibility property of [BMIM][BF$_4$] higher than [BMIM][PF$_6$] Ionic liquid. The elongation strength of cellulose/sb-cd membranes at dry and wet conditions showed in figure 9.2. It can be observed that the cellulose/sb-cd can greatly enhance the flexibility of dry and wet membranes obtained from [BMIM][BF$_4$]. These results propose that the slightly decrease of elongation strength with the 3:1 ratios of cellulose/sb-cd composite membranes in both Ionic liquids. From this strength analysis, each polymer not only contributes to the properties of composite membranes alone but also engages in sb-cd polymer-cellulose polymer interactions which affect the mechanical properties of overall systems [19].

9.2.2. XRD pattern of cellulose, sb-cd and composite membranes

The XRD profiles of the prepared membranes were showed in figure 9.3 a, b, c & d. From figure 9.3a &b exhibits the diffraction pattern probably due to the crystalline structures of the cellulose and sulfated β–cyclodextrin. It is noted that XRD results indicate the crystalline structures of both polymers cellulose and sulfated β–cyclodextrin are mostly disrupted in the composite membranes (Fig. 9.3c & d). The composite membrane from [BMIM][BF$_4$] Ionic liquid exhibited lower crystallinity than [BMIM][PF$_6$] Ionic liquid. The cellulose chains were miscible with the Ionic liquids to disrupt the crystalline structure [20].

9.2.3. FTIR analysis of cellulose, sb-cd and composite membranes

Figure 9.4 a & b shows the FTIR spectra of β-cyclodextrin and sulfated β-cyclodextrin (sb-cd). The -OH stretching absorption displayed a typical broad peak from 3557 cm$^{-1}$ to 3247 cm$^{-1}$(Fig. 9.4a). It indicates that the compound have many numbers of hydroxyl groups. This is the evidence for β-cyclodextrin has many hydroxyl groups in its structure. From 2932 cm$^{-1}$ to 2119 cm$^{-1}$ the peak values represented to the -CH$_2$ stretching. The C-O-C stretching vibration corresponded from 1413 cm$^{-1}$ to 1079 cm$^{-1}$. It is due to the
seven numbers of glucose linkages in β-cyclodextrin structure. The available free hydroxyl
groups indicated with a broad peak at 3207 cm\(^{-1}\). From 2924 cm\(^{-1}\) to 2144 cm\(^{-1}\) peak values
indicates that the -CH\(_2\) asymmetric stretching. The S-O stretching absorption peak showed at
699 cm\(^{-1}\). The asymmetric and symmetric stretching of -SO\(_3\) groups exhibit in the region
from 1152 cm\(^{-1}\) to 699 cm\(^{-1}\). It is the evidence for the sulfonic acid reaction on
β-cyclodextrin and the primary hydroxyl groups may involve sulfonation reaction.

The FTIR spectrum of pure cellulose showed in figure 9.4c. The peak 3418 cm\(^{-1}\)
corresponds -OH stretching and also the -CH\(_2\) stretching corresponds region at 2894 cm\(^{-1}\)
region. The peaks showed at 1110 cm\(^{-1}\) and 1049 cm\(^{-1}\) due to the C-O-C stretching modes.
The FTIR spectrum of cellulose/sb-cd membranes showed in figure 9.4 d &e. The -OH
stretching of alcoholic groups indicates at peak 3269 cm\(^{-1}\). A peak at 2906 cm\(^{-1}\) corresponds
-CH\(_2\) stretching and the peak at 1111 cm\(^{-1}\) represents S-O stretching. This value is the
evidence for functional groups of sb-cd may present in cellulose.

The peaks at 1132 cm\(^{-1}\) and 1044 cm\(^{-1}\) for cellulose, which are moved to a lower
wave number ranges 1102-1013 cm\(^{-1}\) in the composite membrane obtained from
[BMIM]\(^+\)PF\(_6^-\) Ionic liquid. The peaks at which are moved to a lower wave number ranges
1102-1013 cm\(^{-1}\) in the composite membrane obtained from [BMIM]\(^+\)BF\(_4^-\) Ionic liquid

The composite membrane synthesized from [BMIM]\(^+\)BF\(_4^-\) Ionic liquid values move
lower wave number than [BMIM]\(^+\)PF\(_6^-\) assisted composite membrane. These FTIR analysis
results propose that strong hydrogen bonds [21] have been formed among the cellulose and
sulfated β-cyclodextrin (sb-cd). The cellulose and sulfated β-cyclodextrin could be dissolved
in Ionic liquids. Therefore, we suggest that the intra- and inter-molecular hydrogen bonds of
each component were destroyed and the two components were dispersed in Ionic liquids.
9.2.4. Surface morphology of cellulose/sb-cd composite membranes

The SEM images of cellulose/sb-cd composite membrane obtained from Ionic liquids (Fig. 9.5 a,b,c &d). The actual cellulose and β–cyclodextrin polymers are not identified from SEM images. The cellulose system is proposing good linkage between β–cyclodextrin polymer matrices in the membrane formation with Ionic liquids. The [BMIM]⁺BF₄⁻ Ionic liquid obtained cellulose/sb-cd membranes displayed a clear morphology with a non-fibrous structure (Fig. 9.5 a). But less agglomerates observed in cellulose/sb-cd membranes prepared from [BMIM]⁺BF₄⁻ Ionic liquid(Fig 9.5b).The composite membranes obtained from [BMIM]⁺PF₆⁻ Ionic liquid exhibited homogeneous structure with crystalline particles at both magnification (Fig. 9.5 c&d). These results specified that SEM data served as good evidence for complete miscibility between sb-cd and cellulose. It is due to the hydrogen bonding interactions between the hydroxyl groups of the polymer components [22].

9.2.5. TG/DTA analysis of composite membranes

The thermal permanence of cellulose/sb-cd composite membranes showed in figure 9.6. Initially small weight loss exhibits about 1-4% below 100°C for all the membranes and it is assigned to the release of moisture from these membranes. The cellulose and sb-cd polymers shows one-stage degradation within the range of 350-400°C (Fig. 9.6a & b). The major weight loss started from 250°C to 270°C for cellulose/sb-cd membranes (Fig. 9.6c & d). The remaining weight loss of the composite membranes showed in the ranges 350-430°C. The maximum decomposition temperature of the membrane is lower than that of pure cellulose and sb-cd. The maximum decomposition temperature of composite membrane prepared from [BMIM]⁺BF₄⁻ is slightly higher than membrane obtained from [BMIM]⁺PF₆⁻. From these results suggested that the strong intra- and inter-molecular hydrogen bonds of cellulose were partially broken by Ionic liquids and showing relatively high thermal stability.
9.2.6. Antibacterial test

The antibacterial activity synthesized membranes were tested using Gram ‘+ve’ bacteria (S.aures) and Gram ‘-ve’ bacteria (E.coli) for synthesized cellulose/sb-cd composite membranes. The antibacterial activity was determined by colony forming units (CFU) with time intervals. The cellulose/sb-cd membrane prepared from [BMIM]+PF6– Ionic liquid exhibited 87 % of reduction viability for S.aureus and 82% for E.coli in 120 min time interval. Cellulose/sb-cd membrane obtained from [BMIM]+BF4– Ionic liquid exhibited 92 % for S.aureus and 87% for E.coli with maximum bacterial reduction for the time period of 120 min. Cellulose/sb-cd membrane from [BMIM]+BF4– Ionic liquid exhibited maximum antibacterial reduction.

9.3. Conclusion

The cellulose/sb-cd composite membranes have successfully prepared from two Ionic liquids. These membranes were characterized for strength, molecular interaction, crystallinity, morphology and thermal stabilities. These membranes showed relatively good miscibility among the cellulose and the Ionic liquids. The appropriate ratio between cellulose and sulfated β-cyclodextrin levels can enhance the strength of membranes. The XRD studies exhibited the cellulose chains are miscible with the Ionic liquids and to disrupt the crystalline structure of the polymers. The cellulose/sb-cd membrane obtained from [BMIM]+BF4– Ionic liquid showed smooth morphology with a non-fibrous structure. The thermal study TG/DTA proposed that the cellulose/sb-cd membranes showing high thermal stability.
9.4. References


9.5. Legends

9.5.1. Figures

Figure 9.1. Tensile strength of sb-cd/cellulose 1:3 and 3:1 ratio composite membranes from Ionic liquids.

Figure 9.2. Tensile strength of sb-cd/cellulose 1:3 and 3:1 ratio composite membranes from Ionic liquids

Figure 9.3. XRD pattern of Cellulose (a), sulfated β-cyclodextrin (b), sbcd/cellulose membrane from [BMIM]+PF$_6^-$ (c) and sb-cd/cellulose membrane from[BMIM]$^+$BF$_4^-$ (d).

Figure 9.4. FTIR spectra of β-cyclodextrin (a), sulfated β-cyclodextrin (b), cellulose (c), sbcd/cellulose membrane from [BMIM]$^+$PF$_6^-$ (d) and sbcd/cellulose membrane from [BMIM]$^+$BF$_4^-$ (e).

Figure 9.5. SEM images of sb-cd/cellulose membrane from [BMIM]$^+$BF$_4^-$ (a&b) and sbcd/cellulose membrane from[BMIM]$^+$PF$_6^-$ (c &d)

Figure 9.6. TG/DTA curves of Cellulose (a), sulfated β-cyclodextrin (b), sbcd/cellulose membrane from [BMIM]$^+$BF$_4^-$ (c) and sbcd/cellulose membrane from[BMIM]$^+$PF$_6^-$ (d)

9.5.2. Table

Table 9.1: Antibacterial activity of cellulose/sb-cd membrane from [BMIM]$^+$PF$_6^-$ and cellulose/sb-cd membrane from [BMIM]$^+$BF$_4^-$
Figure 9.1: Tensile strength of cellulose/sb-cd 1:3 and 3:1 ratio composite membranes from Ionic liquids
Figure 9.2: Elongation strength of cellulose/sb-cd 1:3 and 3:1 ratio composite membranes from Ionic liquids
Figure 9.3: FTIR spectra of $\beta$–cyclodextrin (a), sulfated $\beta$–cyclodextrin (b), cellulose (c), cellulose/sb-cd membrane from [BMIM]$^+\text{PF}_6^-$ (d) and cellulose/sb-cd membrane from [BMIM]$^+\text{BF}_4^-$ (e).
Figure 9.4: XRD pattern of Cellulose (a), sulfated β-cyclodextrin (b), cellulose/sb-cd membrane from [BMIM]+PF₆⁻ (c) and cellulose/sb-cd membrane from [BMIM]+BF₄⁻ (d)
Figure 9.5: SEM images of cellulose/sb-cd membrane from [BMIM]$^+$BF$_4^-$ (a & b) and cellulose/sb-cd membrane from [BMIM]$^+$PF$_6^-$ (c & d)
Figure 9.6: TG/DTA curves of Cellulose (a), sulfated β-cyclodextrin (b), cellulose/sb-cd membrane from [BMIM]⁺BF₄⁻ (c) and cellulose/sb-cd membrane from [BMIM]⁺PF₆⁻ (d)
<table>
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<td>60 min. %R</td>
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<tr>
<td>Cellulose/sb-cd film (b)</td>
<td>43</td>
<td>71</td>
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*Good antibacterial activity

a=[BMIM]⁺BF₄⁻; b=[BMIM]⁺PF₆⁻