Carbohydrate Polymers 91 (2013) 477–482

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

A comparative study on the chitosan membranes prepared from glycine hydrochloride and acetic acid

Bomou Ma, Xiang Li, Aiwen Qin, Chunju He*

State Key Lab for Modification of Chemical Fibers and Polymer Materials, College of Material Science & Engineering, Donghua University, Shanghai 201620, PR China

ARTICLE INFO

Article history:
Received 12 June 2012
Received in revised form 29 July 2012
Accepted 30 July 2012
Available online 4 August 2012

Keywords:
Chitosan membranes
Gly·HCl
Acetic acid
Solvent

ABSTRACT

In this study, glycine hydrochloride (Gly·HCl) is confirmed to be a promising solvent for dissolving native chitosan and preparing regenerated chitosan membrane. As compared with the chitosan membrane prepared from traditional acetic acid, the membrane prepared from Gly·HCl by dry technique shows excellent tensile strength and initial modulus, i.e. 103.8 MPa and 3.2 GPa, respectively, which is superior to any chitosan membrane and most chitosan blend membranes reported in literatures. Besides, scanning electron microscopy (SEM), wide-angle X-ray diffraction (WAXD) and Fourier transform infrared spectroscopy (FT-IR) were used to visualize the difference between the two kind of regenerated chitosan membranes. The SEM results show that the membrane prepared from Gly·HCl by dry technique presents a novel structure, which ensures its high tenacity. Furthermore, the chitosan microporous membranes were also prepared using PEG as porogen.

1. Introduction

Chitosan is the partially deacetylated polysaccharide of chitin which is the second most abundant natural polymer in the world, and is widely existed in many crustaceans and insects (Pillai, Paul, & Sharma, 2009; Rinaudo, 2006). Chitosan holds many unique properties, i.e. biodegradability, biocompatibility, wound-healing acceleration, etc., and the products made from chitosan can be used in crop protection, food preservation, waste-water treatment, cosmetics, wound dressings, tissue engineering and so on (Di, Sittinger, & Risbud, 2005; Ko, Sfeir, & Kumta, 2010; Muzzarelli et al., 2012; No, Meyers, Prinyawiwatkul, & Xu, 2007; Tchemtchoua, Atanasova, Aqil, Filee, & Colige, 2011). Therefore, many researchers have committed to the field, and some companies have transferred their business to this industry as well. However, the strong hydrogen bonds and semi-crystalline structure of chitosan make it difficult to be dissolved in general solvents. Up to now, only acetic acid is the most commonly used solvent. Furthermore, the poor mechanical and processing properties of pure chitosan products limit its further application. In recent years, much work had been carried out to improve the mechanical property of chitosan matrix.

In the literatures, the blend films of chitosan and hydroxypropyl guar gum were prepared by a conventional solution casting technique (Xiao, Zhang, Zhang, & Zhang, 2003). The results show that the tensile strength of the dry films increases from 43.0 MPa to 58.9 MPa, and the thermal property has been improved properly. The tensile strength of the dry films of chitosan and konjac glucomannan blend even reaches 73.0 MPa (Xiao, Gao, Wang, & Zhang, 2000). Some other blend films were also prepared, i.e. chitosan/cellulose (Shih, Shieh, & Twu, 2009), chitosan/polyvinyl alcohol (PVA) (Costa, Barbosa, Mansur, Vasconcelos, & Mansur, 2009), chitosan/alginate (Zhang, Guo, Zhou, Yang, & Du, 2000), etc. In addition, Fan et al. (2012) used unzipped multiwalled carbon nanotube oxides (UMCNOs) as nanofillers for the reinforcement of chitosan matrix. The prepared UMCNOs/chitosan nanocomposite films present excellent mechanical properties, i.e. tensile strength 142.7 MPa and Young's modulus 6.9 GPa, respectively. Liu, Wu, Chang, and Gao (2011) novelly combined the wet-grinding and high-pressure homogenization to defibrillate chitosan particles into nanoscaled fibrils, and the obtained nanofiber was fabricated to liquid crystal film by self-organization. The liquid crystal film presents a high tensile strength of 100.5 MPa and Young's modulus of 2.2 GPa, respectively. All these studies referred are based on the acetic acid solvent system.

Besides, researchers have been committing to develop new solvents for chitosan. Recently, ionic liquids (ILs), a kind of molten salts, hold many special properties, i.e. thermal stability, negligible vapor pressure, potential for recycling, etc. (Pinkert, Marsh, Pang, & Staiger, 2009; Rogers & Seddon, 2003), present good solubility for polysaccharide (Muzzarelli, 2011; Zakrzewska, Bogel, & Bogel, 2010). Xie, Zhang, and Li (2006) reported that chitosan could be dissolved in 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) to form a semi-clear and viscous solution, which could be used as reversible sorbents for CO_2. Zhu, Han, Cheng, and Wu (2011)

---

* Corresponding author. Tel.: +86 021 6779 2842; fax: +86 021 6779 2855.
E-mail address: chunjuhe@dhu.edu.cn (C. He).

0144-8617/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2012.07.081

Table 1
The signatures of all the chitosan samples ID and "√" refers to the processing technique is chosen.

Sample ID	S_G-1	S_G-2	S_A-3	S_A-4	S_G-5	S_A-6
Wet technique	√	–	√	–	–	–
Dry technique	–	√	–	√	√	√
Solvent	Gly·HCl	Gly·HCl	Acetic acid	Acetic acid	Gly·HCl	Acetic acid

studied the dissolubility of chitosan in four kinds of imidazole-based ILs, i.e. [Bmim]Cl, 1-butyl-3-methylimidazolium acetate ([Bmim]Ac), 1-allyl-3-methylimidazolium chloride ([Amim]Cl) and 1-ethyl-3-methylimidazolium acetate ([Emim]Ac). The results show that the four kinds of ILs can dissolve chitosan, and up to 15.5 wt.% chitosan/[Emim]Ac solution can be prepared at 110 °C. In particular, Li, Yuan, Liu, Yu, and Liang (2012) reported that Gly·HCl was a good solvent for chitosan with different deacetylation degree and molecular weight, and the prepared chitosan solution presented lower viscosity, but the information from this report was very limited.

Do the regenerated chitosan membranes prepared from Gly·HCl present any other special properties than those from acetic acid? Will Gly·HCl be a potential solvent and open a new window for processing chitosan? As a further research, this paper focuses on the structure and properties comparison of chitosan membranes prepared from Gly·HCl and acetic acid, respectively. The SEM results show that the chitosan membrane prepared from Gly·HCl by dry technique presents a novel structure, which presents superior strength than any chitosan membranes and most chitosan blend membranes reported previously. Furthermore, the effect of processing technique and additive on the structure and performance of the membranes are discussed as well.

2. Experimental

2.1. Materials

Chitosan ($\eta = 1000$cp, deacetylation degree > 90%) was purchased from Introduction of Jinhu Crust Product Co. Ltd. (Qingdao, China), and was dried at 105 °C until constant weight before use. Glycine, hydrochloric acid (HCl, 36–38 wt.%), acetic acid, Polyethylene glycol (PEG, Mn = 20,000) and other reagents were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China), and used as received.

2.2. Synthesis of glycine hydrochloride

Glycine hydrochloride (Gly·HCl) was synthesized according to reference (Kou, Tao, He, & Sun, 2005). As follows, 37.5 g glycine and 60.9 g HCl aqueous solution (36–38 wt.%) were added to a round-bottomed flask fitted with magnetic stirring, until glycine was fully dissolved. The mixture was kept at 60 °C for 6 h, and cooled to room temperature. Water was removed through vacuum distillation, the residue was washed with ethyl acetate three times, and kept in vacuum for 24 h, a white crystalline of Gly·HCl was obtained.

2.3. Preparation of chitosan membranes

2 wt.% chitosan solutions were prepared from 2 wt.% acetic acid and 2 wt.% Gly·HCl, respectively. The obtained chitosan solutions were filtered, casted on the mould and regenerated in 5 wt.% NaOH/ethanol coagulation bath. There are two kind of processing technique, one is wet technique, by which the chitosan solution was directly immersed in coagulation for 12 h. Another is dry technique, by which the solution was evaporated at 60 °C for 3 h, and then immersed in coagulation. The primary membranes were washed with water and dried at room temperature. The raw chitosan was named S-0, and the membranes prepared from Gly·HCl by wet and dry technique were named S_G-1 and S_G-2, respectively. Similarly, the membranes prepared from acetic acid by wet and dry technique were named S_A-3 and S_A-4, respectively. Furthermore, the chitosan microporous membranes from Gly·HCl and acetic acid were also prepared by dry technique using PEG as porogen (weight ratio of chitosan/PEG is 100%), named S_G-5 and S_A-6, respectively. The signature of all the samples ID was shown in Table 1.

2.4. Measurement

A Jeol Jsm-5600lv (Jeol Ltd., Tokyo) SEM was used to study the surface morphology of the membranes, which were washed with ether for several times and coated with gold before observation. The WAXD of all membranes was obtained from Rigaku D/Max-2550 (Rigaku Corp, Tokyl) with Cu radiation operated at 40 kV and 200 mA. FT-IR was recorded on Nicolet 8700 (Thermo Electron Corp, USA) in the range of 4000–400 cm^{-1} with attenuated total reflection (ATR) accessory. TGA was performed on TG 209 F1 Iris (Netzsch Gertebau GmbH, Germany) at a heating rate of 10 °C/min under nitrogen atmosphere. DSC was conducted by Q20 (TA, USA) in the range of −30 °C to 120 °C at a heating rate of 10 °C/min. The mechanical property was measured with WDW3020 materials testing system (Changchun Kexin Instrument Co. Ltd., China) at room temperature with a crosshead speed of 5 mm/min, the samples were cut into strips of 80 mm × 10 mm, and five strips were measured for each sample.

3. Results and discussion

3.1. Morphology analysis

The scanning electron micrographs of all the chitosan membranes are shown in Fig. 1. It can be seen that the surface and cross section of S_G-1 present loose structure, which is similar to that of S_A-3. That is because the processing technique plays an important role to determine the morphology of membranes. In general, once the chitosan solution is immersed in coagulation bath, the precipitation occurs, and the morphology of regenerated chitosan membranes is shaped gradually. It is very difficult to change the loose structure into compact one during the subsequent process. On the contrary, the structure of membrane will be denser if the solution is pre-evaporated before being immersed in coagulation, this is confirmed by the cross section morphology of S_G-2 and S_A-4. The surface of S_A-4 is smooth and homogeneous, there are no any flaws, while the surface of S_G-2 presents a novel structure and looks more densification. From the above analysis, it can be inferred that the mechanical properties of S_G-2 and S_A-4 will be superior to that of S_G-1 and S_A-3. S_G-5 and S_A-6 present a porous morphology and the distribution of pores are uniform, but the frame of the pores is very different. Specifically speaking, S_G-5 mainly presents closed pores while the pores in S_A-6 are mutually penetrated. This is due to the difference between their corresponding matrix S_G-2 and S_A-4.

As shown in Fig. 2, the appearance of all the membranes is homogeneous and uniform, and there is a little difference on the photopermeability of them. Overall, the photopermeability of

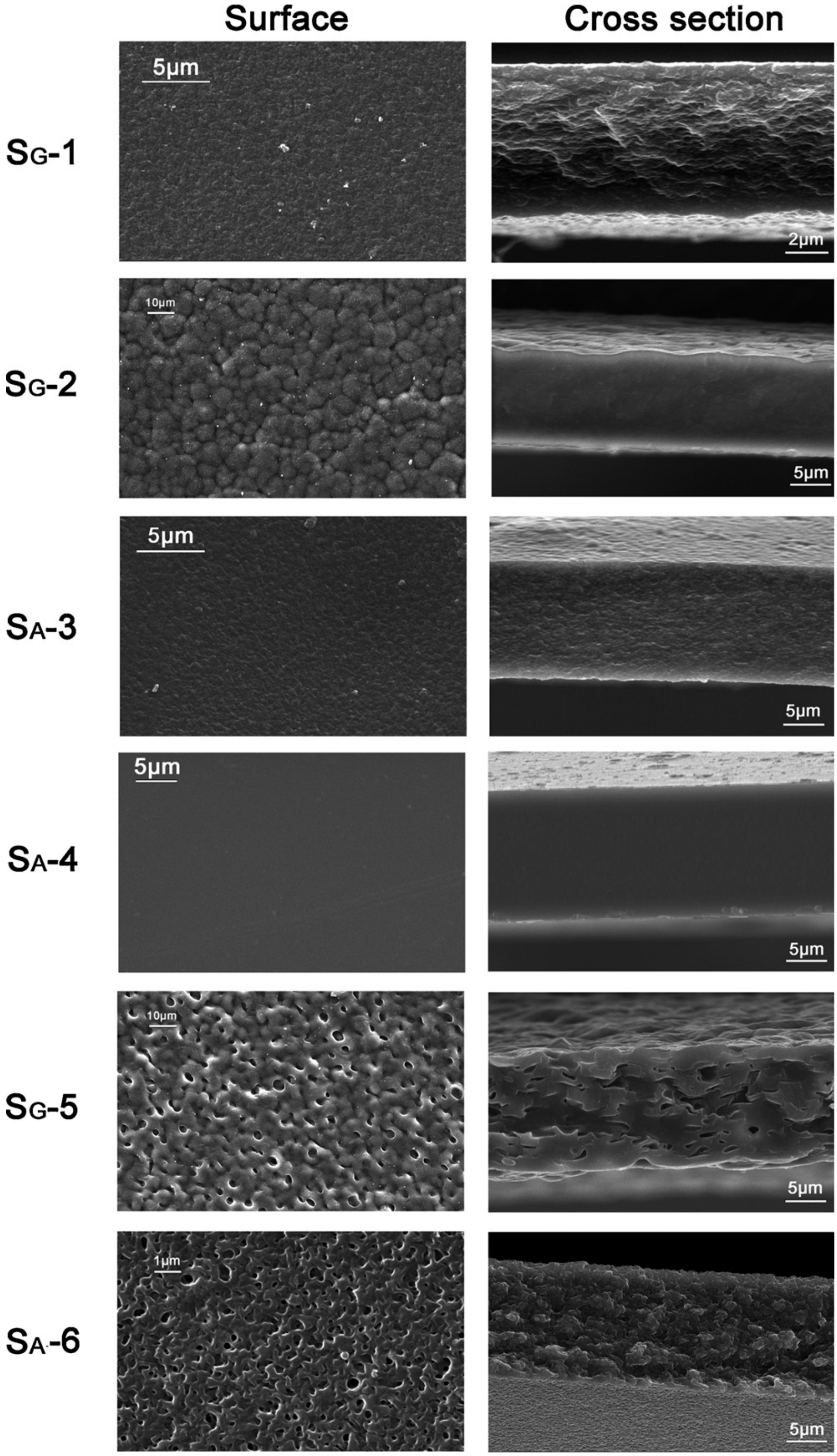

Fig. 1. SEM micrographs of all the regenerated chitosan membranes.

Table 2
Thermal analysis results of all the chitosan samples.

Sample ID	S-0	S_G-1	S_G-2	S_A-3	S_A-4	S_G-5	S_A-6
T_{onset} (°C)	284.4	267.2	268.3	262.5	263.7	270.8	263.2
T_{max} (°C)	305.5	293.2	295.3	283.1	288.3	296.1	284.9
Residual ratio (wt.%)	21.3	40.2	38.6	38.4	37.4	34.5	33.8

membranes prepared from acetic acid is better than that of membranes prepared from Gly·HCl, the membranes prepared by dry technique holds better photopermeability than the membranes prepared by wet technique. Specifically speaking, the photopermeability of S_G-2 and S_A-4 is better than that of S_G-1 and S_A-3. In particular, the photopermeability of S_A-4 is best. This is probably related to the crystallinity and density difference between the crystal phase and the amorphous phase (Liang, 2000). On the other hand, as compared with S_G-2 and S_A-4, the photopermeability of S_G-5 and S_A-6 is lower, which is due to the presence of residual PEG. Although the membrane was washed with deionized water many times, the presence of hydrogen bonds between PEG and chitosan matrix makes it difficult to remove PEG thoroughly (Li, Nan, Chen, & Xu, 2011), this will be demonstrated in the following Section 3.2.

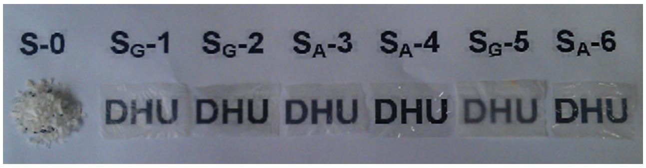

Fig. 2. Images of raw chitosan and all the regenerated chitosan membranes.

3.2. Thermal properties

DSC, TGA and corresponding DTA curves are shown in Fig. 3a, b and c, respectively. It is well known that chitosan is a kind of semi-crystalline polymer, which undergoes thermal degradation prior to melting. As presented in Fig. 3a, no endothermic peaks are detected for the sample S-0, S_G-1, S_G-2, S_A-3 and S_A-4, which is in accordance with the characterization of chitosan. However, for S_G-5 and S_A-6, there is an obvious endothermic peak at 54.5 °C and 56.94 °C, respectively, which is attributed to the melting of PEG existed in the membrane matrix, which also improves the statement in above section.

Fig. 3b and c shows the thermal degradation patterns of all the samples in the range of 50–900 °C, and the numerical data is shown in Table 2. All the samples suffer a weight loss (about 5–10 wt.%) at about 100 °C, which is associated with the volatilization of absorbed water, and a sharp weight loss (about 50–60 wt.%) at about 300 °C, which is associated with the pyrolysis of chitosan matrix. Especially, there exists a second-step decomposition at about 420 °C for S_G-5 and S_A-6, which is associated with the pyrolysis of PEG, this is a further proof for the presence of PEG. As shown in Table 1, the raw chitosan reveals a little higher onset (T_{onset}) and max (T_{max}) decomposition temperature than that of the regenerated chitosan, the T_{onset} and T_{max} of regenerated chitosan prepared from Gly·HCl is higher than that from acetic acid. The processing technique and presence of PEG have little effect on the decomposition temperature of regenerated chitosan. It should be emphasized that the residual of all the regenerated chitosan samples is higher than that of the raw chitosan. That is due to the homogeneous structure of the regenerated chitosan membranes and removal of some relatively unstable impurities and low molecular weight components during the dissolution and regeneration process (Wu, Sasaki, Irie, & Sakurai, 2008).

3.3. WAXD and FT-IR analysis

As shown in Fig. 4, the WAXD profiles of all the samples show an obvious diffraction peaks at about $2\theta = 10°$ and 20°, respectively, which indicate that all the regenerated chitosan samples prepared from Gly·HCl and acetic acid are α-chitosan, which is in accordance with the WAXD result of raw chitosan. It also proves that there is no crystal structure change for chitosan during the dissolution and regeneration process. On the other hand, the peak intensity of all the regenerated chitosan samples is far less than that of the raw chitosan. This indicates that the crystallinity of regenerated chitosan is lower than that of raw chitosan, which is attributed to the full destroy of crystal region of raw chitosan during the dissolution process, and the present crystal of regenerated chitosan is formed during the regeneration process. However, there are still many amorphous areas which cannot be reconstituted to crystal and contribute to the decrease of crystallinity. There is no obvious diffraction peak difference between the regenerated chitosan membranes prepared from Gly·HCl and acetic acid, respectively, which indicates that the crystal structure of regenerated chitosan prepared from the two solvent systems is similar.

Fig. 5 shows the FT-IR spectra of raw chitosan and all the regenerated chitosan membrane samples. More specifically, the absorption band at 3450 cm^{-1} is assigned to the stretching of N—H and O—H of the carbohydrate ring. The peak at 2900 cm^{-1} is assigned to the stretching of C—H, and the strong vibrations

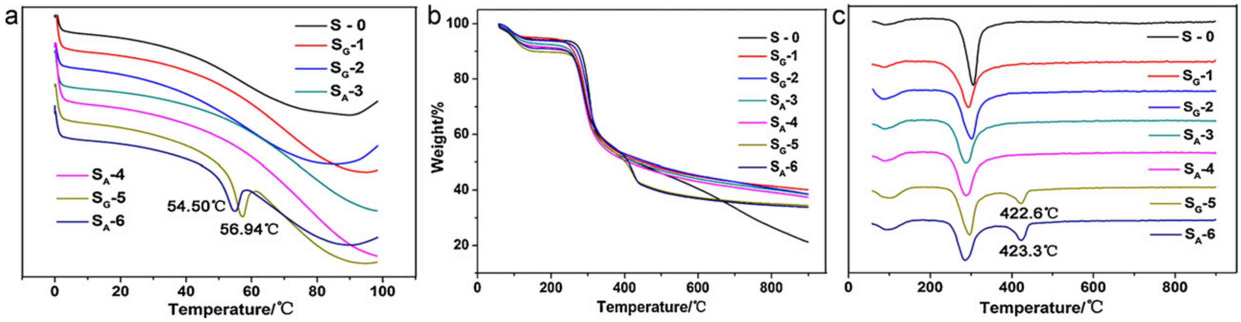

Fig. 3. (a) DSC, (b) TGA and (c) DTA curves of raw chitosan and all the regenerated chitosan membranes.

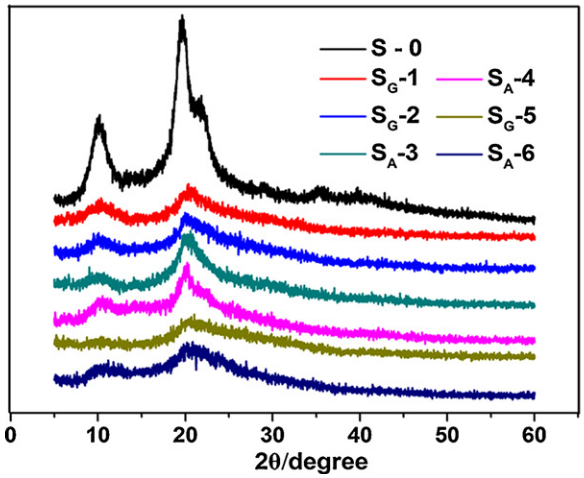

Fig. 4. X-ray diffractogram of raw chitosan and all the regenerated chitosan membranes.

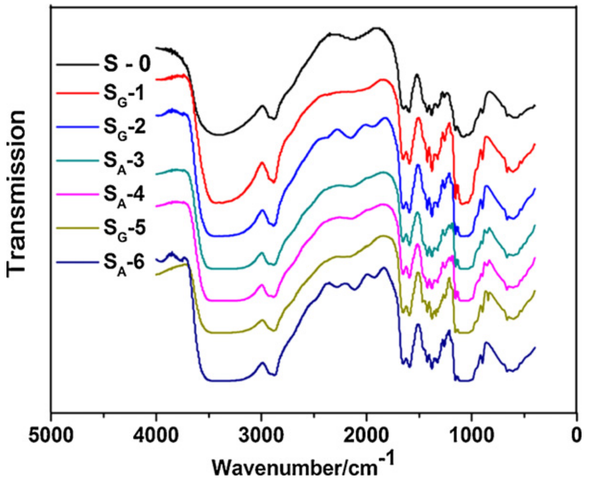

Fig. 5. FT-IR spectra of raw chitosan and all the regenerated chitosan membranes.

at 1650 and 1600 cm^{-1} is assigned to the stretching of amides I and II, respectively. The peaks at 1420 cm^{-1} and 1050 cm^{-1} is corresponded to the flexural vibration of —CH$_2$ and stretching vibration of C—O, respectively (Sangsanoh & Supaphol, 2006; Watthanaphanit et al., 2009; Zhao, Jiang, Sun, Sui, & Shi, 1998). The spectra of all the regenerated chitosan samples are similar to that of raw chitosan, which indicates that no derivatization occurs after regeneration. Furthermore, the absorption band around 3450 cm^{-1} of all the regenerated chitosan samples is broadened as compared with that of raw chitosan. That is due to the regenerated chitosan samples are not fully dried, there are more crystal water and free water presented in the regenerated chitosan samples than that in the raw chitosan (Jiang, 2001).

3.4. Mechanical properties

As shown in Fig. 6a and b, all the samples show a certain tensile strength and elongation except S$_G$-1 since it is so fragile that its tensile strength cannot be detected here. As expected, sample S$_G$-2 and S$_A$-4 display a superior tensile strength and initial modulus than that of sample S$_G$-1 and S$_A$-3. This is ascribed to their different processing technique, which affects the structure and mechanical behavior of chitosan membrane. From the two stages strength–strain curves of S$_G$-2 and S$_A$-4, the second stage is thought to be reorientation of the macromolecule chains. Therefore, the pre-evaporation during dry technique is a simple and effective way to prepare chitosan membrane with high tenacity. Especially, the tensile strength and initial modulus of S$_G$-2 reaches up to 103.8 MPa and 3.2 GPa, respectively, much higher than that of sample S$_A$-4, i.e. 64.6 MPa and 2.1 GPa, respectively, which is superior to any other chitosan membranes and most chitosan blend membranes reported in literatures. Therefore, Gly·HCl is a promising solvent for dissolving chitosan and preparing regenerated chitosan membrane. For S$_G$-5 and S$_A$-6, the porous structure and PEG residual have great effect on the mechanical properties of membranes. As shown in Fig. 6a, the tensile strength of S$_G$-5 decreases 56.2% from 103.8 MPa to 45.5 MPa, while the tensile strength of S$_A$-6 increases 6.7% from 64.6 MPa to 68.9 MPa. This is associated with their corresponding structure. As shown in Fig. 1, although S$_G$-5 and S$_A$-6 present porous structure, the pores in S$_G$-5 are closed, and the pores in S$_A$-6 are mutual penetrated. The closed pores generate flaws in the membrane matrix, which leads to the sharp decrease of tensile strength. However, the mutual penetrated pores generate an interpenetrating network, which enhances the mechanical properties of membrane matrix. On the other hand, as shown in Fig. 6b, the initial modulus of S$_G$-5 and S$_A$-6 is 0.9 GPa and 1.7 GPa, respectively, which is lower than that of S$_G$-2 and S$_A$-4. This is mainly due to the plasticization of PEG.

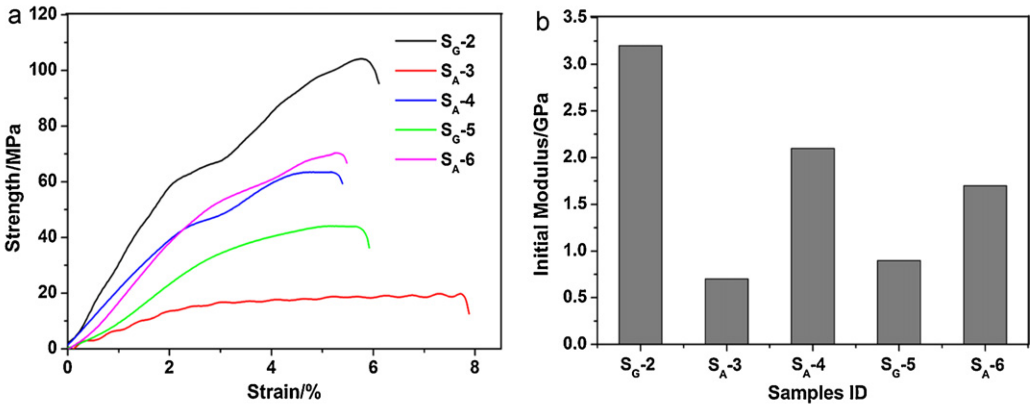

Fig. 6. (a) Stress–strain behavior and (b) initial modulus of the regenerated chitosan membranes.

4. Conclusions

In this study, chitosan membranes were prepared from Gly·HCl and acetic acid, respectively, two kinds of processing technique, i.e. wet technique and dry technique, were studied to show their influence on the properties and structure of the membranes. The SEM results indicate that the membranes prepared from wet technique present loose structure, and the membranes prepared from dry technique present compact structure, and the structure of S_G-2 is the most compact one. The results of TGA indicate that the decomposition temperature of regenerated chitosan membranes prepared from Gly·HCl is a little higher than that of the regenerated chitosan membranes prepared from acetic acid, and all the regenerated chitosan membranes present higher residual than that of raw chitosan. This is due to the homogeneous structure of the regenerated chitosan membrane and remove of some unstable impurities. The WAXD results show that all the regenerated chitosan membranes present structure of α-chitosan, which is accordance with raw chitosan. Especially, the S_G-2 shows excellent tensile strength and initial modulus, i.e. 103.8 MPa and 3.2 GPa, respectively, which is far higher than that of any other membranes and most chitosan blend membranes reported in literatures. On the other hand, porous chitosan membranes are prepared using PEG as porogen, and the pore structure in the two kinds of matrix is different. The pores in chitosan membrane prepared form Gly·HCl are closed, leading to the decrease of tensile strength. However, the pores in chitosan membrane prepared form acetic acid are mutual penetrated, and form an interpenetrating network structure through the cross section, which may enhances the mechanical properties of membrane. Besides, the results of DSC and TGA confirm the residual of PEG in the porous chitosan membrane due to the presence of hydrogen bonds between PEG and chitosan matrix.

Acknowledgements

This work was supported by grants from the National Science Foundation of China (Nos. 51103019 and 21174027), Shanghai Pujiang Program (08PJ1400900), Programme of Introducing Talents of Discipline to Universities (No. 111-2-04) and Innovation Funds for PhD Students of Donghua University.

References

Costa, E., Barbosa, E., Mansur, A., Vasconcelos, W., & Mansur, H. (2009). Preparation and characterization of chitosan/poly(vinyl alcohol) chemically crosslinked blends for biomedical application. *Carbohydrate Polymers*, *76*, 472–481.

Di, M., Sittinger, M., & Risbud, M. (2005). Chitosan: a versatile biopolymer for orthopaedic tissue-engineering. *Biomaterials*, *26*, 5983–5990.

Fan, J., Shi, Z., Ge, Y., Wang, Y., Wang, J., & Yin, j. (2012). Mechanical reinforcement of chitosan using unzipped multiwalled carbon nanotube oxides. *Polymer*, *53*, 657–664.

Jiang, T. (2001). *Chitosan* (1st ed.). Beijing: Chemical Industry Press.

Ko, H., Sfeir, C., & Kumta, P. (2010). Novel synthesis strategies for natural polymer and composite biomaterials as potential scaffolds for tissue engineering. *Philosophical Transactions of the Royal Society A*, *368*, 1981–1997.

Kou Y., Tao, G., He, L., & Sun, N. (2005). Faming zhuanli shenqing gongkai shuomingshu. CN 1631539A.

Li, X., Nan, K., Chen, H., & Xu, Y. (2011). Preparation and characterization of chitosan nanopores membranes for the transport of drugs. *International Journal of Pharmaceutics*, *420*, 371–377.

Li, L., Yuan, B., Liu, S., Yu, S., & Liang, S. (2012). Glycine hydrochloride ionic liquid/aqueous solution system as a platform for the utilization of chitosan. *Journal of Applied Polymer Science*, *123*, 3772–3780.

Liang, B. (2000). *Polymer physics* (2nd ed.). Beijing: China Textile Press.

Liu, D., Wu, Q., Chang, P., & Gao, G. (2011). Self-assembled liquid crystal film from mechanically defibrillated chitosan nanofibers. *Carbohydrate Polymers*, *84*, 686–689.

Muzzarelli, R. (2011). Biomedical exploitation of chitin and chitosan via mechano-chemical disassembly, electrospinning, dissolution in imidazolium ionic liquids, and supercritical drying. *Marine Drugs*, *9*, 1510–1533.

Muzzarelli, R., Boudrant, J., Meyer, D., Manno, N., Demarchis, M., & Paoletti, M. (2012). Current views on fungal chitin/chitosan, human chitinases, food preservation, glucans, pectins and inulin: a tribute to henri braconnot, precursor of the carbohydrate polymers science, on the chitin bicentennial. *Carbohydrate Polymers*, *87*, 995–1012.

No, H., Meyers, M., Prinyawiwatkul, W., & Xu, Z. (2007). Applications of chitosan for improvement of quality and shelf life of foods: a review. *Journal of Food Science*, *72*, 87–100.

Pillai, C., Paul, W., & Sharma, C. (2009). Chitin and chitosan polymers: chemistry, solubility and fiber formation. *Progress in Polymer Science*, *34*, 641–678.

Pinkert, A., Marsh, K., Pang, S., & Staiger, M. (2009). Ionic liquids and their interaction with cellulose. *Chemical Reviews*, *109*, 6712–6728.

Rinaudo, M. (2006). Chitin and chitosan: properties and applications. *Progress in Polymer Science*, *31*, 603–632.

Rogers, R., & Seddon, K. (2003). Ionic liquids—Solvents of the future? *Science*, *302*, 792–793.

Sangsanoh, P., & Supaphol, P. (2006). Stability improvement of electrospun chitosan nanofibrous membranes in neutral or weak basic aqueous solutions. *Biomacromolecules*, *7*, 2710–2714.

Shih, C., Shieh, Y., & Twu, Y. (2009). Preparation and characterization of cellulose/chitosan blend films. *Carbohydrate Polymers*, *78*, 169–174.

Tchemtchoua, V., Atanasova, G., Aqil, A., Filee, P., & Colige, A. (2011). Development of a chitosan nanofibrillar scaffold for skin repair and regeneration. *Biomacromolecules*, *12*, 3194–3204.

Watthanaphanit, A., Supaphol, P., Furuike, T., Tokura, S., Tamura, H., & Rujiravanit, R. (2009). Novel chitosan-spotted alginate fibers from wet-spinning of alginate solutions containing emulsified chitosan citrate complex and their characterization. *Biomacromolecules*, *10*, 320–327.

Wu, Y., Sasaki, T., Irie, S., & Sakurai, K. (2008). A novel biomass-ionic liquid platform for the utilization of native chitin. *Polymer*, *49*, 2321–2327.

Xiao, C., Gao, S., Wang, H., & Zhang, L. (2000). Blend films from chitosan and konjac glucomannan solution. *Journal of Applied Polymer Science*, *76*, 509–515.

Xiao, C., Zhang, J., Zhang, Z., & Zhang, L. (2003). Study of blend films from chitosan and hydroxypropyl guar gum. *Journal of Applied Polymer Science*, *90*, 1991–1995.

Xie, H., Zhang, S., & Li, S. (2006). Chitin and chitosan dissolved in ionic liquids as reversible sorbents of CO_2. *Green Chemistry*, *8*, 630–633.

Zakrzewska, M., Bogel, E., & Bogel, R. (2010). Solubility of carbohydrates in ionic liquids. *Energy & Fuels*, *24*, 737–745.

Zhang, L., Guo, J., Zhou, J., Yang, G., & Du, Y. (2000). Blend membranes from carboxymethylated chitosan/alginate in aqueous solution. *Journal of Applied Polymer Science*, *77*, 610–616.

Zhao, G., Jiang, Y., Sun, L., Sui, D., & Shi, Y. (1998). Comparative study on the properties and infrared spectra of chitosans from different sources. *Journal of Functional Polymers*, *11*, 403–406.

Zhu, Q., Han, X., Cheng, C., & Wu, C. (2011). Study on dissolubility of chitosan in four kinds of imidazole-based ionic liquids. *Acta Polymerica Sinica*, *10*, 1173–1179.