Synthesis of Lignosulfonate Hydrogels cross-linked with PEGDGE

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Introduction

Hydrogels are network based polymers noted for their ability to retain large amounts of water. Industries take advantage of their hydrophilic property to enhance its products; these include drug delivery services, soil rehabilitation, biosorption, etc. Lignosulfonate is a copious lignin-derived byproduct from the pulping process of paper production. Because of the economical and sustainable advantages of using biomass over fossil-fuels, industries are looking towards replacing synthetics with bio-based materials. In this study, sodium lignosulfonate is cross-linked with poly (ethylene glycol) diglycidyl ether (PEGDGE) to form hydrogels. Reaction (PEGDGE mass, lignosulfonate mass, temperature) and application (time, pH) conditions are manipulated to optimize maximum swelling capacity.

Experimental Methods

1. **Hydrogel Preparation:** A water bath with a thin layer of oil was set to heat at various temperatures. 10 ml of deionized water was poured into a screw-top glass vial along with a stir bar. The vial was placed into the water-oil bath. Different amounts of sodium lignosulfonate (code no. 700317) was slowly added to the vial with the while stirring at 900 rpm. The vial is capped and left to stir for 2 hours. After two hours, sodium hydroxide and PEGDGE was added to the mixture. The stir bar was removed and capped vial was removed from the water-oil bath. After the hydrogel formed, it is removed from the vial and washed multiple times with cold water, hot water, and ethanol until the liquid runs clear. Products were freeze dried into xerogel and then ground into a fine powder.
2. **Swelling Capacity Tests:** Approximately 0.20 g of each ground freeze dried hydrogel sample is placed into the bottom of a teabag. The samples were submerged in their respective water baths and left for two hours. After two hours, the teabags are blotted with paper towels and a spatula is used to scoop out the swollen hydrogels for mass measurement. For tests run in respect to time, The samples were submerged into room temperature water baths. At each designated time interval, the teabags are taken out, blotted, and then weighed.

Results and Discussion

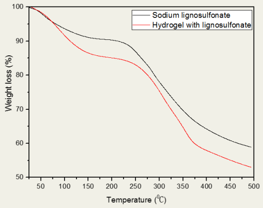
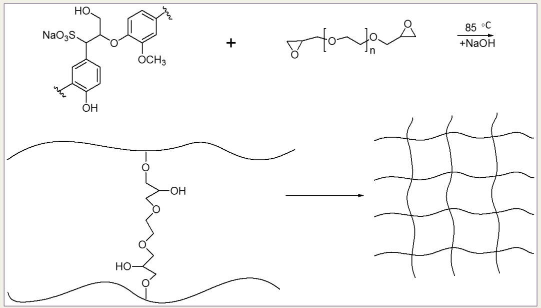


Fig. 1 Thermogravimetric analysis (TGA) of sodium lignosulfonate (SLS) and lignosulfonate hydrogel (SLSH) (5 mg, heating rate 10°C/min, temp. room-500 °C)

SLS and SLSH show similar trends in weight loss. In comparison to SLS, SLSH exhibited greater loss in weight in respect to temperature because of its moisture content.



Scheme 1. Reaction scheme for crosslinking sodium lignosulfonate (SLS) with PEGDGE to synthesize sodium lignosulfonate hydrogel (SLSH)

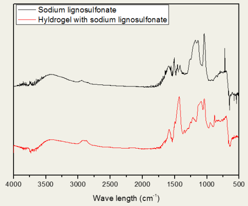


Fig.2 FT-IR spectra of sodium lignosulfonate (SLS) and lignosulfonate hydrogel (SLSH) (scanned scanned 32 times in the range for 4000 to 500 cm^{-1})

There are bands at 1114 and 951 cm-1, which is attributed to C-O-C vibrations. This is evident that crosslinking PEGDGE and SLS was successful.

Reaction Conditions

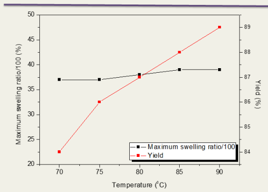


Fig. 3 Different reaction temperature to swelling ratio and yield of SLS hydrogels (4g SLS,1.2g PEGDGE, 10 ml water, 0.5g NaOH, temp. 70-90◦C in increments of 5)

As the temperature condition increases, the swelling ratio increases as well.

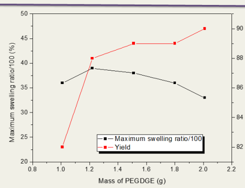


Fig. 4 Different amounts of cross linker to swelling ratio and yield of SLS hydrogels (4g SLS, 85◦C, 10 ml water, 0.5g NaOH, PEGDGE 1.0g-2g in increments of .2)

The swelling capacity of the SLSH increases as the amount increases to 1.2g PEGDGE; it decreases thereafter.

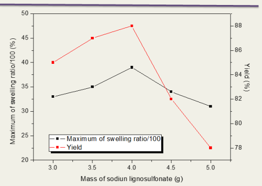


Fig. 5 Different amounts of sodium lignosulfonate to swelling ratio and yield of SLS hydrogels (1.2g PEGDGE, 85◦C, 10 ml water, 0.5g NaOH,SLS 3.0-5g in increments of 0.5)

The swelling capacity of the SLSH increases as the amount increases to 4g SLS; it decreases thereafter.

Application Conditions

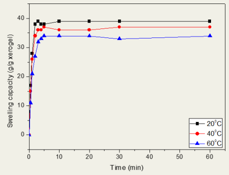


Fig. 6 Relationship between swelling time and swelling capacity (4g SLS,1.2g PEGDGE, 10 ml water, 0.5g NaOH, 85◦C, media pH 3-11 in increments of 2)

SLSH reaches equilibrium within 2 minutes in room temperature media.

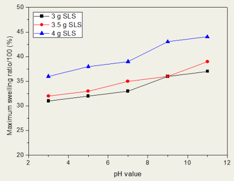


Fig. 7 Variation of the maximum swelling ratio with pH value for different usage of sodium lignosulfonate (4g SLS,1.2g PEGDGE, 10 ml water, 0.5g NaOH, room temperature)

As the pH of the media increases, the swelling ratio of the SLSH increases.

Yield % = $(m_{post\ swelling} - m_{prior\ swelling})/m_{post\ swelling} \times 100$ Swelling ratio (%) = $(m_{swollen} - m_{dry})/m_{swollen}$) X100 Time Swelling ratio (%) = $(m_{time} - m_{dry})/m_{time}$) X100

Conclusion

To optimize the swelling capacity of SLSH, preparation requires 4g SLS and 1.2g PEGDGE synthesized at 85◦C. With 4g SLS, the hydrogel swelling capacity was 39g water/g xerogel; addition of SLS exhibited a decrease in swelling capacity. With 1.2g PEGDGE, the hydrogel swelling capacity was 37g water/g xerogel; addition of PEGDGE exhibited a decrease in swelling capacity. Within 2 minutes, the SLSH reached its maximum swelling capacity.

Future Directions

- Investigate various methods of modifying lignosulfonate hydrogels to increase swelling capacity
- Optimize swelling capacity conditions for lignin amine hydrogels

References

1. Xuliang Liu, Mingsong Zhou, Suya Wang, Hongming Lou, Dongjie Yang,Xueqing Qiu. Synthesis, structure, and dispersion property of a novel lignin-based polyoxyethylene ether from Kraft lignin and poly(ethylene glycol) [J]. ACS Sustain. Chem. Eng., 2(2014):1902-1909]

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