Rheological Characterization of Chemically Modified Hemicellulose

Arja-Helena Vesterinen, Jukka Seppälä

Aalto University School of Chemical Technology, Kemistintie 1, FI-02150 Espoo, Finland

ABSTRACT

Herein, hemicellulose consisting mainly of xylan was modified by using different crosslinking agents containing epoxy or aldehyde group. The changes in hemicellulose during reaction were measured with rotational rheometry. Epoxy formed viscoelastic fluid when content of cross-linker was low. On contrary, aldehyde modification resulted physical gel structure.

INTRODUCTION

Hemicellulose is interesting bio-based polymer. Remarkable fraction of plant or wood biomass consists of hemicellulose. Hemicellulose has little use in industrial applications, mainly because it has poor material properties. Material properties of hemicellulose are typically improved with different plasticizers. [1] Additionally, it is reactive to many chemical groups through its hydroxyl groups. Modification of hemicellulose would increase its usability in different end products. [2]

MATERIALS AND METHODS

Hemicellulose used in this study was beech wood xylan (Sigma-Aldrich). Xylan was dissolved in 0.5 M NaOH solution. After that crosslinking agent; glutaric dialdehyde or 1,4-butanediol diglycidyl ether; was added.

Rheological properties were measured with TA Instruments ARG2 rheometer with 20 mm parallel plate geometry in 1 mm gap. The measurements were made at 25 °C. Frequency sweep was measured at 0.2 % strain. Shear viscosity was measured for the same sample in steady state mode after 5 min equilibrium time.

RESULTS AND DISCUSSION

The reaction occurred between xylan and the crosslinking agent was confirmed with nuclear magnetic resonance spectroscopy and infrared spectroscopy. Both epoxy and aldehyde signals disappeared during reaction.

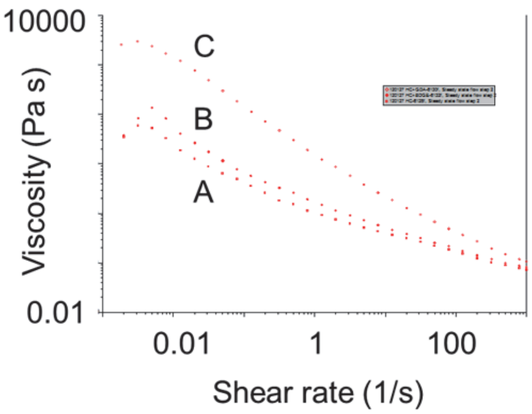

Figure 1. Viscosity with two different crosslinkers A) blank hemicellulose B) butylic diglycidyl ether C) glutaric dialdehyde.

The changes in hemicellulose were measured with rotational rheometry. Fig. 1 presents a flow curve of two different crosslinking agents. It is clear the viscosity increases with aldehyde crosslinker but the same cannot be seen with epoxy crosslinker; even though the chemical reaction occurred in both cases.

The phenomenon can be confirmed with frequency sweep in Fig. 2. Aldehyde modified xylan shows clear gel structure but epoxy modified xylan maintains viscoelastic structure characteristic for this hemicellulose.

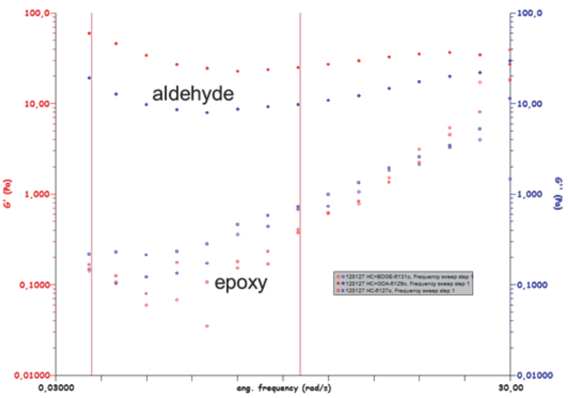

Figure 2. Frequency sweeps of xylan and xylan modified with two different crosslinkers.

After the rheological measurement the films were dried. After that a swelling study was done in order to study whether a covalently crosslinked hydrogel was formed or not. Hydrogel structure was most easily achieved with epoxy cross-linker. (Table 1)

Table 1. Character of hemicellulose composite after modification with crosslinkers.

Epoxy crosslinker	hydrogel
Aldehyde crosslinker	physical gel

Additionally, film forming properties of hemicellulose was studied by visual observation of dried samples. Hemicellulose alone forms weak and fragile film. Good film forming properties of the formed hemicellulose were difficult to achieve even though the chemical reaction itself was successful. Aldehyde crosslinker does not remarkably improve that but significant improvement is observed with epoxy crosslinker. However, none of the methods provided good film forming properties compared to conventional existing polymers.

CONCLUSIONS

Rheological character of xylan can be modified with different crosslinking agents. Epoxy formed viscoelastic fluid when content of cross-linker was low. On contrary, aldehyde modification resulted physical gel structure. Rheological properties could not be directly connected with film forming properties. Hemicellulose with epoxy crosslinker formed better film than the one with aldehyde crosslinker, but it was still rather brittle.

ACKNOWLEDGMENTS

I am grateful for my trainee Minna Hakalahti for careful lab work and for Tapio Saarinen and Anni Karppinen for support regarding rheological issues. Ossi Turunen in the laboratory of bioprocess technology is acknowledged for his support regarding hemicellulose.

REFERENCES

1. Hansen, N.M. and Plackett D. (2008) "Sustainable films and Coatings from Hemicelluloses: A Review", *Biomacromolecules,* **9**, 1493-1505.

2. Voepel, J., Edlund, U., Albertsson A-C., Percec, V. (2011), "Hemicellulose-Based Multifunctional Macroinitiator for Single-Electron-Transfer Mediated Living Radical Polymerization", *Biomacromolecules,* **12**, 253-259.