CELLULOSE CHEMISTRY AND TECHNOLOGY

CHARACTERIZATION OF A RAPIDLY FORMED MIXED ESTER OF CELLULOSE BY PHTHALIC ANHYDRIDE AND LOW TEMPERATURE TRANSITION MIXTURE UNDER MICROWAVE IRRADIATION

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This is the first effort to esterify cellulose with phthalic anhydride and a low temperature transition mixture (LTTM) under microwave irradiation. Oxalic acid-choline chloride mixture (OAC) was used as a representative LTTM. Results indicated that cellulose could be very readily esterified under this OAC. Microwave irradiation allowed a rapid esterification reaction within two minutes. Oxalic acid within the OAC participated as both solvent and reagent. Results revealed that the resulting products were actually mixed esters of cellulose formed by oxalic acid and phthalic anhydride. FTIR and elemental analyses indicated that the difference in esterification rate between phthalic anhydride and oxalic acid depended on the concentration of phthalic anhydride and microwave irradiation time. TGA demonstrated that the reaction of cellulose with higher concentration of phthalic anhydride under longer microwave irradiation increased the carbonization rate of the cellulose under thermal exposure, mainly due to acid degradation. Therefore, this study showed a rapid, yet environmentally-benign cellulose esterification could be possible with phthalic anhydride and OAC under microwave irradiation.

Keywords: cellulose, phthalic anhydride, oxalic acid, low temperature transition mixture, microwave irradiation, mixed ester

INTRODUCTION

Cellulose is the most abundant organic material on earth. The utilization and modification of cellulose has drawn much attention due to its excellent properties, such as sustainability, non-toxicity, biodegradability and functionality.[1,2] Various methods for modification of cellulose have been investigated.[3-6] Not a single method can satisfy the objective completely. Thus, the research must be continued.

The replacement of volatile organic solvents by less volatile ones, such as ionic liquids, with negligible vapor pressure, becomes very important.[7-10] However, the most common imidazolium-based ionic liquids are produced from fossil resources and their synthesis process cannot be considered "green". Also, the costs of the production and purification processes are very high.[9,11,12]

To overcome these limitations of ionic liquids, deep eutectic solvents were proposed on the basis of eutectic mixtures of two compounds; hydrogen bond donor and hydrogen bond acceptor.[8,13,14] Hydrogen bond donors include amides, acids, and alcohols, where the hydrogen bond acceptor is mainly choline chloride. By forming hydrogen bonding, these deep eutectic solvents will produce a homogenous liquid of ions with a significant decrease in freezing points.[11] Since some deep eutectic solvents did not show a definite freezing point, they could be also called as low temperature transition mixtures (LTTMs).[15] These LTTMs, unlike conventional ionic liquids, can be easily prepared at low cost with high purity and low toxicity.[15-17]

Microwave-assisted organic modification moved to the forefront of chemical research. The use of microwave irradiation renders a number of advantages over conventional heating, such as non-contact, instantaneous, and rapid heating with high specificity.[3,6,18,19] It is also known that ionic liquids are especially suitable for microwave irradiation due to their high electron-conductivity.[20] The microwaves selectively heat specific phases, followed by subsequent dissipation of energy throughout the body of a material. Consequently, processing times can be 1000 times faster by using microwave heating.[19] In addition, the microwave heating could be 60 to 70% more energy efficient than conventional heating in some processes.[20]

Therefore, the objective of the present study was to firstly examine the feasibility of esterifying cellulose with phthalic anhydride, which is one of the most common reactions, with non-conventional medium, such as choline chloride-based LTTM medium, under microwave irradiation. Especially, oxalic acid-choline chloride LTTM was mainly used as a treatment medium due to the high acidity of oxalic acid that could act as a catalyst too. The LTTM and treated cellulose powder were characterized by using various instrumental methods.

EXPERIMENTAL

Materials

Cellulose powder (Sigmacell type 20, 20 μm), purchased from Aldrich, was used as cellulose substrate. Chemicals, such as oxalic acid ($HOOCCOOH \cdot 2H_2O$), choline chloride and phthalic anhydride, also purchased from Aldrich Chemicals, were reagent grade and used without further purification.

Preparation of LTTM

The LTTMs were prepared as described in the reference;[7] oxalic acid and choline chloride (1:1) were mixed under stirring at 100 °C until a homogeneous liquid was formed (hereinafter, 1:1 oxalic acid:choline chloride LTTM is referred to as OAC). It should be noted that the melting points of oxalic acid and choline chloride are 102 °C and 302 °C, respectively. However, these two solid compounds demonstrated much lower temperature transition (melting, in this case) because of eutectic mixture formation. The OAC prepared was stable as a liquid state for several weeks with proper protection from moisture.

Esterification of cellulose under microwave irradiation

The cellulose powder was placed in the OAC under stirring in an Erlenmeyer flask and an appropriate amount of phthalic anhydride was added. The flask was placed in a commercial microwave oven (Daewoo Electronics, KR-S340TC, 1500 W), equipped with a stirrer to ensure even treatment. The irradiation time was adjusted as a treatment parameter. The temperature of the system was monitored each time. The treated cellulose powder was washed with 1% NaOH, and rinsed several times with deionized water until it reached a neutral pH. The esterified powder was air-dried and then stored in a standardized chamber (21 ± 1 °C, 65% ± 2% relative humidity) for at least 24 hours before further analyses.

Characterization of LTTM and treated cellulose

A Fourier transform infrared (FTIR) spectroscope with an attached ATR (Bruker, Vertex 70, USA) was used to analyze OAC and esterified cellulose in the spectral region of 4000-600 cm^{-1} with 64 scans at 4 cm^{-1} resolution. A differential scanning calorimeter (DSC, Perkin Elmer, USA) was used to study the thermal characteristics of OAC with a 20 cm^3/min flow of nitrogen at a heating rate of 10 °C/min. The OAC was cooled to -65 °C and heated up to 10 °C. The crystalline structure of the cellulose powder was evaluated by X-ray diffraction (XRD, Bruker, D2 Phaser, Germany) at 30 kV and 10 mA, with 1 minute scanning time, 0.02 increment, and 5-75 2θ range. The thermal characteristics of the cellulose powder were investigated by thermogravimetric analysis (TGA, Mettler, USA). Scanning electron microscopy (SEM) (COXEM, CX-100S, Korea) was employed to study the effect of the treatment on topological characteristics of the cellulose powder. Elemental analysis (Euro Vector E, E/V RE2) was used to determine the amounts of carbon and oxygen in esterified cellulose.

RESULTS AND DISCUSSION

Characterization of OAC and phthalic anhydride

Figure 1 shows a homogeneous liquid state of OAC. A carbonyl stretching peak for oxalic acid was observed at 1724 cm^{-1} in the FTIR spectrum, which showed a hypsochromic shift. The position of this peak was higher than 1690 cm^{-1}, commonly found in a hydrogen-bonded carbonyl of oxalic acid. The hypsochromic shift could be due to two reasons: first, potential esterification of at least one of the two carboxylic acid groups in oxalic acid with a hydroxyl group of choline chloride, or second, the presence of the Cl^- ion, a hydrogen bonding acceptor, in choline chloride preventing intra- or intermolecular hydrogen bond formation in oxalic acid.

We also examined OAC using DSC analysis, as shown in Figure 2. Upon heating of the OAC from -65 °C, two exothermic peaks were observed with onset temperatures of -51 °C and -41 °C. The first onset peak was small and the second peak was more prominent. This type of thermal behavior was consistent with crystallization of a glass state that was followed by melting.[21] Similar thermal behavior was also observed in other LTTM, such as choline chloride-glycerol mixture.[22]

As shown in Figure 3, the FTIR spectrum of phthalic anhydride shows two anhydride carbonyl stretching peaks at 1841 cm^{-1} (unsymmetric) and 1755 cm^{-1} (symmetric) along with aromatic –C=C- at 1594 cm^{-1} and 1462 cm^{-1}, whereas the absorption peaks in the region 897 ~ 705 cm^{-1} could be assigned to out-of-plane bending of carboxyl groups attached directly to the aromatic ring of phthalic anhydride.[2] The presence of these peaks in the FTIR spectrum was used to evaluate the reaction of phthalic anhydride with cellulose.

Esterified cellulose with 1 mole of phthalic anhydride

Figure 4 shows the FTIR spectrum of untreated, pristine cellulose powder. The absorption peaks, such as that at 3331 cm^{-1} for O-H stretching, at 2890 cm^{-1} for C-H stretching, at 1636 cm^{-1} for bending mode of the absorbed water, at 1323 cm^{-1} for O-H bending, at 1154 cm^{-1} for C-O stretching, at 1025 cm^{-1} for C-O-C pyranose ring skeletal vibration, and at 896 cm^{-1} for β-glycosidic linkages between the sugar units, were all related to the typical cellulose molecules.[23] On the other hand, Figure 5 illustrates the FTIR spectra of the esterified cellulose by 1 mole of phthalic anhydride under OAC LTTM medium at various microwave irradiation times. Ester carbonyl stretching peaks were observed at 1738 ~ 1712 cm^{-1} and typical anhydride carbonyl stretching peaks shown at 1841 cm^{-1} and 1755 cm^{-1} in phthalic anhydride (Fig. 3) disappeared in the treated cellulose, indicating the occurrence of the esterification reaction. An analysis of the spectra, however, revealed that the positions of the carbonyl stretching peaks were slightly different at various microwave irradiation times, *i.e.*, 1720 cm^{-1}, 1738 cm^{-1} and 1712 cm^{-1} for 30, 60 and 120 seconds, respectively.

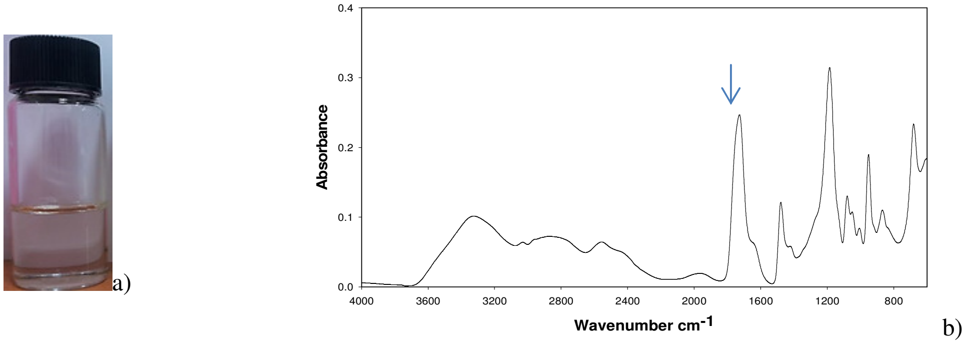


Figure 1: A clear liquid state (a) and FTIR spectrum (b) of OAC

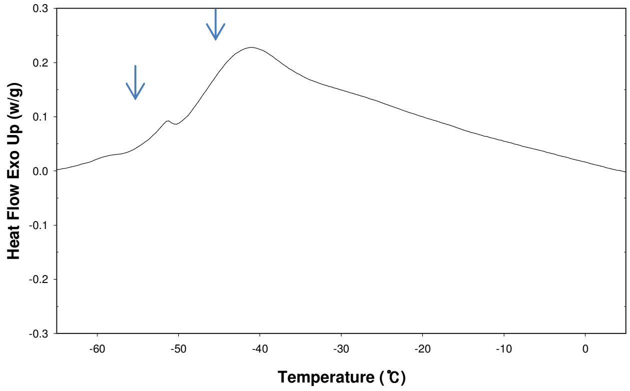


Figure 2: DSC thermogram of OAC

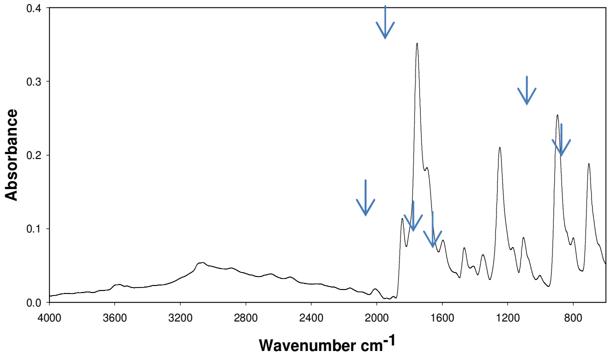


Figure 3: FTIR spectrum of phthalic anhydride

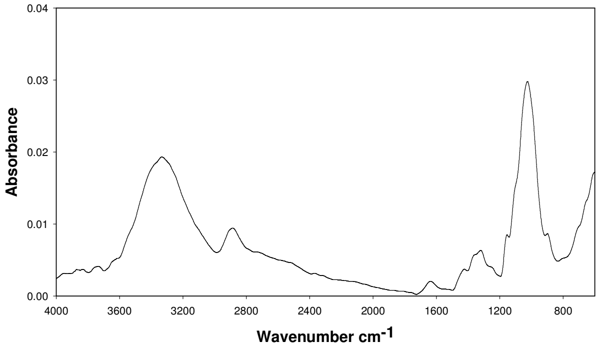


Figure 4: FTIR spectrum of untreated, pristine cellulose powder

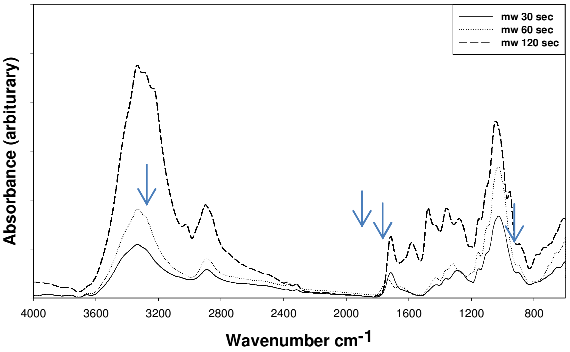


Figure 5: FTIR spectra of esterified cellulose by phthalic anhydride (1 mole) under OAC medium at various microwave irradiation times

The peaks at 1738 cm^{-1} and 1720 cm^{-1} were believed to be due to esterified cellulose with oxalic acid since the absorption peak for aromatic –C=C- was not found in the phthalic anhydride-modified cellulose specimens irradiated for 30 and 60 seconds. On the other hand, the FTIR spectrum of cellulose treated with 1 mole of phthalic anhydride and irradiated at 120 seconds showed clear evidence of phthalic anhydride-cellulose esterification by several absorption peaks: 1712 cm^{-1} for the ester carbonyl peak with aromatic ring conjugation, 1587 cm^{-1} for the aromatic –C=C- stretching peak, 3026 cm^{-1} for aromatic -C-H stretching, and 782 cm^{-1} for the aromatic out-of-plane bending peak, as shown in Figure 3. These results suggested that the esterification of cellulose with 1 mole of PA occurred only at 120 seconds of microwave irradiation.

To confirm the esterification reaction between cellulose and oxalic acid in OAC, cellulose was treated by OAC alone in the absence of phthalic anhydride. As illustrated in Figure 6, the cellulose clearly revealed the evidence of esterification with oxalic acid, by showing an ester carbonyl peak at 1735 cm^{-1}. This substantiated that oxalic acid participated at the esterification reaction as both reactant and solvent (and probably, as a catalyst as well). The easy esterification reaction between cellulose and oxalic acid was probably due to its high acidity with lower pK$_a$ values, 1.23 for pK$_{a1}$ and 4.19 for pK$_{a2}$, than those of phthalic anhydride.

Two possible reactions could have occurred during the esterification of phthalic anhydride or oxalic acid with cellulose molecules: one is a single site reaction, leading to a monoester with a carboxylic pendant group (-COOH) and/or the formation of a diester without a pendant carboxylic group.[2] However, because of the complexity of the system including oxalic acid and phthalic anhydride, the separation of two peaks (ester carbonyl *vs.* acid carbonyl) was difficult.

Esterified cellulose with 2 moles of phthalic anhydride

The spectra of cellulose treated with 2 moles of phthalic anhydride shown in Figure 7 are quite similar to those for the treatment with 1 mole of phthalic anhydride, but the small shoulder at 1641 cm^{-1} for aromatic –C=C- was observed even for 30 seconds of microwave irradiation, in addition to the ester carbonyl stretching peak at 1735 cm^{-1}. This indicated that at high concentration of phthalic anhydride, esterification with both oxalic acid and phthalic anhydride occurred with cellulose for 30 seconds of microwave irradiation time.

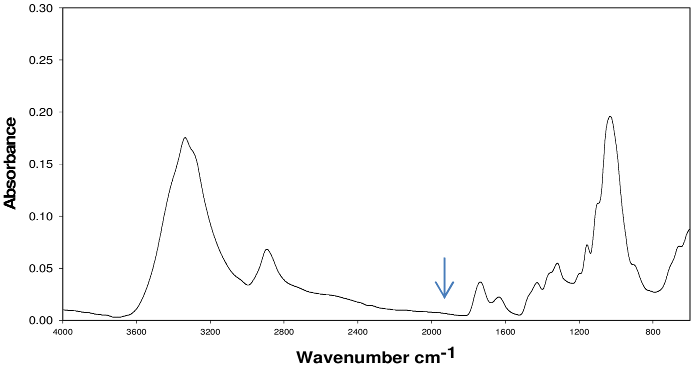


Figure 6: FTIR spectrum of cellulose treated by OAC for 60 seconds of microwave irradiation time (no phthalic anhydride)

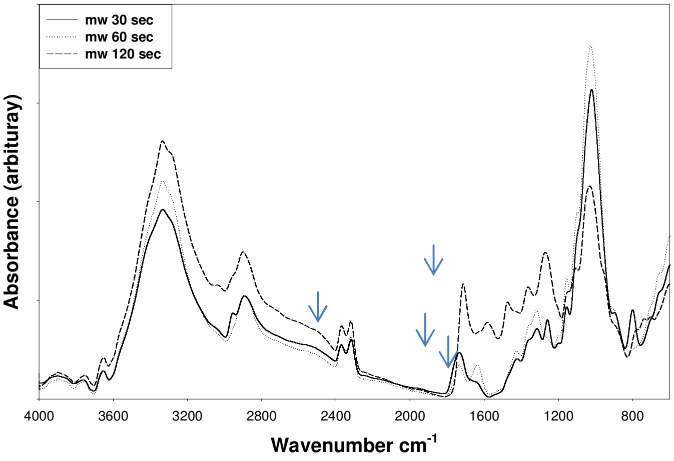


Figure 7: FTIR spectra of esterified cellulose by 2 moles of phthalic anhydride under OAC medium for various microwave irradiation times

Table 1
Peak height ratios of cellulose treated by phthalic anhydride and OAC for different microwave irradiation times

Concentration of PA[a]	Microwave (seconds)	Peak height ratio (1735 cm^{-1}/1716 cm^{-1})
1 mole	30	0.528
	60	0.424
	120	0.383
2 moles	30	0.555
	60	0.528
	120	0.399

[a]phthalic anhydride

With an increase of irradiation time to 60 seconds, ester carbonyl stretching at 1728 cm^{-1} and aromatic –C=C- at 1637 cm^{-1} were easily observed. With 120 seconds of microwave irradiation time, the wavenumber of the ester carbonyl stretching peak shifted to a lower energy region to 1716 cm^{-1}, due to an increase in cellulose esterification with phthalic anhydride, and the peak intensity increased considerably.

By using height ratios of two different ester carbonyl stretching bands, *i.e.*, 1735 cm^{-1} for esters carbonyl formed by oxalic acid and 1716 cm^{-1} for esters formed by phthalic anhydride, we assessed a composition of mixed esters within the treated cellulose molecules. As shown in Table 1, peak height ratios were continuously decreased with increase in microwave irradiation time and this trend was observed at both phthalic anhydride concentrations. In addition, these ratios were slightly higher at 2 mole of phthalic anhydride. This clearly confirmed that esterification of cellulose was more favorable with phthalic anhydride at prolonged microwave irradiation and higher concentration of phthalic anhydride.

When cellulose was added into OAC, a turbid milky white solution was observed and turbidity remained with an increase in time. This indicated that cellulose was insoluble in the OAC. It is known that LTTM, like OAC, has low hydrogen bond basicity, as can be seen in the low value of its Kamlet Taft parameter, β (0.42), and thus does not dissolve cellulose.[22] On the other hand, an ionic liquid with high β (0.92), such as 1-butyl-3-methyl immidazolium chloride, was able to dissolve cellulose molecules. The reaction rate of phthalic anhydride would be much faster than that of oxalic acid in a homogeneous reaction. However, this esterification reaction under OAC medium was a heterogeneous reaction, resulting in the availability of oxalic acid and phthalic anhydride near cellulose, the hydroxyl group became a very important factor in determining the reaction rate. Since oxalic acid has a much smaller molecule than phthalic anhydride, the reaction of cellulose was toward oxalic acid at an initial stage. The esterification of cellulose, however, tended to shift into phthalic anhydride at longer microwave time and higher concentration. This enhancement of the esterification at longer microwave irradiation was most likely due to greater diffusion of phthalic anhydride into cellulose by increasing its mobility and swelling of cellulose molecules in OAC.[23]

It should be also noted that when cellulose was treated by phthalic anhydride under OAC with microwave irradiation, small doublet peaks at 2380 cm^{-1} and 2318 cm^{-1} appeared. These peaks were very weak at 1 mole of phthalic anhydride, but the intensity was substantially increased at 2 moles of phthalic anhydride. In addition, the peaks at 2372 cm^{-1} and 2316 cm^{-1} increased with an increase in microwave irradiation time from 30 seconds to 120 seconds under these conditions. These peaks were believed to be an amino acid zwitterion because of the presence of three components within the system, *i.e.*, phthalic acid, oxalic acid, and choline chloride. This again suggested that OAC acted as both solvent and reagent.

The XRD study also revealed that OAC did not modify the crystalline structure of cellulose molecules under microwave irradiation, as shown in Figure 8. This also re-confirmed that the reaction of phthalic anhydride with cellulose under OAC was a heterogeneous reaction. In addition, no substantial differences were observed in surface morphology of cellulose after esterification under OAC and microwave irradiation, as seen in the SEM micrographs in Figure 9.

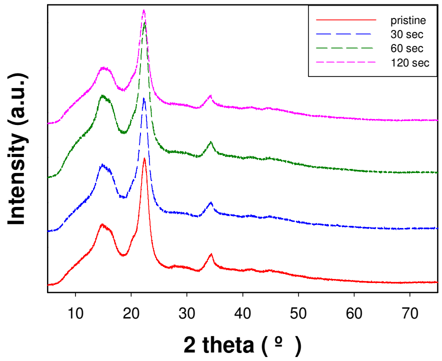


Figure 8: XRD of esterified cellulose with 2 moles of phthalic anhydride under OAC medium at various microwave irradiation times

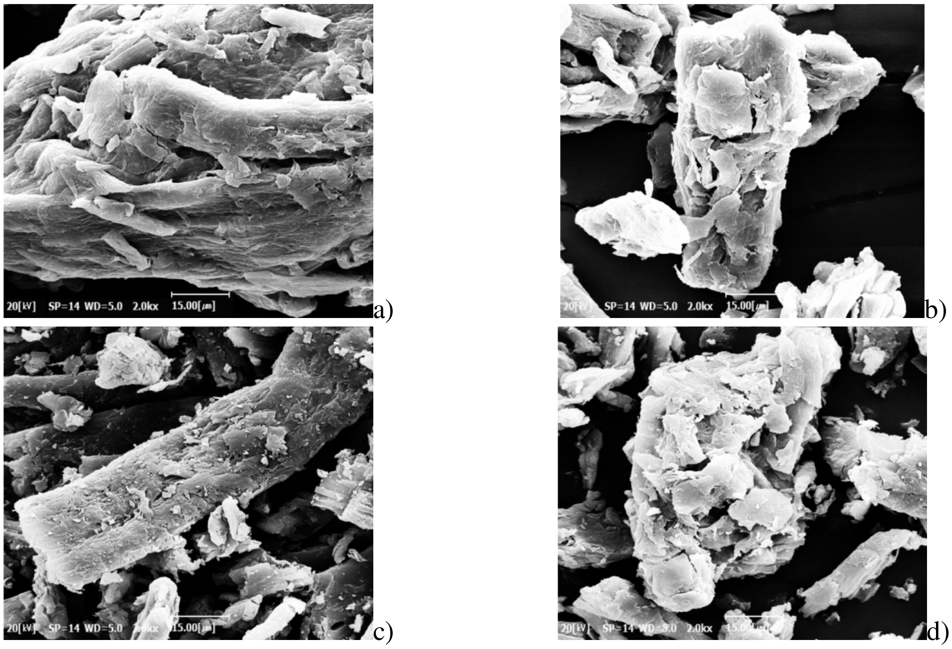
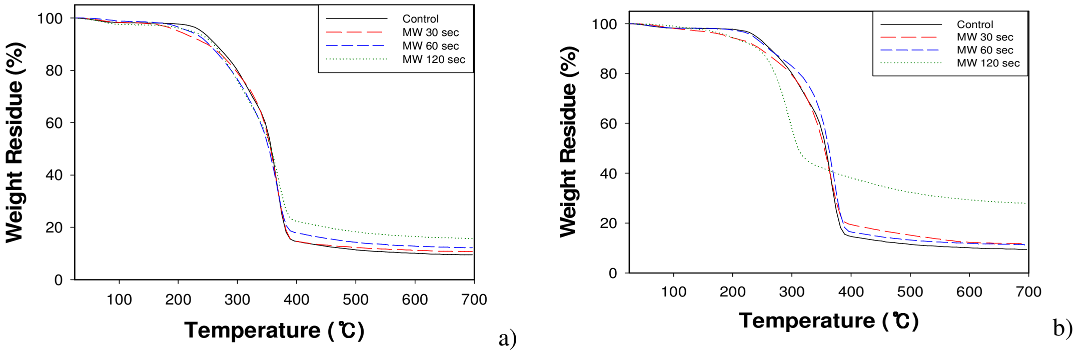


Figure 9: SEM micrographs of esterified cellulose with 2 moles of phthalic anhydride under OAC at various microwave irradiation times; (a) pristine, (b) 30 seconds, (c) 60 seconds and (d) 120 seconds



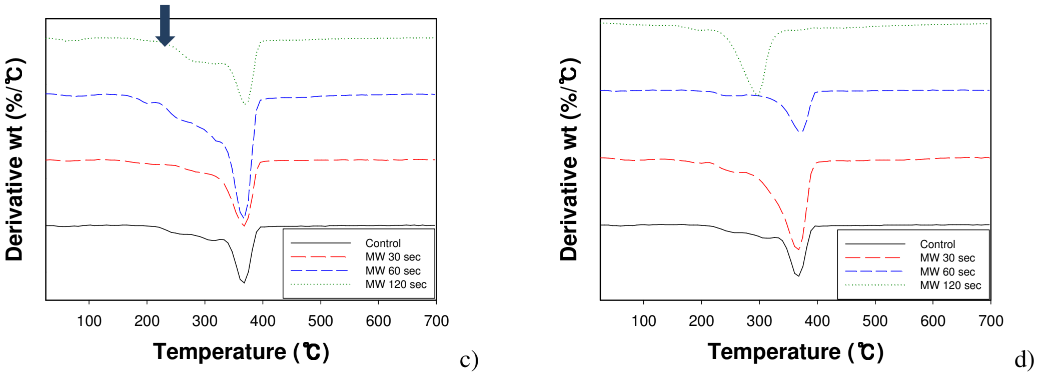


Figure 10: TGA and 1st derivative curves of cellulose treated by phthalic anhydride under OAC medium at various microwave irradiation times: (a) and (c) 1 mole of phthalic anhydride, (b) and (d) 2 moles of phthalic anhydride

TGA analyses of esterified cellulose

Figure 10 illustrates the thermal characteristics of cellulose treated by phthalic anhydride under OAC at different microwave irradiation times. It should be noted that a control sample was also irradiated for 60 seconds by microwaves under OAC in the absence of phthalic anhydride. The results in Table 2 reveal that the residues (%) at 700 °C of cellulose treated with phthalic anhydride were increased with an increase in microwave irradiation time at each concentration of phthalic anhydride. On the other hand, a little disparity appears in the peak temperature of the 1st derivative curve (T_p) due to the reaction with 1 mole of phthalic anhydride. Nevertheless, the 1st derivatives of the TGA curves indicated that the thermal decomposition of cellulose was initiated at much lower temperature at 120 seconds of microwave irradiation, even by the treatment with 1 mole of phthalic anhydride. The same phenomena were also observed in the T_p of cellulose treated with 2 moles of phthalic anhydride. Contrarily, the cellulose sample treated with 2 moles of phthalic anhydride at 120 seconds of irradiation showed quite different results, as indicated by the considerable decrease in T_p and the increase in % residue. The inflection point, T_p, indicates the points of greatest rate change in the weight loss curve. Therefore, this clearly indicates that the reaction of cellulose with higher concentration of phthalic anhydride under longer microwave irradiation increased the carbonization rate of the cellulose under thermal exposure, mainly due to acid degradation. Similar results were obtained with cotton fabrics treated by polycarboxylic acid at an elevated temperature.[3,6]

Furthermore, there was a possibility of forming crosslinks between two adjacent cellulose chains by dicarboxylic acids, such as phthalic anhydride and oxalic acid. This could increase the % residue observed at higher concentration of phthalic anhydride and longer microwave irradiation time, even with faster degradation.

Table 2
TGA analyses of cellulose treated by phthalic anhydride and OAC at different microwave irradiation times

Specimen	Microwave (seconds)	%Residue at 700 °C	T_p[a], °C
OAC-treated	60	9.46	368
	30	10.7	368
1 mole PA	60	12.2	367
	120	15.7	369
	30	11.7	368
2 moles PA	60	11.3	368
	120	27.9	298

[a] T_p is the peak point in the 1st derivative of the weight loss curve

Table 3
Elemental analysis results of esterified cotton fabrics with phthalic anhydride and OAC under microwave irradiation

Cotton	Microwave time (s)	Elemental composition (%)			
		C	H	O	O/C ratio
Pristine	--	46.8±0.2	6.2±0.2	40.9±0.2	0.87
2 moles phthalic anhydride	30	47.3±0.3	6.4±0.1	41.2±0.3	0.87
	60	48.1±0.2	6.3±0.2	40.7±0.2	0.85
	120	50.2±0.4	6.3±0.2	41.0±0.3	0.82

Elemental analyses of esterified cellulose

Elemental analyses of cotton fabric showed that the O/C ratios were generally close to the theoretical O/C ratio of cellulose (0.83) reported in the literature.[2] It must be pointed out that two opposite effects could contribute to the O/C ratio; esterification of cellulose molecule with oxalic acid tended to increase the O/C ratio, whereas esterification with phthalic anhydride decreased the O/C ratio. Because of these two contrary effects, the decrease in the O/C ratio by carbon-rich phthalic anhydride esterification was only marginal at 60 and 120 seconds microwave irradiation, as shown in Table 3.

CONCLUSION

An esterification of cellulose by phthalic anhydride with eco-friendly LTTM under microwave irradiation was carried out and the esterified cellulose was characterized. The OAC mixture was used as a representative LTTM. Results indicated that cellulose was easily esterified under these conditions. Microwave irradiation with LTTM allowed a rapid esterification of cellulose within two minutes. Oxalic acid in the LTTM participated at the reaction both as solvent and reagent (maybe, also as catalyst). Therefore, the resulting products were actually mixed esters of cellulose by phthalic anhydride and oxalic acid.

FTIR and elemental analyses indicated that the difference in the esterification rate between phthalic anhydride and oxalic acid depended on the concentration of phthalic anhydride and on the microwave irradiation time. Therefore, at 1 mole of phthalic anhydride, the cellulose was mainly esterified with oxalic acid for 30 and 60 seconds of microwave irradiation time, whereas cellulose esterification with phthalic anhydride only occurred for 120 seconds. Contrarily, with 2 moles of phthalic anhydride the evidence of cellulose esterification with phthalic anhydride appeared even for 30 seconds of microwave irradiation time. TGA demonstrated that the cellulose sample treated with 2 moles of phthalic anhydride at 120 seconds of irradiation showed a considerable decrease in T_p (inflection point) and an increase in % residue. This clearly revealed that the reaction of cellulose with higher concentration of phthalic anhydride under longer microwave irradiation increased the carbonization rate of the cellulose under thermal exposure, mainly due to acid degradation.

Therefore, this study showed that a rapid microwave-assisted cellulose esterification is feasible with phthalic anhydride for two minutes using an environmentally-benign solvent, LTTM.

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