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Dissolution of cellulose with NMMO by microwave heating

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A B S T R A C T

Environmentally friendly microwave heating process was applied to the dissolution of cellulose in *N*-methylmorpholine-*N*-oxide (NMMO) with 105–490 W and 2450 MHz microwave energy until the dissolution completed. Microwave heating caused the decrease in the dissolution time and energy consumption. Cellulose/NMMO/water solutions with different cellulose concentrations were converted to the membrane to measure the crystallinity and degree of polymerization. It was shown that microwave heating with the power of 210 W is an alternative heating system for dissolution of cellulose in NMMO. The membranes obtained with two different heating methods showed the same crystallinity and degree of polymerization. As a result, microwave heating has an advantage in shortening reaction times, compared to conventional heating.

1. Introduction

Cellulose constitutes the most abundant, renewable polymer resource available today worldwide, mostly are combined with lignin and other polysaccharides (so called hemicelluloses) in the cell wall of woody plants. Cellulose is converted by large scale industrial processing into cellulose derivatives (ethers and esters) and regenerated materials (fibers, films, food casing, membranes, and sponges, among others) (Fink, Weigel, Purz, & Ganster, 2001).

Cellulose is a homopolysaccharide polymer composed of β-D-glucopyranose units which are linked together by (1 → 4) glycosidic bonds and is a structural component of plant cell walls. Cellulose molecules are completely linear and have a strong tendency to form intra- and intermolecular hydrogen bonds. Bundles of cellulose molecules are thus aggregated together in the form of micro fibrils, which build up fibrils and finally cellulose fibers. It is widely known that cellulose does not melt, but it will undergo thermal degradation at high temperature. Cellulose must therefore be converted into a liquid form by either direct dissolution or by derivatization and subsequent dissolution of the derivative. The strong inter-chain and intra-chain hydrogen bonding involved in the crystalline regions make reactions and dissolution of cellulose difficult (Klemm, Schmauder, & Heinze, 2003).

Commercial regeneration of cotton or wood cellulose in the form of fibers and films has been based on solvent systems such as those used in the xanthate and cuprammonia processes. There has been an intensive search for the commercial regeneration of cellulose because of the environmental problems associated with the xanthate process. Recently, tertiary amine oxides have drawn attention as powerful cellulose solvents, with *N*-methylmorpholine-*N*-oxide (NMMO) being the most common (Fink et al., 2001).

Regenerated cellulose fiber produced by the NMMO method was industrialized and a lot of studies on the manufacturing and characterization of the fiber have been carried (Frank & Varga, 1979; Eichinger et al., 1993; Luo, Roscelli, Neogi, & Jewell, 2001). NMMO process is environmentally friendly process and in this process, cellulose dissolution has been realized at high temperature and under low vacuum (Fink et al., 2001; Rosenau, Potthast, Sixta, & Kosma, 2001). In order to dissolve the cellulose with NMMO solvent, microwave heating has been considered as an alternative approach in the present study. There is a wide and continuously increasing literature available in the area of using microwave techniques in organic synthesis and wood liquefactions because of its high heating efficiency and easy operation. (Caddick, 1995; Krzan & Kunaver, 2006). In the literature, it was shown that microwave heating was successfully applied in the dissolution of cellulose with ionic liquids (Swatloski, Spear, Holbrey, & Rogers, 2002), but microwave dissolution with NMMO solvent has not been reported. In this work we have used microwave heating technique for the dissolution of cellulose with NMMO and the effect of the heating system was shown by characterizing the membranes prepared from the resultant solution.

2. Experimental

2.1. Materials and chemicals

Bleached linters pulp, obtained from commercial sources, was used as cellulose sample, which is characterized by the data given

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in Table 1. Linters pulp was powdered by grinding with a mill. *N*-methylmorpholine-*N*-oxide (NMMO)/H_2O (50/50 wt) mixture, supplied from Fluka, was used as a solvent for dissolution of the cellulose. *N*-propylgallate (Aldrich) was used as an antioxidant to avoid oxidation and degradation during the cellulose dissolving.

2.2. Membrane preparation

An adequate amount of cellulose pulp, NMMO/H_2O and antioxidant were added into a 250 ml beaker, which was positioned at the centre of a rotating circular glass plate in the microwave oven. The mixture was heated by microwave irradiation until the dissolution completed. The dissolution process was ended when the amount of distilled water was reaching the nominal value. This value was calculated as a function of desired final water content in solution. The weight loss of the mixture was determined by weighting the mixture during interrupting the flow of microwave energy.

The cellulose solution was cast onto a glass plate by a doctor blade, with a clearance of 120 μm. Before casting, the glass plate and doctor blade should be held at 90 °C to prevent the crystallization of NMMO monohydrate. The glass plate was immersed immediately into a water bath at 5 °C for 30 min, then washed with hot distilled water a few times and dried in a vacuum oven at room temperature for 24 hours. The membranes were prepared at different cellulose concentrations (5, 8 and 10%) and microwave heating capacities (105, 210, 350 and 490 W). In this study an Arçelik, ARMD-580 microwave oven was used. It has frequency of 2450 MHz, a microwave output power of 700 W, four microwave energy steps, a convection heat power of 1400 W, a thermostat which can be adjusted between 40 and 250 °C and turbo circulation. Microwave energy creates a magnetic field in the oven. For this reason it is difficult to measure the temperature inside the oven by means of conventional laboratory methods. Therefore, temperatures were measured by a thermocouple for each measurement by interrupting the flow of microwave energy. For temperature measurements, a Testo-Term 900 type precision thermometer with a Cr–Ni probe and accuracy of ±0.1 °C was used.

2.3. Membrane characterization

The membranes from cellulose/NMMO/H_2O solution prepared with microwave dissolution were characterized. The standard cupriethylene-diamine solution method is used for determining the intrinsic viscosity and DP of cellulose membranes by using Ubbelohde viscometer and calculated from the following equation.

$$DP = 95x\frac{[cx\eta]}{m}$$

m – Sample weight, g.
$[cx\eta]$ – Intrinsic viscosity

Scanning electron micrographs (SEM) of the membranes were taken with a JEOL JSM-6335 F “Field Emission Scanning Electron” microscope. The surface of membranes coated with gold were observed and photographed.

Table 1
The properties of linters pulp

Properties	Methods	Results
Moisture content (%)	TAPPI 208	7.5
Alpha cellulose content (%)	TAPPI T 203 cm-93	94
Degree of polymerization	TAPPI T 230	623
Kappa number	ISO 302	0.2
Lignin content (%)	ISO 302	0.03
Ash content (%)	TAPPI 211	0.08

Infrared spectra of the membrane samples were recorded with a Perkin Elmer Spectrum One Fourier transform-infrared spectrometer (FT-IR). Test specimens were measured directly.

The crystallinity of milled cellulose samples was determined by X-ray diffraction patterns which were taken by Karadeniz Technical University with a Rigaku 3D/Max series diffractometer. The radiation was Ni-filtered Cu–Ka radiation of wavelength 0.1542 nm.

The empirical method proposed by Segal, Creely, Martin, and Conrad (1959). was used for calculation of degree of crystallinity.

$$\mathrm{Cr_I} = \frac{[I_{002} - I_{\mathrm{amorph}}]}{I_{002}} \times 100$$

where $\mathrm{Cr_I}$ is the degree of crystallinity, I_{002} is the maximum intensity of the (002) lattice diffraction and I_{amorph} is the intensity diffraction at 18° 2θ degrees.

3. Results and discussion

3.1. Dissolution of cellulose

The loss of water in the cellulose solution was measured to show the effect of microwave irradiation power on the dissolution time. Three different cellulose/NMMO/Water solution having different cellulose concentrations were prepared. The amount of evaporated water increased with the reduction in the cellulose concentration. The microwave power was also effective parameter in the evaporation of water present in the cellulose/NMMO casting solution. Figs 1–3 show the change of the water evaporation time at different microwave powers according to the cellulose concen-

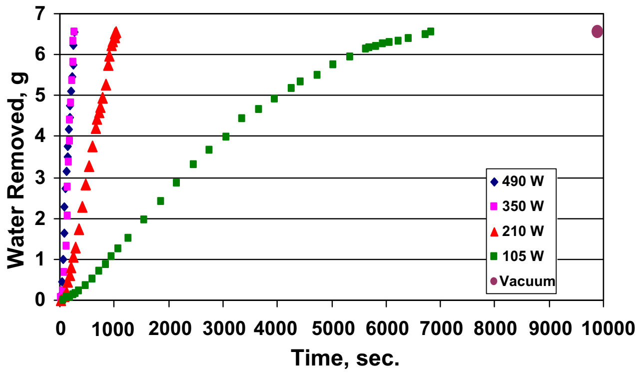


Fig. 1. Water removed in g with regard to the reaction mass at different microwave powers for 5% with cellulose concentrations.

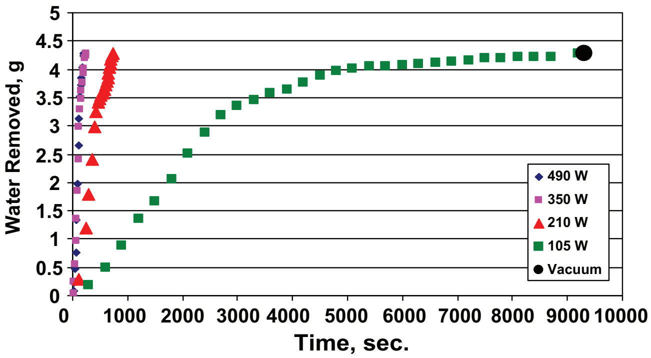


Fig. 2. Water removed in g with regard to the reaction mass at different microwave powers for 8% with cellulose concentrations.

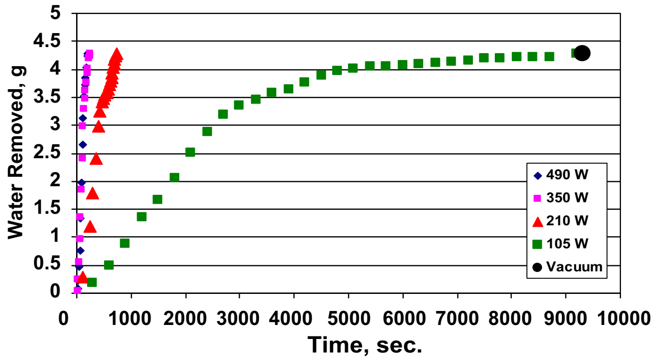


Fig. 3. Water removed in g with regard to the reaction mass at different microwave powers for 10% with cellulose concentrations.

trations. During the preparation of the cellulose solution with 5% concentration, the evaporation time for 6.54 g of water measured was as 2 h 45 min, 1 h 45 min, 17 min, 4 min, 4 min, under the condition of vacuum, 105, 210, 350 and 460 W, respectively. It was estimated that the increase in the cellulose concentration caused the decrease in the evaporation time because of the content of less water in the solution. Whereas no differences observed with the solution of 8% and 10% cellulose concentration.

The temperature in the microwave oven was measured using a suitable thermocouple and the maximum temperature was determined as 126 °C at the microwave powers of 350 and 490 W. Wendler, Grane, and Heinze (2005) reported that both cleavage of the cellulose and degradation of the solvent NMMO started at a temperature of 85 °C. The loss in the degree of polymerization in Fig. 4 is proving this expression.

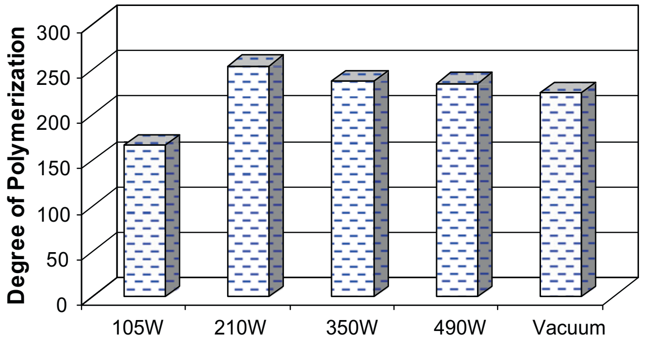


Fig. 4. Degree of polymerization values for cellulose concentration with 8% under different heating conditions.

3.2. Degree of polymerization of membranes

The cellulose/NMMO solutions with different cellulose concentrations after microwave dissolution was converted to membrane form. The average viscometric degree of polymerization represents the average number of glucose units in the cellulose and these values can range from 800 to 1600 U with the most probable value being about 1200. In order to measure the viscosity of a cellulose sample it must first be dissolved in a suitable solvent system. Such a solvent system that works well for dissolving cellulose is a cupriethylene-diamine solution. In this study, the degree of polymerization of linters pulp prepared by soda pulp production method was measured as 623. During the preparation of membrane from the dissolved linters cellulose, polymer chains degrade into smaller units. These membranes can be called as regenerated cellulose membranes. Because of the polymer degradation, it is expected that degree of polymerization of cellulose based membranes would be lower than original linter pulp. The results showed that under microwave and vacuum dissolution conditions for the same cellulose concentrations, degree of polymerization data of all membranes are almost the same as shown in Fig. 4.

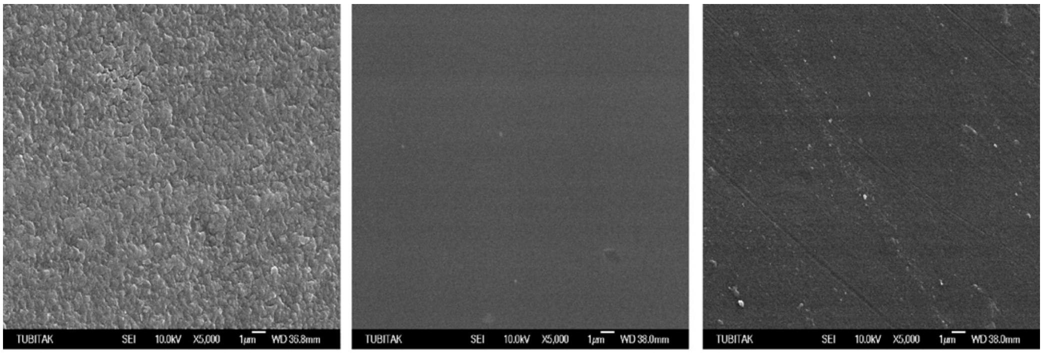
3.3. Morphology of membranes

Fig. 5 shows the scanning electron microscope (SEM) photographs of cross-sections of the cellulose membranes from casting solutions of the different cellulose concentrations with microwave powers of 210 W. As shown in Fig. 5, the membranes prepared from cellulose concentrations of 8% and 10% have homogenous nonporous structure whereas that of cellulose concentration of 5% have non homogenous porous structure. The results indicated that the decrease in the cellulose concentration resulted in the formation of porous structures in the membrane because of the lower polymer chain entanglement and larger free chain mobility (Bang, Lee, Park, & Cho, 1999).

The FT-IR spectra of cotton linters and membranes are shown in Fig. 6. The qualitative analysis of the FT-IR spectra shows that membranes prepared from cellulose/NMMO solution are made up of crystalline cellulose II and amorphous cellulose. As it has been expected, no significant peak shifts were observed in Fig. 6 when different microwave powers are applied for dissolution.

3.4. Crystallinity of membranes

Crystallinity of cellulose membranes was calculated from diffraction intensity data using the empirical method proposed by Segal. In this study, the degree of crystallinity of the commercial membrane cellophane membrane and NMMO based membrane was measured around 78.8% and 79.5%, respectively. The crystal-



5 % 8 % 10 %

Fig. 5. Scanning electron micrograph photographs of the membranes prepared from different cellulose concentration with microwave heating with the power of 210 W.

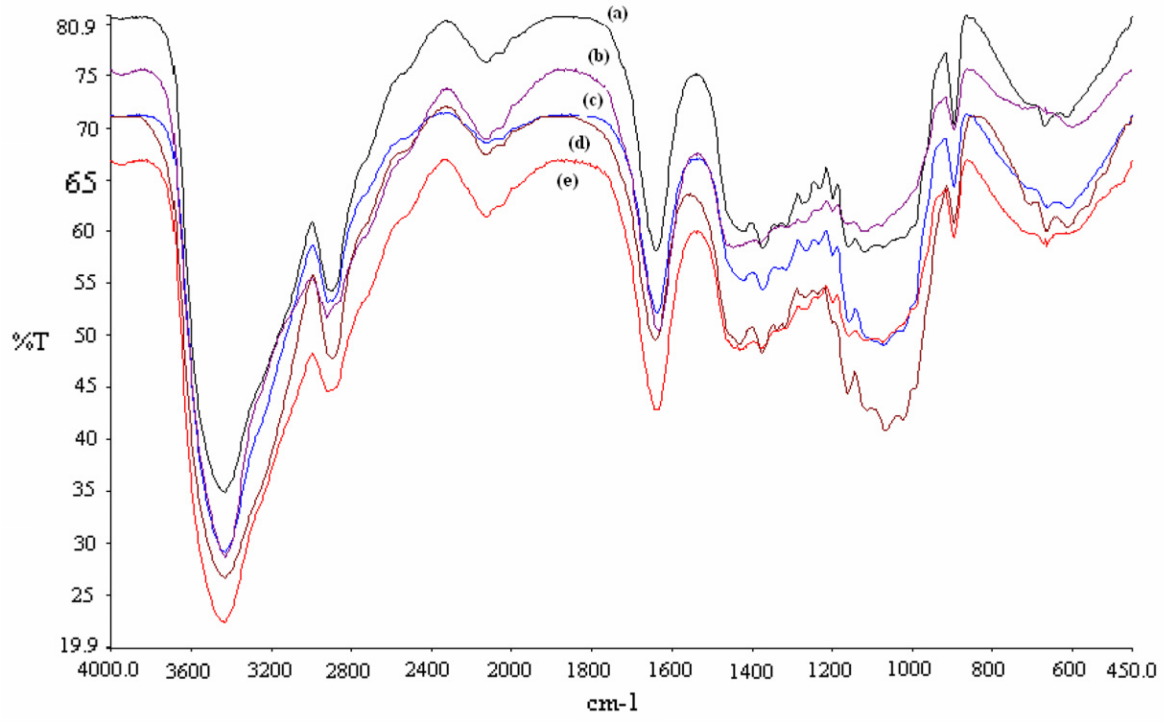


Fig. 6. FT-IR spectra of membranes and linter pulp (a) Linter cellulose (b) 350 W (c) 490 W (d) 105 W (e) 210 W.

Table 2
Degree of crystallinity of membranes

	I_{002}	I_{Amorph}	Degree of crystallinity (%)
Cellophane	88757	18804	78.8
M105W	12516	2619	79.1
M210W	20692	4198	79.7
M460W	10849	2311	78.7
MV	73417	15258	79.2

linity of both membranes does not show any differences as shown in Table 2. The studies carried out by Fink et al. (2001) indicated that crystallinity degree of cellophane and NMMO based membrane have 45% and 40% respectively by using the Ruland-Vonk method.

The difference between the criystallinities can be interpreted with the application of different measurement and calculation method. Thygesen, Oddershede, Lilholt, Thomsen, and Stahl (2005) also showed the differences of four methods (Segal, Ruland-Vonk, Rietveld and Debye) in the determination of cellulose crystallinity. Segal method was based on the intensity measured at two points in the diffractogram and Ruland-Vonk method was based on a separate measurement of an amorphous standard scaled to the diffraction pattern.

The results showed that microwave heating and different microwave powers did not have any effect on the degree of crystallinity.

4. Conclusions

The dissolution of cellulose in NMMO by microwave heating has been investigated. For the last decade it was accepted that microwave heating has an advantage of shortening reaction times, compared with conventional heating. The experiments have shown that cellulose dissolution in NMMO can be efficiently carried out using microwave heating. The dissolution time of cellulose by microwave heating was measured according to the nominal value of water in the solution. Cellulose concentration caused the decrease in the evaporation time of water in the solution because of the content of less water in the solution, whereas no differences observed with the solution of 8% cellulose concentration. Under microwave and vacuum dissolution conditions for the same cellulose concentrations, degree of polymerization data of all membranes are almost the same proving that this heating method reduced the dissolution time and energy consumption. Cellulose/NMMO/water solutions with different cellulose concentrations were converted to the membrane to measure the crystallinity and degree of polymerization. It was showed that microwave heating with the power of 210 W is an alternative heating system for dissolution of cellulose in NMMO.

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