4. MICROWAVE TREATMENT OF CELLULOSE

4.1. Introduction

Microwave heating has been used to disrupt the recalcitrant structures of lignocellulose (Hu and Wen, 2008). Microwave pretreatment could also disrupt the silicon-containing waxy surface which otherwise could inhibit polysaccharide hydrolysis (Ma et al., 2009).

4.2. Microwave chemistry

Since the late 1980s, interest has been growing in the field of microwave-assisted chemistry. Microwave irradiation lies between radio and infrared in the electromagnetic spectrum as shown in the Figure 4.1. The advantage of microwave chemistry is the increased efficiency of heating the material by “microwave dielectric heating effects”, which depends on the ability of a material (solvent or reagent) to absorb the microwave energy and convert it into heat (Gedye et al., 1986).

There are two main mechanisms through which interaction occurs: dipolar polarization and ionic conduction. When polar molecules are exposed to a strong electric field, the displaced positive and negative charges will orientate opposite to the direction of the electric field. Heat is then dissipated as the distortions within the molecule relax to their original orientation. The ability to convert electromagnetic energy into heat under given microwave conditions is strongly dependent on the “loss
Studies on solvolytic structural transformation and degradation of cellulose

factor”, expressed as tan δ. This value is calculated as tan δ = ε* / ε#, where ε* is the dielectric loss, a measure of the efficiency of conversion of electromagnetic energy to heat, and ε# the dielectric constant, which represents the molecule’s ability to be “polarized by the electric field”. A high tan δ value is required for efficient absorption of the microwave energy and hence a greater rate of heating. Microwave energy can also cause a heating effect through ionic conduction.

Microwave chemistry offers many advantages over conventional methods of heating. Overall the process is more energy efficient, as microwave irradiation heats the whole volume of a sample while conventional heating heats the sample in contact with the reaction vessel before the bulk. Unlike conventional heating methods, the heating effect is almost instantaneous, there is no time spent waiting for the source to heat up or cool down. Microwave reactor operating system allows easy control of pressure and temperatures.

4.3. Microwave treatment of cellulose

As microwave heating is a kind of volumetric and rapid heating technique with high efficiency and no temperature gradient, it has been used for organic reactions and the pretreatment of lignocellulosic materials (Zheng et al., 2007; Azuma et al., 1984; Ooshima et al., 1984; Miura et al., 2004; Kitchaiya et al., 2003; Hu & Wen, 2008).

Microwave heating, as an alternative to conventional heating technique, has been proved to be more rapid, uniform and efficient. The development of microwave-assisted chemistry such as synthesis, catalysis, analytical chemistry, etc., has witnessed an explosive growth (Zhang & Hayward, 2006). In particular, there is an increasing interest in the use of microwave irradiation to speed up chemical reactions (Navarro & Stortz, 2005). Microwave radiation lies in the range of the electromagnetic spectrum between infrared and radio frequencies and corresponds to wavelengths of 1 cm to 1 m (frequencies of 30 GHz to 300 MHz). When a molecular is irradiated with microwaves it rotates to align itself with the applied field. The frequency of molecular rotation is similar to the frequency of microwave radiation.
Microwave (MW) heating is a potentially attractive technique as it provides a volumetric heating process at improved heating efficiencies as compared with conventional techniques (Appleton et al, 2005). Microwave irradiation is one of the powerful techniques of non-contact heating, because the dielectric substances with large dielectric loss constant vigorously fever by vibration and rotation of permanent dipoles in microwave field. Microwave has been used for reacting, heating and drying cellulose materials. The microwave energy can easily penetrate to particle inside and all particles can be heated simultaneously, thus reducing heat transfer problems.

In microwave processing, energy is supplied by an electromagnetic field directly to the material. This results in rapid heating throughout the material thickness with reduced thermal gradients. Volumetric heating can also reduce processing times and save energy. The microwave field and the dielectric response of a material govern its ability to heat with microwave energy (Thostenson and Chou, 1999).

In most cases, replacing classical heating by microwave irradiation led to spectacular accelerations, due to the efficient internal heating produced by the direct coupling of microwave energy with the molecules present in the reaction mixture as opposed to a slow and inefficient energy transfer when using classical heating (Kappe, 2008). In addition to the higher speed and efficiency, microwave irradiation also led to more specific and selective reactions. Microwave energy has been recently explored as a potential technology to enhance the pretreatment of various lignocellulosic materials for the production of biofuels (Eskicioglu et al., 2007a,b; Taherzadeh and Karimi, 2008; Alvira et al., 2010; Shi et al., 2011; Jackowiak et al., 2011). It has more rarely been applied to the specific extraction of lignin, either as a pretreatment technique prior to enzymatic mild acidolysis (Zoia et al., 2008) or in combination with ionic liquids (Tan et al., 2009; Sun et al., 2009; Fu et al., 2010).

Environmentally friendly microwave heating was usually applied to the dissolution of cellulose in solution so as to obtain cellulose derivatives and regenerated materials. Antova, et al., (2004) studied the synthesis of cellulose stearate.
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by transesterification of methylstearate with low-molecular microcrystalline cellulose under microwave heating. Sarotti, et al., (2007) reported the microwave-assisted pyrolysis of cellulose into levoglucosenone with high yield.

Dogan and Hlimioglu (2009) reported the dissolution of cellulose with N-methylmorpholine-N-oxide by microwave heating. Possidonio, et al., (2009) reported the microwave-assisted cellulose dissolution in ionic liquids without changing degree of polymerization of microcrystalline cellulose.

Microwave-assisted organic synthesis (Biswal et al., 2007; Takano et al., 2007) has gained popularity in recent years because microwave irradiation was found to accelerate remarkably a wide variety of reactions. Particularly, a solvent-free microwave-assisted reaction provides an opportunity to work with open vessels thus avoiding the development of high pressure and provides a possibility of up-scaling the reaction on a preparative scale and helps the induction of the reaction under dry conditions. Considerable efforts have also been devoted to investigate the modification of polymer materials (Satge et al., 2002; Shogren & Biswas, 2006).

The microwave irradiation has been used in the dyeing processing of cellulose fabric. In the conventional processing of fabric, a large amount of energy is consumed. Some new techniques and methods for saving energy were investigated and microwave is one of them. (Liu et al., 2004; Xie et al., 2007b, 2007c). However, the microwave irradiation could affect the chemical and morphological structure of cellulose, including some physical properties. The report of the effect of microwave irradiation on the physical properties and morphological structure of cellulose was scarce.

Ha et al., (2011) found that microwave heating not only increased cotton cellulose solubility in ionic liquids, but also reduced the degree of polymerization in the regenerated cellulose obtained after the pretreatment compared with pretreatment at 110 °C without microwave. They suggested that internal heating by microwave irradiation was more effective for polar solvents such as ionic liquids. Casas et al. (2012) used microwave successfully as a thermal source to reduce dissolution time required for Pinus radiata and Eucalyptus globulus woods in the following ionic
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liquids: [C\textsubscript{2}mim]OAc, [C\textsubscript{4}mim]OAc, [C\textsubscript{2}mim]Cl, [C\textsubscript{4}mim]Cl, and [Amim]Cl. Despite its advantages, microwave heating also has significant drawbacks. Apart from increased equipment cost and scale-up difficulties, another drawback for microwave heating is that uneven heating may cause pyrolysis of cellulose due to high temperatures (Feng and Chen, 2008).

Hou et al., (2008) investigated the effect of microwave irradiation on the physical property and morphological structure of cotton cellulose, cellulose fabric was treated with microwave irradiation at different conditions. The morphological structures and thermal stabilities of the untreated and treated cellulose were investigated with differential scanning calorimetry (DSC) and X-ray diffraction. The results show that the physical properties of the treated cellulose fabrics were improved and the recoverability had not significant change. The thermal stability of the treated cellulose was changed. The crystallinity and preferred orientation of the treated cotton cellulose increased.

Microwave assisted method has been accepted as an efficient technology in materials preparation, and has various advantages such as reduced energy consumption, high reaction rate, shorter reaction time, enhanced reaction selectivity, and higher product yield (Tsuji et al., 2005).

4.4. Experimental Part

4.4.1. Materials

The cellulose used in the study was fibrous cotton linter, shredded in the form of powder in an ultra-centifugal mill and oven dried. Analytical grade reagents were used as received.

4.4.2. Method

The microwave treatment of cellulose was performed in Erlenmeyer flask (250 ml) by mixing cotton linter with distilled water in the bath ratio 1:100. The microwave used in the study was model no. IFB 30 SC2 of 30 Litres capacity. The microwave of the following technical specifications was used for irradiation: Power
Source at 230V / 50Hz; Power Consumption at 1400 W; Output Power of the microwave was at 900W while microwave frequency worked at 2450MHz. The flasks were kept irradiated for 10 minutes which was repeated 15 times with a break of 10 min. After the microwave irradiation of the samples, it was centrifuged to remove unhydrolysed residue. The supernatant was analysed for the total reducing sugars while residues were air-dried, stored kept in desiccators and was analysed for crystallinity by X Ray Diffraction. Following flow chart at Figure 4.2 demonstrates the procedure for the microwave treatment of cellulose.

![Flowchart](image)

**Figure 4.2. Microwave treatment of cellulose**

### 4.4.3. Total reducing sugar analysis

The estimation of total reducing sugars (%) was carried out by the DNS method (Miller, 1959). 1.0 ml aliquots of the supernatant was placed into the test tubes and 3 ml of DNS reagent was added to it. The mixture was then boiled for 5 min., cooled to room temperature, and 16 ml of distilled water was added to it and mixed well. The absorbance of the samples was recorded at 550 nm. All the absorbance values were measured against a reagent blank in UV–vis spectrophotometer. The concentration of TRS (%) was calculated based on a standard curve obtained with glucose.
4.4.4. Crystal structure measurements

The crystallinity of untreated cotton linter cellulose fibers was examined by wide-angle X-ray diffraction (WAXD) technique, using Ni-filtered Cu Kα radiation (λ = 1.5406Å), equipped with computerized data collection and analytical tools. XRD measurements were performed on a Philips PANalytical X’Pert PRO system in order to estimate the crystalline – amorphous ratio of the initial cellulose samples and of the residues. The X-ray source was operated at a voltage of 45 kV and a filament current of 40 mA. Samples were scanned from 2θ=5º to 2θ=45º with a step size of 0.016º.

4.4.5. Crystallinity index

Crystallinity for the X-ray diffractograms of all samples was analyzed using the empirical procedure of Segal et al., (1959). The calculation of the crystallinity index (Cr. I.) followed the Eq. (1):

\[
\text{Cr.I. (\%)} = \frac{I_{(0,0,2)} - I_{(am)}}{I_{(0,0,2)}} \times 100 \quad \cdots(1)
\]

where \(I_{(0,0,2)}\) is the maximum intensity of diffraction of the (0 0 2) lattice peak at a 2θ angle of between 22º and 23º, and \(I_{am}\) is the intensity of diffraction of the amorphous material, which is taken at a 2θ angle between 18º and 19º where the intensity is at the minimum (Roncero et al., 2005). Taking the Lorentzian distribution function as the shape of the resolved bands, cellulose I and cellulose II components were resolved into four and three reflections, respectively (Oh et al., 2005).

4.5. Results and discussion

4.5.1. Estimation of reducing sugars

The process of microwave treatment of cellulose resulted in the slight degradation of the cellulose molecule. The total reducing sugar (%) obtained for the microwave treatment with a treatment time of 10 min. was about 0.67 ± 0.05% while for control the values obtained were 0.36 ± 0.03% as shown in Table 4.1 and corresponding graphical representation at Figure 4.3.
Table 4.1. Total reducing sugars for microwave treatment of cellulose.

<table>
<thead>
<tr>
<th>Description</th>
<th>Total Reducing Sugars (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Controlled</td>
<td>0.36 ± 0.03</td>
</tr>
<tr>
<td>Microwave treatment</td>
<td>0.67 ± 0.05</td>
</tr>
</tbody>
</table>

Figure 4.3. TRS obtained by the treatment of cellulose with microwave treatment.

4.5.2. Wide-angle X-ray diffraction (WAXD) analysis

The X-ray diffraction pattern of control cotton linters (untreated) is presented in Figure 4.4, which shows a pattern which is quite similar to the native cellulose (cellulose I). The characteristic peaks of the untreated cotton linters are approximately located at 20 = 14.7°, 16.8°, 22.7°, and 34.8°, which are the positions of the (1 0 1), (1 0 –1), (0 0 2) and (0 4 0) crystallographic plane reflections, respectively. The diffractogram (Figure 4.4) revealed a relatively ordered structure with narrow peak at 22.7° (0 0 2) and a diffuse peak between 14.7° and 16.8° (1 0 1 and 1 0 –1). The sharper diffraction peak at 22.7° (0 0 2) indicates region of higher crystallinity. The
linear cellulose molecules are linked laterally by hydrogen bonds to form linear bundles, giving rise to a crystalline structure. Individual fibrillar units consist of long periods of ordered crystalline regions interrupted by completely disordered amorphous regions. The findings are in agreement with observations reported by earlier researchers (Alemdar & Sain, 2008; Berlant & Khalifa, 1991; Chen et al., 2011; Davidson et al., 2004; Ouajai & Shanks, 2005; Quddiani et al., 2011; Sotton et al., 1978).

![Figure 4.4. TRS obtained by the treatment of cellulose with microwave treatment](image)

**Figure 4.4.** TRS obtained by the treatment of cellulose with microwave treatment

### 4.5.3. X-ray diffraction analysis of microwave treated cotton linter

A flow chart at Figure 4.2. mentions the procedure of cotton linter undergone the microwave treatment of cellulose. The characteristic peaks obtained for the cellulose after the microwave treatment were similar to the untreated cotton linters and were approximately at the same position. The minor difference in the height of the characteristic peaks was observed, which resulted in minor decrease in the crystallinity (Figure 4.5). The treatment microwave does not cause much change in the crystal packing of chains of cellulose I (chains aligned in parallel). There is almost
no effect on the structural transformation of cellulose I polymorph of cotton linter undergone the microwave treatment (Figure 4.6).

Figure 4.5. WAXD of cotton linters undergone microwave treatment.

The Crystallinity index decreased for the cellulose treated with microwave as compared to the untreated cellulose. There was a minor decrease in all the characteristic peaks intensity at $2\theta = 14.7^\circ$, $16.8^\circ$, $22.7^\circ$, and $34.8^\circ$ for cellulose I polymorph from control. The crystallinity index of the control and cotton linters treated with microwave was calculated according to the method developed by Segal et al. (1959) and the results are depicted in Table 4.2. The crystallinity index for control cotton linter was observed as 90.8% and for microwave treated cotton linters was 90.1%. There was little and a gradual fall in the height of the characteristic peaks, which resulted in the decrease in crystallinity index. This can be explained by the fact that microwave being a physical parameter alone was unable to dissociate hydrogen bonds available in cellulose I polymorph, leading to no significant change in the cellulose crystallinity which is only of (0.7%). Figure 4.6 shows comparative graphs of cotton linters treated with microwaves and of controlled.
Figure 4.6. WAXD of microwave treated cotton linters & control

Table 4.2. Crystallinity index of the cellulose undergone the treatment

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Treatment</th>
<th>Type of Cellulose</th>
<th>Crystallinity Index (Cr. I.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Untreated cotton linters</td>
<td>I</td>
<td>90.8%</td>
</tr>
<tr>
<td>2</td>
<td>Cotton linters undergone microwave treatment</td>
<td>I</td>
<td>90.1%</td>
</tr>
</tbody>
</table>
4.6. References


