FABRICATION OF AGAR/BIOPOLYMER BLEND AEROGELS IN IONIC LIQUID AND CO-SOLVENT MIXTURE

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In the present study, a biopolymer (cellulose, rice starch or zein protein) was dissolved in the ionic liquid (1-butyl-3-methylimidazolium chloride) and co-solvent (dimethyl sulfoxide) mixture (1:1 weight ratio), and then blended with the agar solution, followed by gelation at low temperature. The blends were soaked and shaken in 250 mL distilled water, washed and freeze-dried. The agar/biopolymer contents were varied as 1:1, 1:1.5 and 1:2 weight ratios. The bulk densities, melting point temperatures (T_m), FTIR spectra, surface morphologies, surface areas and pore size diameters of the blend aerogels were determined and characterized. The lowest bulk density (25.69 mg cm^{-3}) was obtained for agar/rice starch, at a 1:2 weight ratio. DSC thermograms indicated depression in T_m with the addition of biopolymers. FTIR spectra showed the presence of functional groups of blend aerogels components. SEM micrographs of blend aerogels indicated the presence of pores in their internal surface. The BET surface areas and pore size diameters of the blend aerogels (1:2 weight ratio) ranged from 371 to 478 m^2 g^{-1} and from 34 to 63 nm, respectively. This study led to the conclusion that the mixture of 1-butyl-3-methylimidazolium chloride and dimethyl sulfoxide could be used as a blend medium for the fabrication of agar/biopolymer blend aerogels.

Keywords: agar, biopolymer, blend aerogel, ionic liquid, co-solvent

INTRODUCTION

Aerogels are porous solids with the lowest bulk density, air being one of their major components. Aerogels have been used in sensors (ultrasonic and gas), thermal insulation (cryogenic to high temperatures), waste management (gas absorption, radioactive waste confinement), optics and light-guides, electronic devices, capacitors, energy storage, high-explosives research, various dry processes (including particle separation), imaging devices, catalysts, X-ray laser research, high-impact strength materials, etc.[1-3] Most aerogels are made of silica, carbon and alumina,[4] however biopolymer-based aerogels have attracted the researchers' interest, as the biopolymers are abundant, natural, non-toxic, biodegradable, biocompatible, renewable and low-cost materials. Previous studies have shown that cellulose is most frequently used in the fabrication of aerogels,[5-10] followed by chitin[11] and chitosan derivatives.[12]

Ionic liquids have low melting point temperature (commonly <100 °C), extremely low vapour pressure (being non-volatile), high stability, high polarity, high thermal stability, good solubility of organic and inorganic materials, being miscible with certain organic solvents and/or water and able to dissolve and process a number of biopolymers without derivatization.[13] They are also non-inflammable, chemically inert, recyclable and can be customized.[14] These outstanding solvent properties make ionic liquids suitable for being used as a medium for the fabrication of aerogels from biopolymers.[15] Nevertheless, the ionic

liquids (*e.g*. 1-butyl-3-methylimidazolium chloride, 1-ethyl-3-methylimidazolium acetate, 1-butyl-3-methylimidazolium thiocyanate, 1-allyl-3-methylimidazolium chloride, etc.) usually used to dissolve biopolymers are highly viscous, scarce and expensive.[16]

In this study, ionic liquid (1-butyl-3-methylimidazolium chloride) was used together with a co-solvent (dimethyl sulfoxide) for the fabrication of blend aerogels. A co-solvent was added to the ionic liquid to decrease viscosity, dissolution temperature and to reduce the dependence on the ionic liquid (ionic liquid-to-biopolymer weight ratio). This approach is absolutely inexpensive and less time-consuming than the development of new precursors or new synthesis methods for creating new types of ionic liquids.[17,18] Dimethyl sulfoxide was selected as a co-solvent since this liquid has a high boiling point (189 °C), low toxicity, low cost, being weakly acidic and relatively mild as an oxidizer.[19] In addition, the most important feature of dimethyl sulfoxide is its miscibility in a wide range of organic solvents, including ionic liquids, as well as water.

The use of agar as a blend component of aerogels has been regarded as interesting and important, since it can act as a gelling agent, therefore no cross-linking agent is required to build networks for gel formation. Several common biopolymers, *e.g.* cellulose, rice starch and zein protein were used in different weight ratios to fabricate blend aerogels. The influence of biopolymers content and type on the bulk density of blend aerogels was investigated. The thermal, chemical and morphological properties, as well as the surface area and pore size diameter of agar/biopolymer blend aerogels were also characterized and studied.

MATERIALS AND METHOD

Materials

Cellulose microcrystalline powder, 20 μm, with the bulk density of 500 mg cm^{-3} (product number 310697) was purchased from Sigma Aldrich. Rice starch (product number S7260) and zein protein from maize (product number Z3625) were purchased from Sigma Aldrich. 1-Butyl-3-methylimidazolium chloride, ≥95% (product number 38899) and dimethyl sulfoxide, 99.8% (product number 494429) were also acquired from Sigma Aldrich. Agar granules, with the bulk density of 550 mg cm^{-3}, (product number 101614) were bought from Merck. All chemicals were used as received, without further activation treatments.

Fabrication of agar/biopolymer blend aerogels

0.3 g of biopolymer (cellulose, rice starch or zein protein) was dissolved in 10 g of 1-butyl-3-methylimidazolium chloride and dimethyl sulfoxide mixture (1:1 weight ratio) at 95 °C, with stirring. The 0.3 g of agar was dispersed and stirred in 10 g of distilled water, at 95 °C. The biopolymer solution was blended with the agar solution and kept under stirring at constant temperature (95 °C), until a homogenous solution was obtained. Then, the solution was cast in a Teflon mould and allowed to cool to 4 °C in the freezer for gelation. The gels were removed from the mould and soaked in 250 mL of distilled water, then shaken at room temperature (25 °C), overnight, in an incubator shaker (150 rpm), then washed with distilled water and dried in a Christ freeze dryer for 48 h, at a temperature of -52 °C, and chamber pressure of 10^{-3} mbar. The temperature of the final samples was of 25 °C. The weight of agar was fixed at 0.3 g, whereas the contents of biopolymers were varied – 0.3 g, 0.45 g and 0.6 g –, which led to weight ratios of the blend aerogels of 1:1, 1:1.5 and 1:2. For the sake of comparison, the aerogel containing only agar has also been fabricated by the above procedures. All fabrications were carried out in quintuplicate.

Characterization

The volume and mass of agar and blend aerogels were determined by simply measuring and weighing the samples. The bulk density of each aerogel sample was calculated by dividing the mass by the volume of the sample. The data were taken from an average of 15 samples, for each weight ratio. The melting point temperature (T_m) was measured with a differential scanning calorimetry (DSC) apparatus (Mettler Toledo DSC822^e), using STAR analysis software, under a constant stream of nitrogen, at a flow rate of 50 mL min^{-1}. The samples were tightly sealed in aluminium pans and first heated at 100 °C, to eliminate the thermal history. The analysis was carried out over a temperature range of 25 to 250 ºC, at a heating rate of 10 ºC min^{-1}, to obtain the T_m value determined from the thermogram during the programmed reheating steps. Fourier transform infrared (FTIR) characterization was carried out with a Perkin Elmer Spectrum 100 Series FTIR spectroscopy, to determine the presence of functional groups in the agar/biopolymer blend aerogels and also to investigate the interaction between them. The FTIR spectra were recorded using a universal attenuated total reflectance accessory (UATR). Each sample was scanned for 16 times, in the wavenumber range of 4000-280 cm^{-1} and resolution of 4 cm^{-1}. All spectra were rationed against the reference spectrum of the background. The surface morphology of the samples was examined on a scanning electron microscope (SEM), LEO model 1455 VPSEM. The samples for SEM micrographs were fractured by making a cut with a knife and breaking at room temperature, followed by sputter-

coating with gold. The surface areas of agar/biopolymer blend aerogels cross-sections were determined by the Brunauer–Emmett–Teller (BET) method, from their nitrogen adsorption and desorption isotherms, measured with a Quantachrome Autosorb-1 instrument at -195.7 ºC, after vacuum pre-treatment of the samples for 9 h (outgassing the samples at 100 ºC under vacuum until a stable $5x10^{-2}$ Torr pressure was obtained without pumping). The pore size diameters of the agar/biopolymer blend aerogels were determined from the desorption of isotherms by the BJH method.

RESULTS AND DISCUSSION

Bulk density

Table 1 lists the bulk densities of agar and agar/biopolymer blend aerogels at room temperature (25 ºC). The bulk density of the blend aerogels containing agar and biopolymer in a 1:1 weight ratio indicated no significant difference with the bulk density of agar aerogel, except for the agar/rice starch blend aerogel, which has lower bulk density (37.91 mg cm^{-3}). Table 1 also shows that, at a 1:1.5 weight ratio, all blend aerogels demonstrated low bulk density compared to the values for the 1:1 weight ratio. A similar trend was also observed for blend aerogels at a 1:2 weight ratio, with lower bulk density than at a 1:1.5 weight ratio, therefore as the biopolymers content increases, the bulk density of blend aerogels decreases. The various weight ratios of the agar/biopolymer have been tested in the initial experiments – only the 1:1, 1:1.5 and 1:2 weight ratios were considered suitable for the fabrication of blend aerogels. The maximum content of biopolymers added to blend aerogels is indicated at a 1:2 weight ratio. If the biopolymers contents are higher than this ratio, the gels will become fragile, difficult to handle and will normally break when soaked and shaken in distilled water overnight. This generally occurs when the biopolymer content exceeds the limit for the agar, which causes the decrease of gels strength.

Even if the duration of soaking and shaking is shortened, to prevent gel breakage, amounts of liquid mixture are still left in the gel network, so that the samples are not completely dried out in the final stage of freeze-drying, because of the low vapour pressure of the ionic liquid. Therefore, the samples should be soaked and shaken overnight in an incubator shaker. These procedures are extremely important for the removal of the ionic liquid and co-solvent mixture, allowing the entrapment of distilled water inside the gel network prior to freeze-drying.

Table 1
Bulk densities of agar and agar/biopolymer blend aerogels at room temperature (25 ºC) with different weight ratios

Sample	Weight ratio	Bulk density (mg cm^{-3})	Standard deviation
Agar	1:0	42.57	0.91
Agar/cellulose	1:1	41.55	2.04
Agar/cellulose	1:1.5	34.22	1.42
Agar/cellulose	1:2	33.15	2.33
Agar/rice starch	1:1	37.91	1.55
Agar/rice starch	1:1.5	29.66	1.38
Agar/rice starch	1:2	25.69	1.68
Agar/zein protein	1:1	40.66	2.17
Agar/zein protein	1:1.5	33.09	2.58
Agar/zein protein	1:2	32.52	1.79

The analysis of bulk density results led to an unexpected observation: the agar/rice starch blend aerogel recorded the lowest bulk density (25.69 mg cm^{-3}) at a 1:2 weight ratio, followed by agar/zein protein and agar/cellulose, with bulk densities of 32.52 and 33.15 mg cm^{-3}, respectively. Thus, the low bulk density of agar/biopolymer blend aerogels depends not only on the biopolymer content, but also on the type of biopolymers used for the fabrication of blend aerogels. This may be related to the relatively different density of biopolymers and agar. The agar aerogel shows the highest bulk density (42.57 mg cm^{-3}), since pristine agar is denser than the biopolymers used.

DSC characterization

DSC is the most common instrument to ascertain polymer blend miscibility through glass transition temperature (T_g) or the melting point temperature (T_m). Figure 1 shows the thermograms of agar and agar/biopolymer blend aerogels with a 1:2 weight ratio, as determined by DSC. The T_m obtained from DSC thermograms represents the crystalline melting point temperature of the samples (listed in Table 2). The T_m of the agar aerogel observed at 131.82 °C, a high value compared to the T_m value reported in literature,[20] is probably due to the effect of the high molecular weight of agar.[21] The T_m of biopolymers could not be measured as they decompose at elevated temperatures. Table 2 shows that the T_m of the agar/biopolymer blend aerogels is different from that of the agar aerogel, in other words, the T_m value of the blend aerogels is significantly lower than the T_m of agar aerogel. This result shows that the T_m of the agar/biopolymer blend aerogels decreases with the addition of biopolymers. The miscible binary polymer blends frequently exhibit[22] a depression in T_m, or a single transition between the T_g values of the two components.[23] All blend aerogels exhibited a depression in T_m, therefore miscible blends were obtained.

The T_m of a miscible polymer blend is usually lower than that of the pristine polymer, because of some thermodynamic factors (polymer-polymer interactions).[22] The functional group of agar and biopolymers is the major reason for their mixing through intermolecular interaction. Besides, the tendency to interact with each other is good, since both the agar and the biopolymers were blended in solvent medium, where the polymer chains were more extended, which also contributed to their miscibility.

Table 2
Melting point temperatures (T_m) of agar and agar/biopolymer blend aerogels (1:2 weight ratio) as determined from DSC data

Sample	T_m (ºC)
Agar	131.82
Agar/rice starch	112.55
Agar/zein protein	98.42
Agar/cellulose	95.63

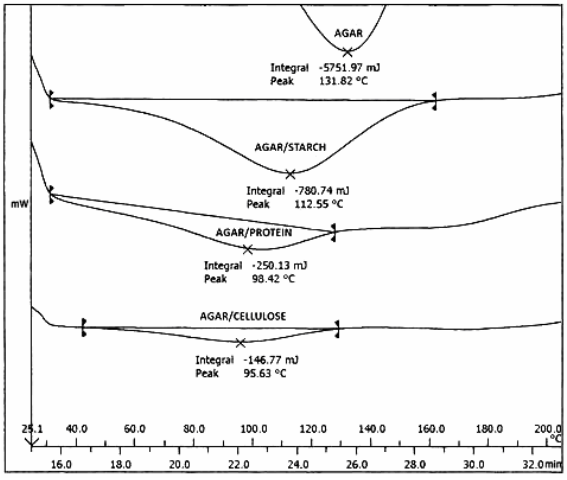

Figure 1: Thermograms of agar and agar/biopolymer blend aerogels (1:2 weight ratio) obtained from DSC

On the other hand, the high T_m value of the agar/rice starch blend aerogel displayed a strong intermolecular interaction between agar and starch, compared to the other blend aerogels. Conversely, the T_m value of the agar/cellulose blend aerogel was lower than those of the agar/zein protein and agar/rice starch blend aerogels, which could be attributed to the weak

intermolecular interaction between the agar and the cellulose chains, thereby less energy was required to break their interaction upon melting. The intermolecular interaction between agar and biopolymers was further determined by FTIR spectroscopy.

FTIR characterization

Figure 2 shows the FTIR spectra of agar, cellulose, rice starch, zein protein and blend aerogels with a 1:2 weight ratio, the bands of the FTIR spectra being given in Table 3. The functional groups were determined on the basis of specific bands and molecular motions. Despite the fact that the spectra contain numerous bands, not all of them can be attributed explicitly to the structural groups of the samples, the 4000-3500 cm^{-1} region providing no useful information on the samples and being, therefore, not considered for further analysis. As shown in Figure 2, the FTIR spectra of all samples (except zein protein) exhibit strong intensity broad bands at 3349-3293 cm^{-1}, which could be assigned to the O–H stretching of the alcohol group. Nevertheless, the bands at 3289-3285 cm^{-1}, associated with the N–H stretching of the amine group, belong to the pristine zein protein and to its blend aerogel. Noticeably strong intensity bands at 2928-2897 cm^{-1}, responsible for the C–H stretching of the alkane group, are observed in every sample. The strong intensity bands at 1644-1638 cm^{-1}, attributed to the absorbed water, indicate the presence of tightly bound water in all samples. The strong intensity bands at 1531-1524 cm^{-1} reveal the N–H bending of the amine group, present only in the pristine zein protein and in its blend aerogel. CH_3 bending of the alkane group results from the medium intensity bands at 1371-1368 cm^{-1}, present only in pristine agar and in the agar/biopolymer blend aerogels. The bands caused by the C–O stretching of the ether group indicated at 1159-1148 cm^{-1}, with strong intensity, were found in every sample, with the exception of pristine zein protein, since this group is a common linkage in agar, cellulose and starch. The bands at 1056-1000 cm^{-1} correspond to the C–O stretching of the alcohol group and have been remarked in all samples (except zein protein). The FTIR spectra showed the presence of functional groups of blend components in all blend aerogels, which demonstrates that no significant changes occurred in the chemical structure of agar and biopolymers in the blend aerogels, after being processed with the ionic liquid and co-solvent mixture.

However, the bands of blend aerogels are slightly different from their individual components because, when agar is blended with different types of biopolymers, changes in bands take place, which is an evidence of intermolecular interaction. The bands of the O–H stretching of the alcohol group for agar/cellulose and agar/rice starch shifted to lower wavenumbers, compared to the bands of O–H stretching for agar. A similar behaviour was remarked for the bands of both N–H stretching of the amine group for agar/zein protein and C–O stretching of the alcohol group for agar/rice starch. This is due to the increased formation of intermolecular hydrogen bonding between the hydroxyl groups of agar with the hydroxyl or amine groups from the biopolymers. Therefore, these observations indicate the existence of intermolecular interactions between agar and biopolymers, which causes the miscibility of blend aerogels. This result also explains the decrease in the T_m of blend aerogels, as indicated by DSC results.

Table 3
FTIR bands of agar, cellulose, rice starch, zein protein and agar/biopolymer blend aerogels (1:2 weight ratio)

Wavenumber (cm^{-1})	Molecular motion	Functional group
3349-3293	O–H stretching	Alcohol
3289-3285	N–H stretching	Amine
2928-2897	C–H stretching	Alkane
1531-1524	N–H bending	Amine
1371-1368	CH_3 bending	Alkane
1159-1148	C–O stretching	Ether
1056-1000	C–O stretching	Alcohol

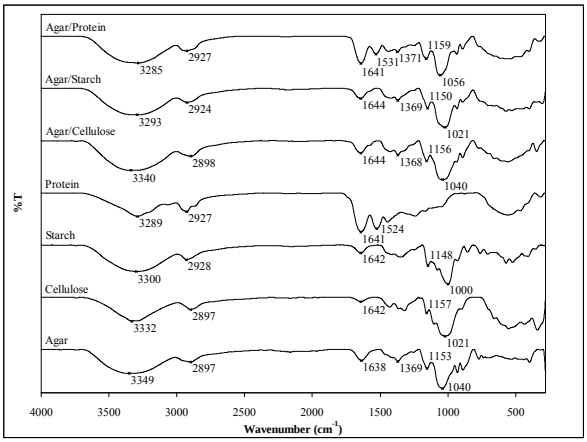

Figure 2: FTIR spectra of agar, cellulose, rice starch, zein protein and agar/biopolymer blend aerogels (1:2 weight ratio)

Moreover, the small shift in the wavenumbers of the O–H stretching of the alcohol group in the agar/cellulose blend aerogel, compared to the agar/rice starch and agar/zein protein blend aerogels, describes the low T_m of this blend aerogel, while the large shift in the wavenumbers of both O–H and C–O stretching of the alcohol group in the agar/rice starch blend aerogel, compared to the agar/zein protein blend aerogel, explains the high T_m of this blend aerogel.

Morphological analysis

Surface morphologies were observed by using scanning electron microscope (SEM) with accelerating voltages of 20.0 kV, at 160× magnification. Figures 3 to 6 show SEM micrographs of the fracture surface (inner section) of the samples of agar and agar/biopolymer blend aerogels (1:2 weight ratio). The SEM micrographs of the agar/biopolymer blend aerogels indicate that the boundary between the agar and biopolymer phase cannot be clearly seen, and no phase separations are observed. This observation suggests a fine phase morphology and homogeneous blends were obtained. In the miscible phase area, only one phase can be observed,[23] which implies that the blends have good miscibility. This is most likely caused by the intermolecular hydrogen bonding, as previously mentioned in the FTIR results, which also explains the absence of phase separation in the SEM micrographs. Additionally, the formation of such a tear surface (Fig. 5) towards the fracture force indicates that there are strong interactions[23] between the agar and starch phases.

SEM micrographs (Fig. 3) indicate that agar has the largest pore size, while Figures 4 and 6 for agar/cellulose and agar/zein protein blend aerogels, respectively, show smaller pore sizes, compared to those of agar. Furthermore, an obvious morphological difference was observed for the agar/rice starch blend aerogel (Fig. 5), which has the smallest pore size. Generally, when the size of the pores is small, the lateral surface is large and bulk density is high, because of the increased amount of matter. Although the bulk density of the agar/biopolymer blend aerogels showed the opposite trend, the size of the pores could not be directly related to the bulk density results. This is because the agar used in the fabrication of aerogel has a high density, compared to biopolymers. BET analyses were performed to confirm the differences between aerogels by measuring surface area and pore size diameter.

BET characterization

The results of the surface area and pore size diameter are plotted in Figure 7. The BET surface areas of the agar/cellulose and agar/zein protein blend aerogels were 371 m^2g^{-1} and 451 m^2g^{-1}, respectively. The agar/rice starch blend aerogel had the highest surface area, of 478 m^2g^{-1}, while the agar aerogel had only 162 m^2g^{-1}. On the contrary, the pore size diameter of agar and of the agar/biopolymer blend aerogels showed an opposite pattern. The pore size diameter of agar aerogel was of 100 nm, significantly higher than that of the agar/biopolymer blend aerogels. The agar/cellulose and agar/zein protein blend aerogels showed pore size diameters of 63 and 43 nm, respectively. The lowest pore size diameter, of 34 nm, was obtained for the agar/rice starch blend aerogel. This shows that the pore size diameter for blend aerogels depends on the

biopolymer type, and decreases linearly with increasing the surface area. Hence, the addition of biopolymers to agar does not only provide a high surface area, but also causes a decrease in pore size diameter. The differences between them are entirely correlated with the observations obtained from surface morphology results, although the nanometer-ranged pore sizes of the blend aerogels could not be fully observed by SEM.

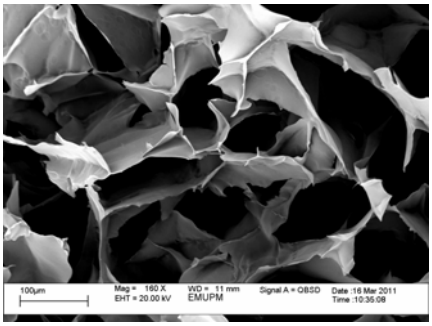

Figure 3: SEM micrograph of agar fracture surface (magnification: 160×)

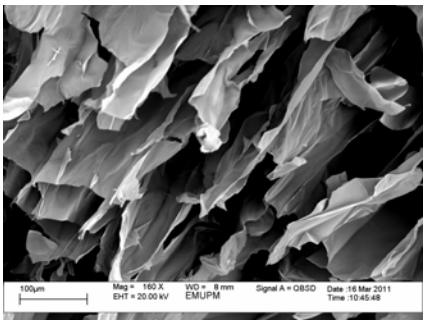

Figure 4: SEM micrograph of agar/cellulose blend aerogel fracture surface (1:2 weight ratio; magnification: 160×)

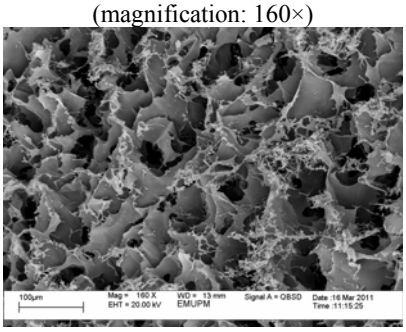

Figure 5: SEM micrograph of agar/rice starch blend aerogel fracture surface (1:2 weight ratio; magnification: 160×)

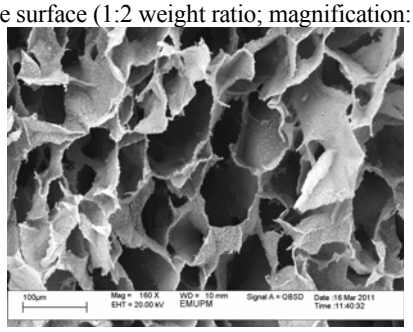

Figure 6: SEM micrograph of agar/zein protein blend aerogel fracture surface (1:2 weight ratio; magnification: 160×)

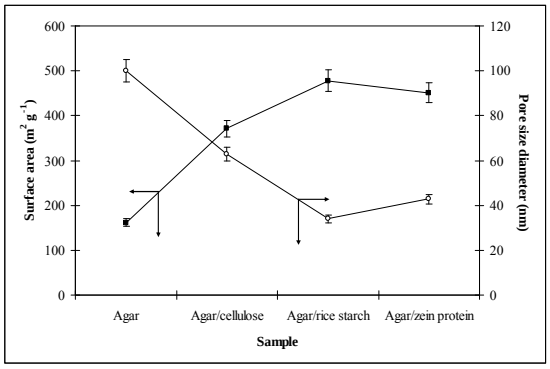

Figure 7: Surface areas and pore size diameters of agar and agar/biopolymer blend aerogels (1:2 weight ratio)

CONCLUSIONS

This study shows that the agar/cellulose, agar/rice starch and agar/zein protein blend aerogels can be fabricated by using the mixture of ionic liquid (1-butyl-3-methylimidazolium chloride) and co-solvent (dimethyl sulfoxide), where the mixture acts as a blend medium. The content and type of biopolymers necessarily play a significant role in influencing the bulk density of blend aerogels. DSC thermograms show that miscible blend aerogels were obtained, while FTIR spectra prove the presence of intermolecular hydrogen bonding among the components of the blend aerogels. SEM micrographs of blend aerogels indicate the absence of phase separation. The BET surface areas and pore size diameters of the blend aerogels have been correlated with their surface morphology results.

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