

# APPLICATIONS OF IONIC LIQUIDS AND THEIR MIXTURES FOR PREPARATION OF ADVANCED POLYMER BLENDS AND COMPOSITES: A SHORT REVIEW

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**Abstract.** In this paper, we reviewed the applications of hydrophilic and hydrophobic ionic liquids including their mixtures particularly between ionic liquids and chemical compounds for preparation of advanced polymer blends and composites. In the preceding researches we have found that ionic liquids and their mixtures could be effectively used as environmentally friendly solvent, plasticizer, coupling agent and compatibilizer. These materials have the ability to improve properties of polymer blends and composites that consisted of natural and synthetic polymers. On the other hand, we also included our previous and other studies that consumed the mixture of ionic liquids and chemical compounds for preparation of polymer blends and composites in the form of aerogels, films, composite films and biocomposites.

## 1. INTRODUCTION

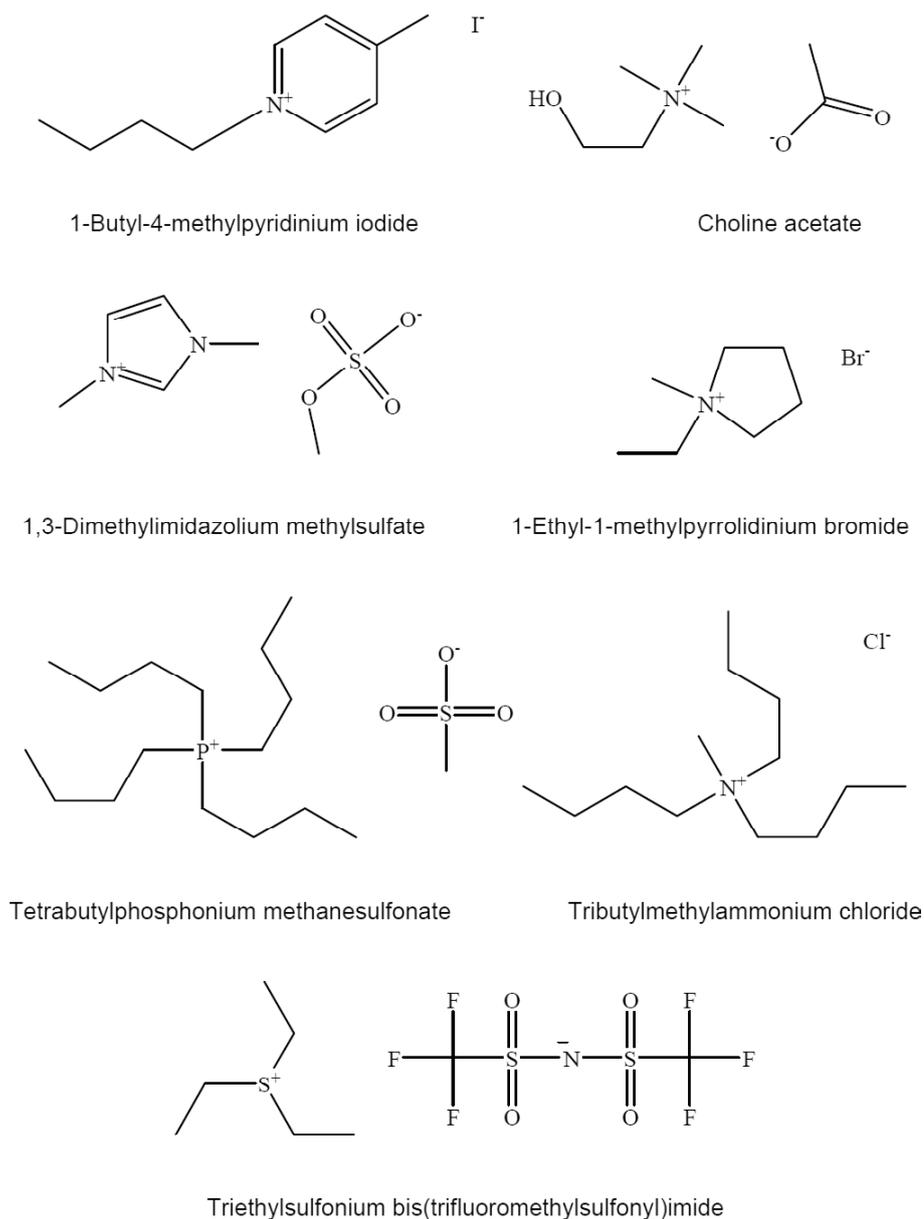
The existence of ionic liquids has given new developments in materials chemistry research. The use of ionic liquids was also brought significant changes in various industrial applications such as chemical, pharmaceutical, biotechnology, energy, gas handling, processing and recycling of materials [1-6]. Several reactions have been proposed to produce the ionic liquids such as alkylation, metathesis, protonation and complexation reactions. Nevertheless, some of these reactions required a long time and high cost to obtain the desired ionic liquids [7-12]. This review has focused on the applications of ionic liquids and the mixtures of ionic liquids and chemical compounds. Nevertheless, the review has only been concentrated on their usage for preparation of advanced polymer blends and composites. Therefore, this review discusses how ionic liquids and their mixtures with chemical compounds ca-

pable acted as solvent, plasticizer, coupling agent and compatibilizer. With availability of these materials, they can also be applied in the large-scale production of advanced materials and polymeric products.

## 2. IONIC LIQUIDS

Salts melt below the boiling point of water (< 100 °C) are ionic liquids. They are composed of cations and anions that are poorly coordinated. Chemical structures of ionic liquids with different cations and anions are indicated in Fig. 1. Ionic liquids are generally regarded as environmentally friendly solvents because they are non-volatile, recyclable, and expected to be alternative solvents that are attractive and robust than conventional organic solvents that are toxic and volatile. Besides having a low melting point temperature, they have a very low vapour pressure makes them non-volatile. Ionic liquids have

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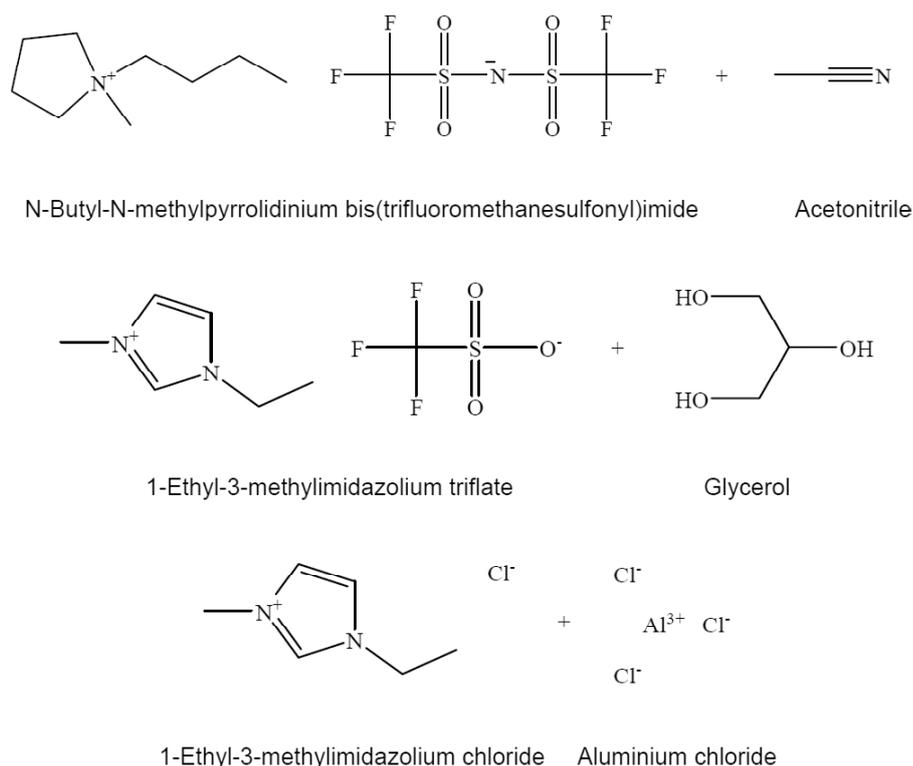
**Fig. 1.** Chemical structures of ionic liquids with different cations and anions.

unusual solvent properties such as very stable, polar, non-flammable, higher thermal stability (> 250 °C), electrically conductive, soluble in organic solvents including water, can be a reaction medium, able to dissolve and solvate many of organic and inorganic materials comprising gas, liquid and solid. They also useful in processing a large number of polymers and biopolymers, chemically inert while maintaining the ability to dissolve wide variety of chemical compounds as well as can be designed and modified according to the needs [13-21].

### 3. IONIC LIQUID MIXTURES

Mixing of the ionic liquids with chemical compounds is one of alternative steps to minimize the use of

ionic liquids which currently considered expensive due to their production costs that are quite high, as well as to save time for preparing new ionic liquids. During the literature review, we have found that the use of the ionic liquids and chemical compounds mixtures is less and the information related with their preparation is also quite little. For that reason, a holistic approach has been committed in our previous studies by mixing ionic liquids and chemical compounds that easily available to create new mixtures. From an economic and environmental point of view, the mixtures of ionic liquids and chemical compounds may be gained a tremendous amount of attention from both the industries and researchers. Improvement of the physicochemical proper-



**Fig. 2.** Examples of ionic liquid mixtures with different chemical compounds.

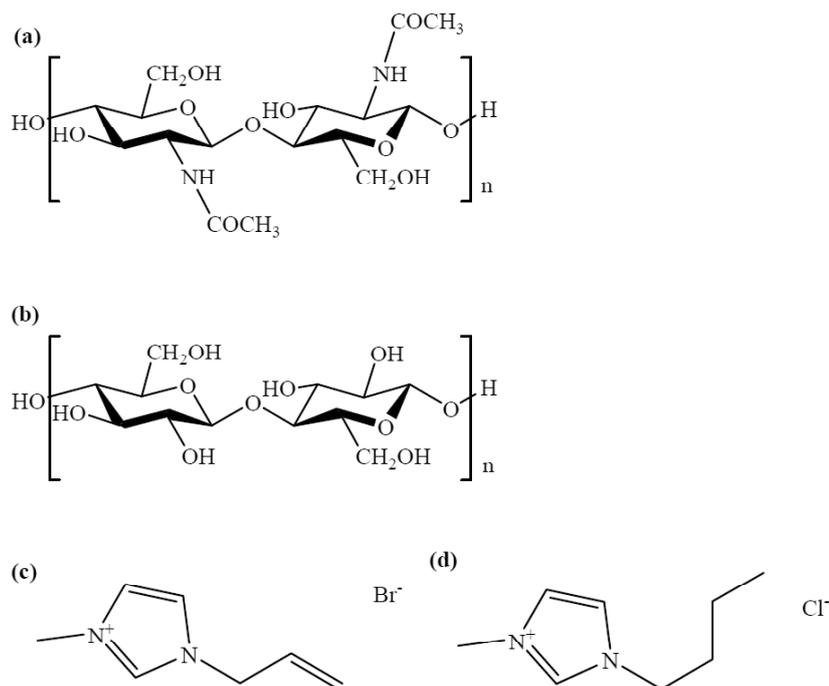
ties of the common ionic liquids into the mixtures that have superior properties are a unique approach to make them interacted much better with the components of materials used [22-24]. Examples of ionic liquid mixtures with different chemical compounds are exhibited in Fig. 2.

#### 4. IONIC LIQUIDS AS SOLVENT

The ability of ionic liquids to interact with polysaccharides through hydrogen bonding makes them usually utilized as solvent for dissolving and processing the biopolymers. Therefore, they can be applied in the preparation of polymer blends. The use of ionic liquids as solvents for different types of biopolymers such as chitin and cellulose in preparation of blend gels and films was studied by Takegawa et al. 2010 [25]. They have used two types of ionic liquids specifically 1-allyl-3-methylimidazolium bromide (AmimBr) and 1-butyl-3-methylimidazolium chloride (BmimCl). The chemical structures of chitin and cellulose biopolymers as well as AmimBr and BmimCl ionic liquids are displayed in Fig. 3. In their study, the chitin and cellulose were dissolved in AmimBr and BmimCl ionic liquids, respectively to produce biopolymers solutions. The homogeneous mixtures of both solutions in the desired ratio were acquired by mixing them at 100 °C. The mixtures were leaved for 4 days

to obtain the blend gels. On the other hand, the mixtures were also casted on glass plates, soaked in water and dried to prepare the blend films. Good miscibility between biopolymers and ionic liquids in the samples was verified by XRD and TGA results. They have found that the ratio of chitin to cellulose in the samples played an important role in changing the mechanical properties of the blend gels and films.

Stefanescu et al. 2012 [26] have successfully prepared chitosan and cellulose blends by using 1-butyl-3-methylimidazolium acetate (BmimAc) ionic liquid as a solvent. Chemical structures of chitosan biopolymer and BmimAc ionic liquid are showed in Fig. 4. In their study, the solutions were manually spreaded on the flat surface and the biopolymers from the blends were precipitated into the mixture of methanol and water to prepare the films. Most of the absorbed water was removed by freeze drying under vacuum condition to avoid the films shrinkage. From the FTIR results, they have found that there are shifts of FTIR bands corresponding to amide groups of chitosan. Furthermore, the specific XRD diffraction peaks were disappeared, the activation energy of thermal decomposition MTGA of all polymeric blends was increased, and the SEM images indicated no phase separation from both biopolymers and also an apparent homogeneous structure was present. All these clearly evidenced



**Fig. 3.** Chemical structures of (a) chitin and (b) cellulose biopolymers as well as (c) AmimBr and (d) BmimCl ionic liquids.

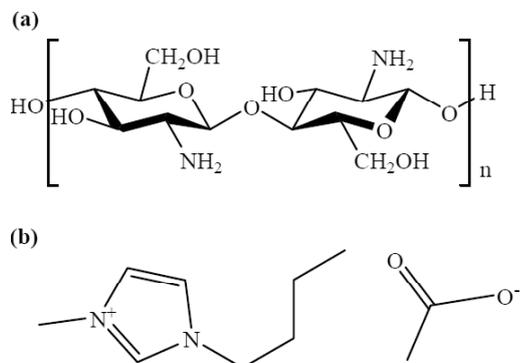
that by using BmimAc, the blends between chitosan and cellulose in the solid state is fully miscible.

On the other hand, corn starch/cellulose blend films have been prepared by Liu and Budtova in 2012 [27]. The biopolymers were mixed into 1-ethyl-3-methylimidazolium acetate (EmimAc) ionic liquid. Chemical structures of starch biopolymer and EmimAc ionic liquid are demonstrated in Fig. 5. The blends in the liquid state and the film state that obtained via wet casting were characterized. They have found that even at high biopolymers concentration (~10 wt.%) which was studied, there is no phase separation was observed in the blends. Coagulation of corn starch/cellulose blends in water and ethanol were done to obtain the blend films. The absence of any new chemical bonds formed

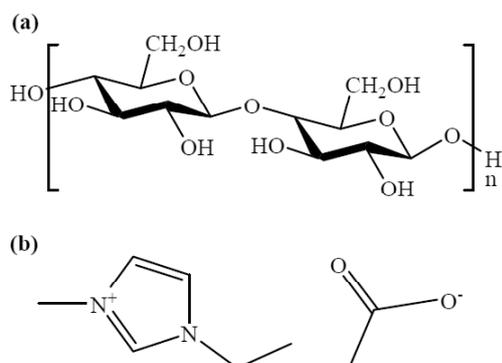
between the components of dry films was confirmed by FTIR analyses, and the significant decrease in crystallinity was validated by XRD results. They also discovered that the starch was entrapped in a three-dimensional network of cellulose when the blends were coagulated in ethanol. However, starch was partially leached, created pores and channels when the blends were coagulated in water. Moreover, the pore size of the freeze-dried wet films could be varied by changing the composition of the blends and varying the coagulation bath as proved in morphology results.

## 5. IONIC LIQUIDS AS PLASTICIZER

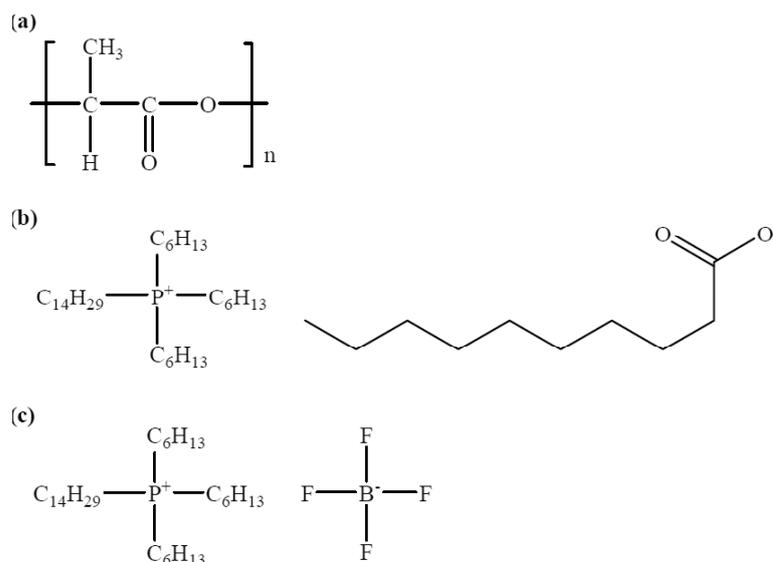
Plasticizing of natural polymers with ionic liquids has given the same increment in physical proper-



**Fig. 4.** Chemical structures of (a) chitosan biopolymer and (b) BmimAc ionic liquid.



**Fig. 5.** Chemical structures of (a) starch biopolymer and (b) EmimAc ionic liquid.



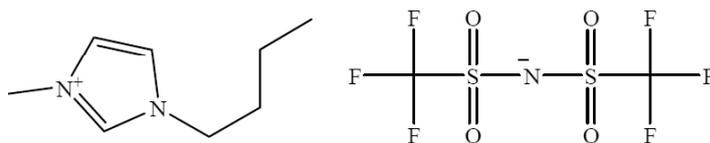
**Fig. 6.** Chemical structures of (a) PLA biopolymer as well as (b) TtphD and (c) TtphBF<sub>4</sub> ionic liquids.

ties as ionic liquid-plasticized synthetic polymers. It is indicated that ionic liquids can be used as plasticizer for various types of polymers without assistance of common plasticizers. The study by Sankri et al. 2010 [28] have also showed that natural polymers such as thermoplastic starch (TPS) could be plasticized with BmimCl ionic liquid. The samples were prepared through melt processing. They have found that the TPS samples plasticized with BmimCl are less hygroscopic than the TPS samples plasticized with glycerol based on the electrical conductivity results. In addition, the BmimCl is essentially seemed to be more efficient plasticizer for the starch with lower water absorption. Compared with the glycerol plasticized TPS samples, the BmimCl plasticized TPS samples have higher elongation at break in elastic condition. They discovered that the presence of ionic liquid caused high reduction of hydrogen bonding between starch chains and extraordinarily led to decrease of elastic Young's modulus of TPS. Their interpretations have also been supported by the detailed FTIR analysis.

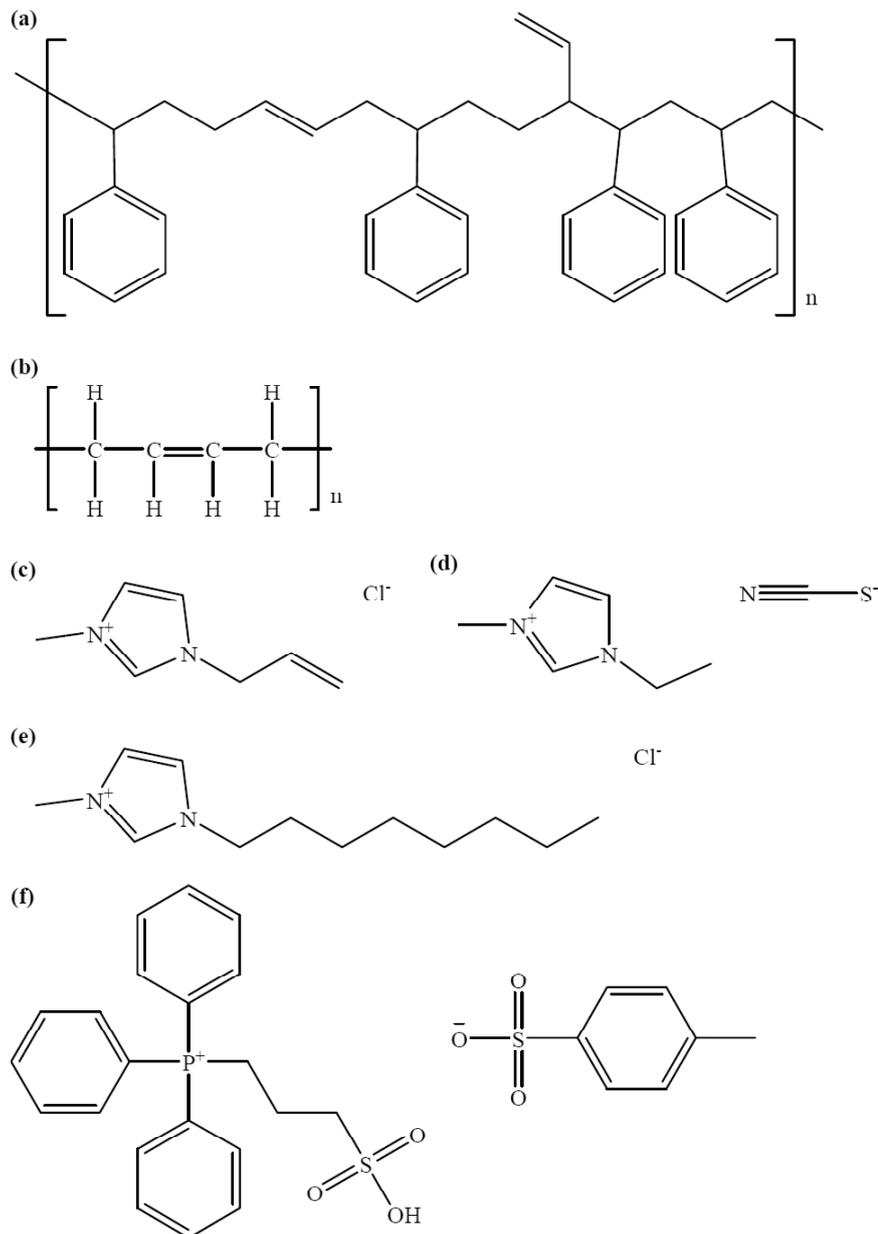
On the other hand, the another study by Park et al. 2010 [29] have used two types of ionic liquids with different anions (decanoate and tetrafluoroborate) but with the same phosphonium-based cation specifically trihexyltetradecylphosphonium decanoate (TtphD) and trihexyltetradecylphosphonium tetrafluoroborate (TtphBF<sub>4</sub>) to evaluate their potential as plasticizer and lubricant for poly(lactic acid), PLA. Chemical structures of PLA biopolymer as well as TtphD and TtphBF<sub>4</sub> ionic liquids are indicated in Fig. 6. The SEM images indicated both ionic liquids at 5 wt.%

are dispersed well and partially miscible with PLA. It is supported by glass transition temperature ( $T_g$ ) values and the calculations of solubility parameters. TGA results showed the thermal stability of ionic liquid containing tetrafluoroborate anions is higher compared with ionic liquid containing decanoate anions. They have found that the PLA incorporated with both ionic liquids also showed the similar trend for thermal properties. Additionally, ionic liquid containing tetrafluoroborate anions has provided more significant lubrication effect as evidenced by the low coefficient of friction values and it is could be associated with a low contact angle. Therefore, based on reduction of elastic modulus and brittleness as well as decrease of  $T_g$  values, the ionic liquid containing tetrafluoroborate anions could generally be considered more effective as a plasticizer than ionic liquid containing decanoate anions.

Mahadeva and Kim 2011 [30] have reported the influence of addition 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BmiTfsi) room-temperature ionic liquids on the thermal and mechanical properties of regenerated cellulose. Chemical structure of BmiTfsi ionic liquid is exhibited in Fig. 7. They have found that the thermal stability of regenerated cellulose was increased with addition of BmiTfsi during the dissolution of cellulose. The improved thermal stability of regenerated cellulose is basically due to the good thermal stability of BmiTfsi at high temperature. Moreover, low vapour pressure of BmiTfsi resulted in good performance with less evaporation or leaching in comparison with other plasticizers that were used for regenerated cellulose. They also discovered that there is intermo-



**Fig. 7.** Chemical structure of BmiTfsi ionic liquid.

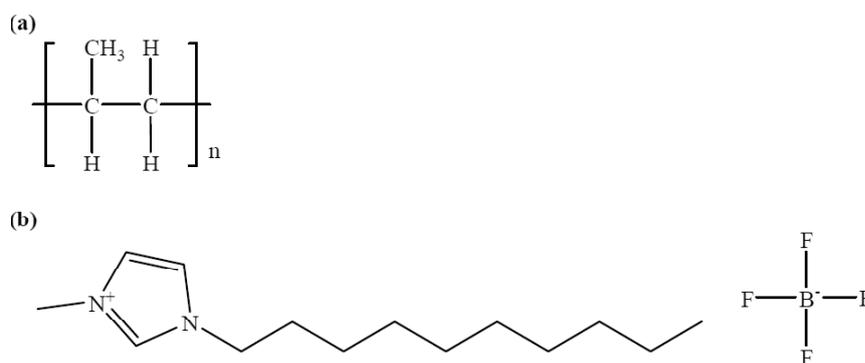


**Fig. 8.** Chemical structures of (a) styrene-butadiene, and (b) polybutadiene rubbers as well as (c) AmimCl, (d) EmimTc, (e) MoimCl, and (f) TphsT ionic liquids.

lecular interaction between the molecules of cellulose and BmiTfsi as proved by the analyses of UV-Vis and FTIR spectroscopes. In addition, effectiveness of BmiTfsi as plasticizer for regenerated cellulose at wide variety of environmental humidities and temperature conditions is because of the immiscible nature of BmiTfsi with water and its stability against moisture.

## 6. IONIC LIQUIDS AS COUPLING AGENT

Besides dissolving and plasticizing polymers, ionic liquids could also be used as coupling agent since they can interact directly with both matrices and fillers. This has improved the physicochemical properties of prepared polymer composites. Das et al.



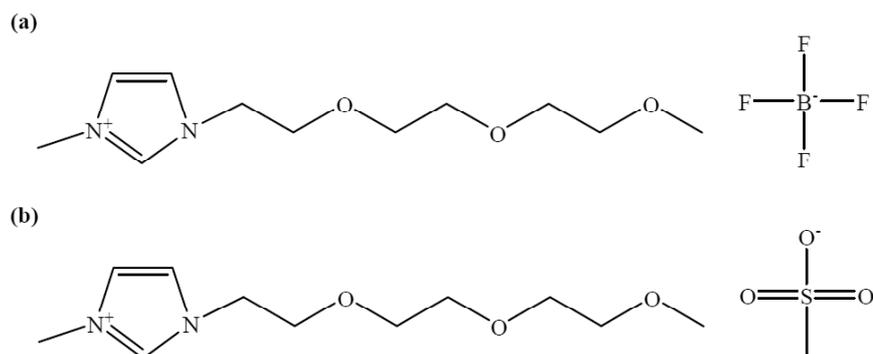
**Fig. 9.** Chemical structures of (a) PP and (b) DmimBF<sub>4</sub> ionic liquid.

2009 [31] have reported the use of ionic liquids as coupling agent in polymer composites. They have studied the coupling activity of ionic liquids for enhancing interaction and dispersibility multi walled carbon nanotube (MWCNT) with diene elastomer polymer matrix. The 1-allyl-3-methylimidazolium chloride (AmimCl), 1-ethyl-3-methylimidazolium thiocyanate (EmimTc), 1-methyl-3-octylimidazolium chloride (MoimCl), 3-(triphenylphosphonic)-1-sulfonic acid tosylate (TphsT) and TtphD ionic liquids were tested. Chemical structures of styrene-butadiene and polybutadiene rubbers as well as AmimCl, EmimTc, MoimCl and TphsT ionic liquids are demonstrated in Fig. 8. They have found that for the styrene-butadiene/polybutadiene rubber blends that were used as the basic elastomer and < 3 wt.% MWCNT loading showed threefold increase of tensile strength with the addition of AmimCl. The composite could be stretched up to 456 % without mechanical failure at the low concentration of MWCNT. In addition, the electrical conductivity of the composite was increased with the incorporation of the ionic liquid. Furthermore, with the aid of AmimCl there are specific interactions between the MWCNT and rubber molecules as supported by Raman spectroscopy analysis. The good dispersion of MWCNT together with cellular-like structure of the CNT in the rubber matrix was also confirmed by TEM images.

On the other hand, the study used a 1-decyl-3-methylimidazolium tetrafluoroborate (DmimBF<sub>4</sub>) ionic liquid as a liquid coupling agent for preparation of the polypropylene (PP)/silica composites was reported by Donato et al. 2010 [32]. Chemical structures of PP and DmimBF<sub>4</sub> ionic liquid are showed in Fig. 9. The silica-ionic liquid xerogel hybrid obtained as free flowing aggregated spherical particles was prepared via sol-gel method. The extraction and calcination of silica-ionic liquid hybrid were done to prepare silica without ionic liquid. The composites

with ionic liquid and without ionic liquid have been prepared by melt blending isotactic PP with silica-ionic liquid hybrid and silica without ionic liquid, respectively. They have found that the improvement of silica dispersion in a polymer matrix and no compression of the silica particles are considerably caused by the presence of DmimBF<sub>4</sub> on the surface of silica-ionic liquid hybrid. Furthermore, the crystallization temperature of the composite with ionic liquid is significantly higher which indicated that the silica-ionic liquid hybrid filler acted as nucleating agent. In addition, with the presence of ionic liquid, the thermal decomposition resistance of the composites was enhanced as well.

Donato et al. 2011 [33] have used DmimBF<sub>4</sub>, 1-triethylene glycol monomethyl ether-3-methylimidazolium tetrafluoroborate (TemimBF<sub>4</sub>) and 1-triethylene glycol monomethyl ether-3-methylimidazolium methanesulfonate (TemimMs) ionic liquids for preparation of epoxy/silica nanocomposites via sol-gel process and epoxy networks development, simultaneously. Chemical structures of TemimBF<sub>4</sub> and TemimMs ionic liquids are indicated in Fig. 10. They have found that the silica structure and the interphase interaction between silica and epoxy matrix could be controlled and modified by using the different methylimidazolium-based ionic liquids. Therefore, hybrids with various morphologies and mechanical properties could be prepared and improved. Moreover, the hybrid formation and their final properties were influenced by both anionic and cationic components of ionic liquids. Whereas, both hydrolysis and condensation in sol-gel process as well as self-assembly ordering of ionic liquid were promoted by the use of DmimBF<sub>4</sub> together with HCl as acid catalyst. It has significantly increased the elastic modulus of the nanocomposites and provided hybrid morphology which very fine with good dispersion of silica nanodomain. In addition, they also explained that



**Fig. 10.** Chemical structures of (a) TemimBF<sub>4</sub> and (b) TemimMs ionic liquids.

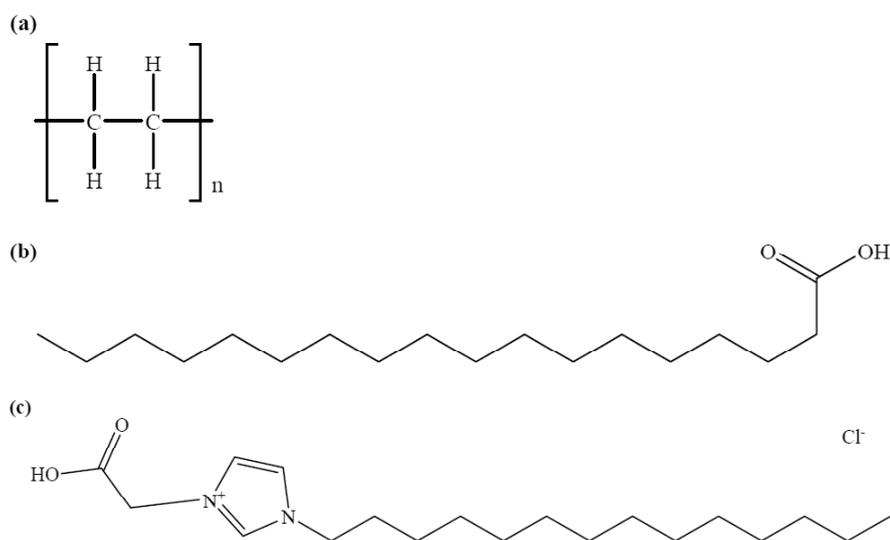
the non-polar interaction between C<sub>10</sub> long alkyl chains (decyl substitution) of DmimBF<sub>4</sub> cations resulted in an ordered structure. This has formed physical crosslinking which increased the final properties of nanocomposites.

## 7. IONIC LIQUIDS AS COMPATIBILIZER

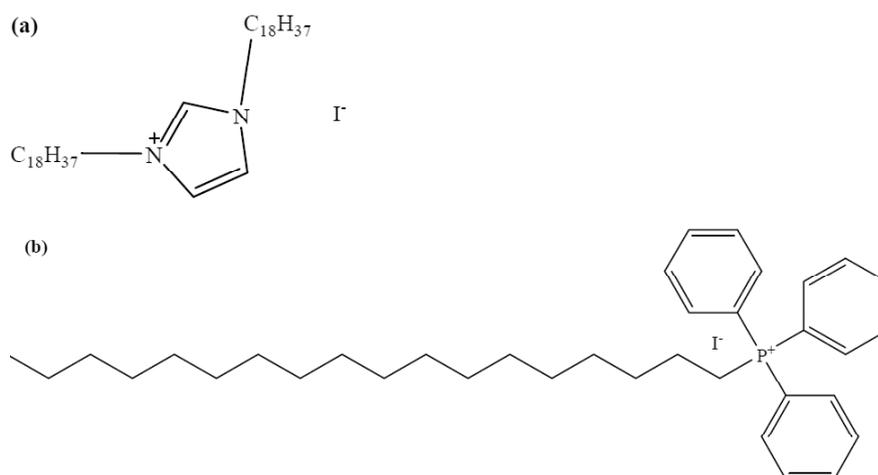
Generally, the low compatibility of fillers with polymers in the polymer composite systems is due to the different hydrophobicity between them. Recently, the ionic liquids have also been utilized in the systems for compatibilizing hydrophilic fillers with hydrophobic polymers. Ding et al. 2011 [34] have used 1-tetradecyl-3-carboxymethylimidazolium chloride (TcmimCl) ionic liquid to modify magnesium hydroxide (Mg(OH)<sub>2</sub>), and then TcmimCl-Mg(OH)<sub>2</sub> was incorporated into linear low density polyethylene (LLDPE) to obtain LLDPE/TcmimCl-Mg(OH)<sub>2</sub> composites through melt mixing. The LLDPE/Mg(OH)<sub>2</sub> composites and LLDPE/SA-Mg(OH)<sub>2</sub> composites (SA is stearic acid) have been prepared and their

properties were characterized in the same way for comparison purposes. Chemical structures of LLDPE, SA and TcmimCl ionic liquid are exhibited in Fig. 11. They have found that TcmimCl acted as efficient lubricant and compatibilizer for Mg(OH)<sub>2</sub> and LLDPE which caused large increase in processability and mechanical properties of LLDPE/TcmimCl-Mg(OH)<sub>2</sub> composites. This is due to the TcmimCl interacted with Mg(OH)<sub>2</sub> through chemical bonds. The composites have sufficiently high flame retardancy and showed very high char formation as well as effectively eliminated the melt drips.

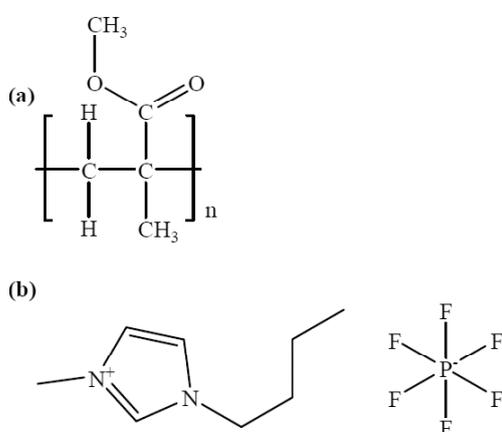
Livi et al. 2010 [35] have synthesized N-octadecyl-N-octadecylimidazolium iodide (OoimI) and octadecyltriphenylphosphonium iodide (OtpI) ionic liquids to be used as new surfactants for cationic substitution of layered silicates such as montmorillonite (MMT). Chemical structures of OoimI and OtpI ionic liquids are demonstrated in Fig. 12. MMTs modified with the synthesized imidazolium or phosphonium ions have possessed higher thermal decomposition compared with quaternary ammonium salts that commonly used for modification of MMT.



**Fig. 11.** Chemical structures of (a) LLDPE, (b) SA and (c) TcmimCl ionic liquid.



**Fig. 12.** Chemical structures of (a) Ooiml and (b) Otpl ionic liquids.



**Fig. 13.** Chemical structures of (a) PMMA and (b) BmimPF<sub>6</sub> ionic liquid.

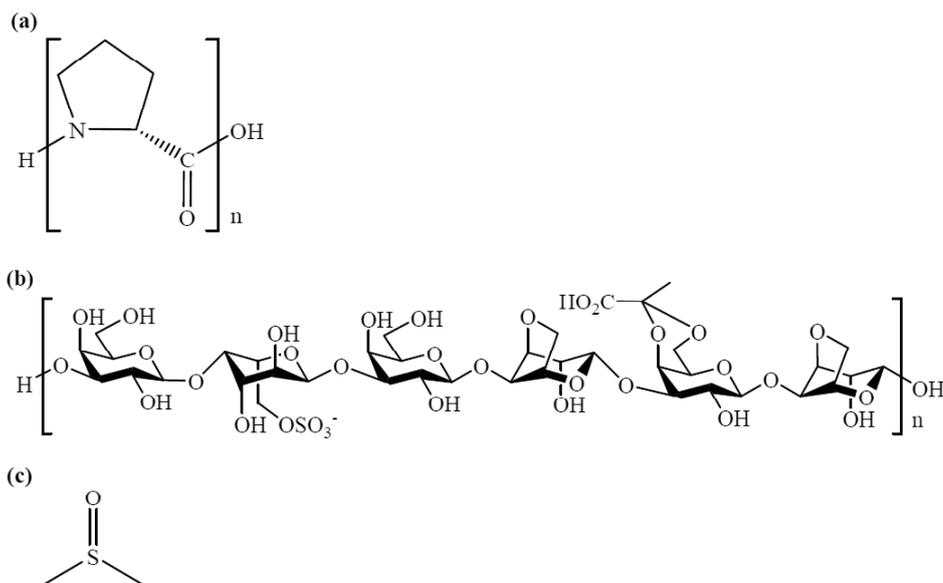
They have found that even after washing the modified clays, their thermal decomposition temperatures are still could be shifted toward higher temperatures. The modified MMTs were added into the polyolefin such as high density polyethylene (HDPE) via melt processing to prepare thermoplastic nanocomposites and also to prove the effect of the thermal resistance of the ionic liquids. From the analysis, they have discovered that with only 2 wt.% of thermal stable clays have slightly increased the thermal stability of nanocomposites. Furthermore, the strong increase of the modulus was achieved with both thermal stable clays without loss of fractured properties, this has caused the stiffness-toughness properties are much improved. Moreover, organic species physically adsorbed on the surface of unwashed thermal stable clays has acted like compatibilizer. It is helped dispersion into the HDPE matrix and improved the interface quality of clay/matrix, consequently provided better mechanical performance.

The study by Zhao et al. 2012 [36] have prepared poly(methyl methacrylate) (PMMA)/MWCNT

nanocomposites in the presence of 1-butyl-3-methylimidazolium hexafluorophosphate (BmimPF<sub>6</sub>) room-temperature ionic liquid. The nanocomposites were prepared through homogeneous dispersion of MWCNT by simple melt mixing method. Chemical structures of PMMA and BmimPF<sub>6</sub> ionic liquid are showed in Fig. 13. They have found that in preparation of the nanocomposites, the ionic liquid used in their study was able to act as multifunctional agents. Firstly, BmimPF<sub>6</sub> acted as an effective compatibilizer for substantially increasing the dispersion of MWCNT in PMMA matrix. Secondly, BmimPF<sub>6</sub> drastically induced reduction of the  $T_g$  value for the PMMA matrix as an efficient plasticizer. Thirdly, BmimPF<sub>6</sub> acted as a processing aid for melt processing PMMA/MWCNT nanocomposites. Fourthly, BmimPF<sub>6</sub> increased the electrical conductivity as a dopant for prepared nanocomposites.

## 8. IONIC LIQUID MIXTURES AS SOLVENT

Some of the ionic liquids that are typically used to dissolve biopolymers often have high viscosity properties. It is required higher temperature for reducing the viscosity of ionic liquids. Thus, co-solvent could be used to overcome this drawback. In our previous study [37], we have used the BmimCl ionic liquid and dimethyl sulfoxide (DMSO) co-solvent mixture (1:1 weight ratio) to dissolve a biopolymer (cellulose, rice starch or zein protein). The biopolymer solution was blended with the agar solution, followed by gelation at low temperature. The blends were soaked and shaken in distilled water, washed and freeze-dried to obtain blend aerogels. The agar/biopolymer contents were varied as 1:1, 1:1.5 and 1:2 weight ratios. Chemical structures of zein protein (polyproline) and agar biopolymers as well as



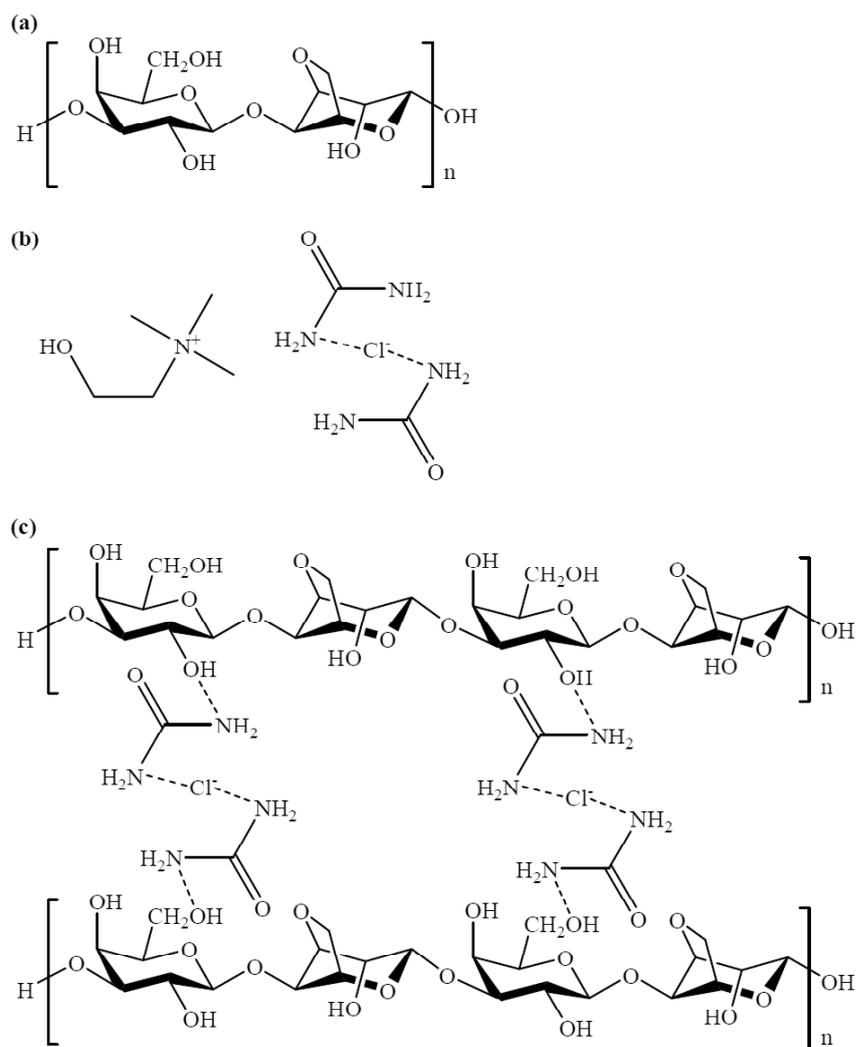
**Fig. 14.** Chemical structures of (a) zein protein and (b) agar biopolymers as well as (c) DMSO co-solvent.

DMSO co-solvent are displayed in Fig. 14. In this study, we have found that the lowest bulk density was obtained for agar/rice starch, at a 1:2 weight ratio. The depression in melting point temperature ( $T_m$ ) values of blend aerogels with the addition of biopolymers was indicated in DSC thermograms. On the other hand, the presence of functional groups of blend aerogels components was proved by FTIR spectra. Additionally, the existence of pores in internal surface of blend aerogels was indicated in SEM micrographs.

Lv et al. 2012 [38] have studied the rheological properties of cellulose which dissolved in two types of ionic liquids specifically AmimCl and BmimCl with DMSO co-solvent in the cellulose concentration range from 0.07 to 6.0 wt.%. In their study, the addition of DMSO in the concentration range from 0 to 100 wt.% has dramatically decreased the viscosity of ionic liquids. They have found that the friction coefficient of monomer in cellulose solution was reduced by DMSO co-solvent which resulted in reduction of solution viscosity. Additionally, the rheological properties are roughly independence on ionic liquids for cellulose/ionic liquids/DMSO solution. They also discovered that the ionic liquids/DMSO mixture is more like theta solvent for cellulose as shown by the dependence on the specific viscosity of cellulose concentration. The thermodynamic properties of the ionic liquids for cellulose at 25 °C are similar with the ionic liquids/DMSO mixtures. Moreover, either in the dilute or even concentrated state, the addition of DMSO has not changed the conformation of cellulose in ionic liquids.

## 9. IONIC LIQUID MIXTURES AS PLASTICIZER

The typical ionic liquids that were utilized for plasticizing polymers are too complicated to be prepared. Moreover, the cost of their precursors is too high and this would increase the total cost of plasticizers production for large applications. In our preceding research [39], we have used the ionic liquid mixture as plasticizer for agarose films. ChCl/Urea eutectic-based ionic liquid (also known as deep eutectic solvent) which was prepared from the mixture of choline chloride and urea through complexation at a 1:2 mole ratio has been added into the films from 30 to 70 wt.%. The films were prepared by dissolving ChCl/Urea in distilled water followed by dispersion of agarose at 95 °C. The solutions were gelled at room temperature, and the formed gels were dried in an oven for overnight at 70 °C. From mechanical testing results, we have found that the agarose film containing 60 wt.% ChCl/Urea had higher tensile extension and tensile strain at break compared to the pristine agarose film. The  $T_g$  values of agarose films were reduced with the addition of ChCl/Urea. The surface roughness of cross-section agarose films was disappeared with addition of ChCl/Urea as showed in SEM images. The presence of intermolecular hydrogen bonding between agarose and ChCl/Urea was confirmed by FTIR spectra. The amorphous phase was obtained when ChCl/Urea was added as validated by XRD patterns. We also found that the agarose films containing more ChCl/Urea have higher transparency as measured by UV-Vis spectrometer. Chemical structures of

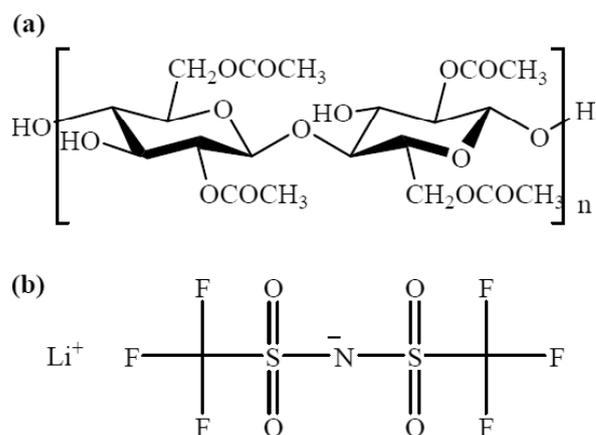


**Fig. 15.** Chemical structures of (a) agarose biopolymer, (b) ChCl/Urea mixture, and (c) interaction between agarose and ChCl/Urea.

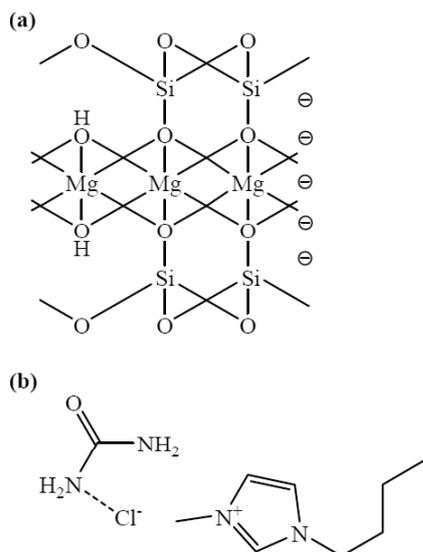
agarose biopolymer, ChCl/Urea mixture and interaction between agarose and ChCl/Urea are indicated in Fig. 15.

Very recently, Ramesh et al. 2013 [40] have prepared polymer electrolytes by using materials such as cellulose acetate (CA), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and ChCl/Urea via solution casting technique. Chemical structures of CA biopolymer and LiTFSI salt are exhibited in Fig. 16. They have found that when ChCl/Urea content enhanced, the CA:LiTFSI:ChCl/Urea was well plasticized and the ionic conductivity with the chemical integrity were also gradually increased. The CA:LiTFSI:ChCl/Urea sample at composition of 28 wt. %:12 wt. %:60 wt. % was identified has the highest conductivity and possessed the greatest ability to maintain the room-temperature ionic conductivity over the entire 30 days of storage time. Moreover, when different content of ChCl/Urea added into CA:LiTFSI, changes in FTIR peaks have

been clearly seen. This is due to the complexation which caused the collapse of the crystallinity of the CA matrix as observed from reduction of XRD dif-



**Fig. 16.** Chemical structures of (a) CA biopolymer and (b) LiTFSI salt.



**Fig. 17.** Chemical structure of (a) talc and (b) BmimCl/Urea mixture [41].

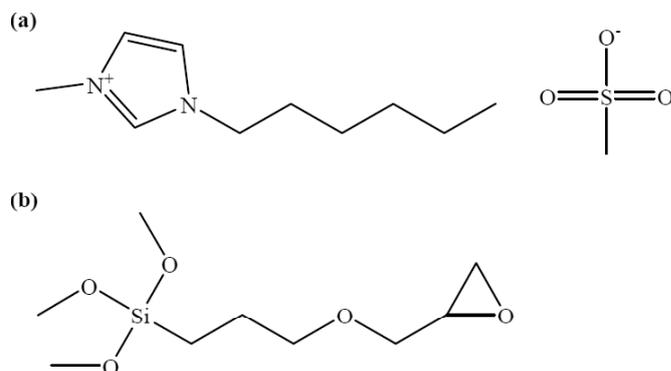
fraction peaks intensity. In comparison with pure CA, ChCl/Urea plasticized sample was found to be more heat stable. They also discovered that at the minimum addition of ChCl/Urea, the thermal stability of CA:LiTFSI was improved, nonetheless the heat resistance was reduced with more addition of ChCl/Urea.

## 10. IONIC LIQUID MIXTURES AS COUPLING AGENT

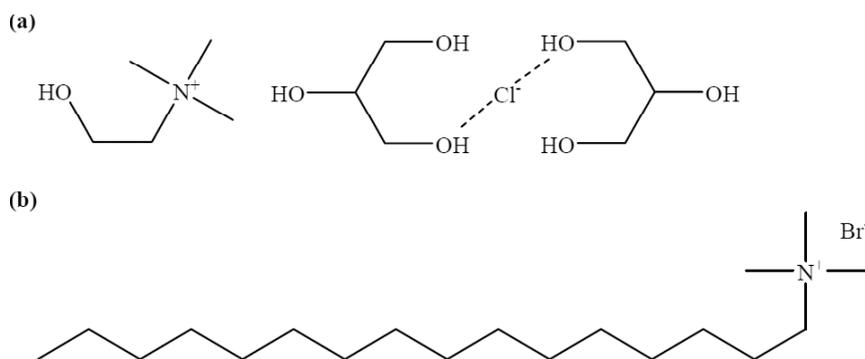
In recent times, the ionic liquids and chemical compounds mixtures were prepared to create balanced interaction between both polymers and fillers. This has increased the effectiveness of the ionic liquids to act as coupling agent for the polymer composites. In our prior study [41], the BmimCl/Urea mixture was created by blending BmimCl ionic liquid with urea chemical compound at 1:1 mole ratio. The gelation method was used to acquire the agarose/talc composite films containing the BmimCl/Urea

mixture. The content of BmimCl/Urea was varied from 0 to 10 wt.%, while the weight ratio of agarose and talc was fixed at 4:1 relative to the overall weight of the composite films. Chemical structures of talc and BmimCl/Urea mixture are demonstrated in Fig. 17. We have found that the optimum BmimCl/Urea content in the composite film was 8 wt.% based on the tensile stress and modulus results. SEM micrographs demonstrated that the talc particles were embedded in the agarose matrix and there were no pulled-outs for the composite films containing BmimCl/Urea. The  $T_g$  values of the composite films were increased with the addition of BmimCl/Urea. We also discovered that the existence of interaction between agarose and talc has improved their interfacial adhesion as validated by FTIR and FT-Raman spectra.

Donato et al. 2012 [42] have studied the effects of using ionic liquids and the mixtures of ionic liquid and coupling agent on the mechanical properties of epoxy diglycidyl ether bisphenol A (DGEBA)/silica nanocomposites. Ionic liquids such as TemimMs, 1-N-hexyl-3-methylimidazolium methanesulfonate (HmimMs) and DmimBF<sub>4</sub> together with HCl as acid catalyst and 3-glycidyloxypropyltrimethoxysilane (GTMS) coupling agent were used in their study. Chemical structures of HmimMs ionic liquid and GTMS coupling agent are showed in Fig. 18. They have found that the use of all three of the ionic liquids significantly caused stiffness in the DGEBA/silica nanocomposites system. More balanced tensile properties were achieved with the use of HmimMs ionic liquid which promoted the formation of nanocomposites with high modulus and tensile strength as well as high extensibility and toughness. Nevertheless, the nanocomposites with the best balanced tensile properties were prepared by using combination of ionic liquid and coupling agent. Nanocomposites with TemimMs and 20 to 30% of GTMS mixtures showed higher modulus, tensile



**Fig. 18.** Chemical structures of (a) HmimMs ionic liquid and (b) GTMS coupling agent.



**Fig. 19.** Chemical structures of (a) ChCl/Gly ionic liquid and (b) HTAB surfactant [43].

strength and energy to break as much as ~ 450% and ~ 500%, respectively compared with unmodified one-step DGEBA/silica nanocomposite. Such mixtures also provided an increase in toughness without losing substantial stiffness of the nanocomposites.

## 11. IONIC LIQUID MIXTURES AS COMPATIBILIZER

The compatibility of ionic liquids could also be further increased with the addition of other chemical compounds that have amphiphilic character. This has induced components of polymer composites to interact with each other for the best performance. In our latest research [43], choline chloride/glycerol (ChCl/Gly) eutectic-based ionic liquid was prepared at a 1:2 mole ratio. The ChCl/Gly was added with the different content of hexadecyltrimethylammonium bromide (HTAB) surfactant. Surfactant was used in the preparation of the ionic liquid mixture due to it has polar and non-polar parts (amphiphilic) [44]. Moreover, HTAB has been chosen since it could be acted as intermediary between polar (hydrophilic) and non-polar (hydrophobic) polymers [45,46]. The HDPE/agar biocomposites were introduced with ChCl/Gly-HTAB through melt mixing. Chemical structures of ChCl/Gly ionic liquid and HTAB surfactant are showed in Fig. 19. The impact strength and tensile extension of the biocomposites were increased with the introduction of the ChCl/Gly-HTAB mixture as indicated in the mechanical testing results. The significant decrease in the number of agar fillers pull-out,  $T_m$  and thermal decomposition temperature of the biocomposites are also due to the ChCl/Gly-HTAB as exhibited in SEM, DSC and TGA results. The biocomposites introduced with the ChCl/Gly-HTAB mixture demonstrated the presence of physical interactions which contributed to the increase of compatibility between both HDPE and agar as confirmed by FTIR spectra and XRD patterns.

## 12. SUMMARY

The applications of hydrophilic and hydrophobic ionic liquids as well as their mixtures predominantly between ionic liquids and chemical compounds in preparation of advanced polymer blends and composites have been reviewed. In the previous researches, we have found that ionic liquids and their mixtures could be effectively used as environmentally friendly solvent, plasticizer, coupling agent and compatibilizer. The properties of polymer blends and composites that consisted of natural and synthetic polymers could be improved with the use of these materials. In addition, polymer blends and composites in the form of aerogels, films, composite films and biocomposites could also be prepared by using the mixture of ionic liquids and chemical compounds as exhibited in our previous and other studies.

## 13. RECOMMENDATIONS FOR FUTURE RESEARCH

Preparation and characterization of only one type of ionic liquid and chemical compound mixture which be able to act as solvent, plasticizer, coupling agent and compatibilizer in preparation of advanced polymers blends and composites can be conducted for future research. The ionic liquid and chemical compound mixture can be composed of either hydrophilic or hydrophobic ionic liquid with the liquid or solid chemical compound which is neutral or charged in nature. This is important to find the ionic liquid mixture which very versatile and possesses many functions for preparation of advanced materials and polymeric products. On the other hand, the function of the mixture can also be changed whether as solvent, plasticizer, coupling agent or compatibilizer according to the percentage of its content. Finally, the related things that should be considered when choosing the ionic liquid and chemical compound

for creating the mixtures are cost, ability, availability, stability, miscibility, toxicity, et cetera.

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