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MODIFICATION OF MICROCRYSTALLINE CELLULOSE FILLER WITH SUCCINIC ANHYDRIDE - EFFECT OF MICROWAVE AND CONVENTIONAL HEATING

In this work the microcrystalline cellulose (MCC) filler was chemically modified by esterification with succinic anhydride (SA) in order to improve the compatibility of MCC with the hydrophobic polymer matrix. The effect of the microwave irradiation and conventional heating on the chemical structure, particle morphology and thermal stability of the cellulosic filler was evaluated by FTIR/ATR, TGA and light microscopy. The extent of surface modification of microcrystalline cellulose gradually increased with an increasing reaction time up to 90 min, and the effect was significantly pronounced under microwave irradiation as compared to conventional heating. A decreasing decomposition temperature was observed for the samples modified with SA as compared to the reference sample as a result of introducing functional side groups into the cellulose backbone and developing the surface of the MCC powder. A decrease in MCC particle sizes was observed as a result of chemical modification, especially under microwave irradiation, indicating partial hydrolysis of the amorphous regions of cellulose in an acidic environment. Smaller particles can be more equally dispersed in a polymer matrix. Applying microwave irradiation enhanced the efficiency of surface modification and produced MCC with a wider range of surface properties. Microcrystalline cellulose with adjusted surface properties can be applied as a reinforcing filler for fully biodegradable 'green' composites.

Keywords: microcrystalline cellulose, surface modification, esterification, microwave, succinic anhydride, natural filler, biocomposites

MODYFIKACJA MIKROKRystalicznej CELULOZY JAKO NAPEŁNIACZA POLIMEROWEGO ZA POMOCĄ BEZWODNIKA BURSZTYNOWEGO - WPŁYW OGRZEWANIA KONWENCJONALNEGO ORAZ MIKROFALOWEGO

Przedstawiono wstępne badania nad chemiczną modyfikacją mikrokrystalicznej celulozy przez estryfikację bezwodnikiem bursztynowym w celu poprawy jej kompatybilności z hydrofobowymi osnowami kompozytów polimerowych. Określono wpływ prowadzenia syntezy w polu promieniowania mikrofalowego oraz w warunkach ogrzewania konwencjonalnego na strukturę chemiczną, rozmiary cząstek i stabilność termiczną napelnacza celulozowego, stosując metody FTIR/ATR, TGA oraz mikroskopię optyczną. Efektywność estryfikacji MCC bezwodnikiem bursztynowym rosła z czasem reakcji do 90 min i była wyraźnie większa w warunkach pola promieniowania mikrofalowego w porównaniu z ogrzewaniem konwencjonalnym. Obserwowano obniżenie temperatur degradacji modyfikowanej MCC w porównaniu z materiałem niemodyfikowanym na skutek wprowadzenia bocznych grup funkcyjnych w łańcuch celulozy i rozwinięcia powierzchni ziaren MCC. Zmniejszenie rozmiarów ziaren napelnacza na skutek modyfikacji chemicznej, szczególnie w warunkach ogrzewania mikrofalowego, wskazywało na zachodzenie częściowej hydrolizy obszarów amorficznych celulozy w kwaśnym środowisku reakcji. Mniejsze cząsteczki potencjalnie umożliwiają uzyskanie bardziej równomiernej dyspersji napelnacza w osnowie polimeru. Prowadzenie reakcji estryfikacji w warunkach pola mikrofalowego umożliwi uzyskanie napelnacza o większym stopniu zmodyfikowania powierzchni, a przez to wytwarzanie MCC o szerszym zakresie właściwości powierzchniowych i jej zastosowanie jako napelnacza wzmacniającego w całkowicie biodegradowalnych kompozytach polimerowych.

Słowa kluczowe: mikrokrystaliczna celuloza, modyfikacja powierzchniowa, estryfikacja, ogrzewanie mikrofalowe, bezwodnik bursztynowy, naturalne napelnicze, biokompozyty

INTRODUCTION

Nowadays, materials from renewable sources can be successfully used to replace the shrinking petroleum resources. Among others, the increasing global demand for the discovery of natural and biodegradable components induces the development of environmentally

friendly polymeric composites. Numerous branches are interested in products from various renewable raw materials, for example the automobile industry [1]. Cellulose, as the most abundant organic polymer, is widely used as a reinforcing filler in order to obtain

'green' composites [2]. Cellulose is a homopolymer consisting of anhydroglucose units, each joined by $\beta(1-4)$ -glycosidic linkages, with strong inter- and intramolecular hydrogen bonding [3]. It is also characterized by a high degree of crystallinity. Unfortunately, the hydrophilic character of this material causes certain limitations in dispersing it in most hydrophobic polymer matrices. In order to enhance the compatibility of a cellulose filler, chemical modification is often required [4].

In the classical synthesis of cellulose derivatives, the esterification of cellulose can be performed under both heterogeneous and homogeneous reaction systems [3]. Typically, most cellulose reactions are carried out as heterogeneous reactions, due to the two-phase structure of cellulose, which is composed of crystalline and amorphous areas [4]. The hydroxyl groups in the amorphous region more easily react with various chemicals, but the crystalline areas are not freely accessible because of their close packing and extensive hydrogen bonding. Therefore, the reaction occurs mainly in the amorphous phase and on the surface of crystallites.

Microcrystalline cellulose (MCC) is widely used in many industries. For example, in cosmetics or pharmaceutical industries it is used as a suspension stabilizer and as a reinforcing filler for tablets [5]. MCC is a purified, partially depolymerized form of cellulose that occurs as a white, odorless and crystalline powder composed of porous particles. MCC can be made from any natural material with a high cellulose content. For example, coconut shells [6], ramie fibers [7] or wheat and rice straws [8, 9] have been studied as raw materials for MCC synthesis. Cellulose from different sources differs in properties such as crystallinity, surface area, porous structure, molecular weight, etc. [5]. Acid or base mild hydrolysis is commonly used as a pretreatment method in preparing MCC from different cellulose materials [10]. Mineral acids, such as sulphuric or phosphoric acid, are commonly used as hydrolysis agents [11].

The hydroxyl groups of cellulose can be esterified by reaction with acids or anhydrides, including succinic anhydride. The scheme of cellulose esterification with succinic anhydride is shown in Figure 1. The reaction of cellulose with a cyclic anhydride, such as succinic anhydride, does not yield a by-product, leaving the modified polymer with covalently bonded carboxylic groups. In the case of a reaction at temperatures above 100°C, the formation of diesters was observed, which resulted in cross-linking within the cellulose chains [4].

Generally, the esterification reaction of cellulose which receives energy by the conventional heating method takes longer periods of time for the reaction to be completed than microwave radiation, which proved to be a more effective heating source in chemical reactions. Therefore, microwave irradiation has drawn the attention of numerous researchers in recent years. The effectiveness of microwaves as a heating source and its promoting effect on the reaction extent has been widely examined. Several studies have focused on the esterification of cellulose under microwave heating [12-14]. For example the study carried out by Ratanakamnuanet et al. [3] showed a considerable decrease in the reaction times of cellulose esterification using different fatty acid chlorides, including butyryl chloride (C4), capryloyl chloride (C8), and lauroyl chloride (C12). The results showed that the optimum times for esterification with C4, C8, and C12 under conventional heating were 2 h at 100°C, 12 h at 80°C, and 12 h at 60°C, respectively, while the optimum conditions for MCC esterification with C4, C8, and C12 under microwave heating irradiation were 60 s at 360 W, 60 s at 270 W, and 150 s at 180 W, respectively.

In the current work the influence of microwave irradiation and conventional heating on the reaction efficiency, particle morphology and thermal stability of the filler was studied in the process of chemical surface modification of microcrystalline cellulose filler with succinic anhydride. The progress of the reaction was monitored by the FTIR method.

MATERIALS AND METHODS

A. Materials

Microcrystalline cellulose (MCC), trade name UFC100 (Ultrafine Cellulose), used in this work was purchased from JRS Rettenmaier and Söhne GmbH+ Co KG, Germany. The material had the form of a loose, white and odorless powder with an average diameter of 8 μm , as supplied by the manufacturer. The reagent grade succinic anhydride (SA) was provided by Sigma Aldrich and used as received to modify MCC. It was in the form of white crystals with a pungent odor. An organic solvent - anhydrous reagent grade dimethylformamide (DMF), used as the reaction environment, was produced by Avantor Performance Materials Poland. Anhydrous pyridine (99.8%) provided by Sigma Aldrich was used as the esterification catalyst.

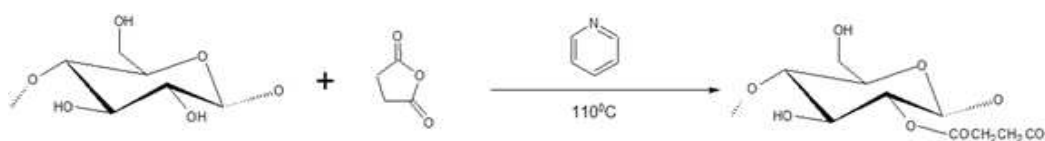


Fig. 1. Scheme of cellulose esterification with succinic anhydride

Rys. 1. Schemat reakcji estyfikacji celulozy bezwodnikiem bursztynowym

B. Laboratory equipment

The Milestone multimodal microwave reactor model RHS-2 with an integrated control program MODEL 320 was used to generate microwave heating.

Centrifugation was used to separate the solvents and unreacted modifier from the solid modified MCC product. For this purpose, a laboratory centrifuge model MPW-531 from MPW Med. Instruments was used.

The ultrasonic homogenizer SONIC RUPTOR 250 produced by the Omni International company, USA, was used at 50% power and for 10 min in order to obtain a water suspension of MCC and break down the residual agglomerates.

Freeze drying of previously frozen substances was carried out using a lyophilizer FreeZone Plus 2.5 from Labconco. This process allowed structural changes in the obtained material to be avoided that could occur as a result of cellulose hornification.

C. Sample preparation

The 2% cellulose suspension was prepared as follows: 0.5 g of dry MCC and 16 ml of DMF were placed in a 100 ml three-necked flask with the stirrer in place. The flask was placed in a heating bowl with an integrated thermocouple and inert gas was connected. Initially, the reaction mixture was heated to 90°C. 10 ml of DMF was placed in a separate beaker and 4.63 g of succinic anhydride was dissolved therein. When the heated mixture reached the set temperature, the contents of the beaker were added to it, and then 0.026 ml of pyridine as the catalyst was quickly added. When using microwave irradiation, the flask was immediately placed in the microwave reactor. The control temperature program consisted of two segments: a 0.5 min dynamic segment at 350 W and then an isothermal segment at 200 W. If a conventional heating method was applied the reaction mixture was heated to 110°C. In both heating methods samples of MCC were taken after: 10, 20, 30, 45, 60, 90 and 120 minutes. Each sample was centrifuged, DMF and the excess SA was decanted and the precipitate was then sonicated for 10 minutes in distilled water. Next the modified cellulose was put into dialysis membranes for 4 days. Afterwards, the samples were sonicated again and frozen with liquid nitrogen. All the samples were freeze dried under vacuum at -82°C for another 4 days and then kept in desiccators prior to each analysis. MCC acetylation was performed using an excess of succinic anhydride (SA) (1 mole of cellulose hydroxyl groups to 5 moles of succinic anhydride).

The scheme of the cellulose esterification reaction with succinic anhydride is shown in Figure 1. The SA content in the cellulose product was monitored as a function of reaction time so the names of samples go as follows: for the conventional heating method (K): MC-K10, MC-K20, MC-K30, MC-K45, MC-K60, MC-K90, MC-K120; for microwave irradiation (M): MC-M10, MC-M20, MC-M30, MC-M45, MC-M60,

MC-M90, MC-M120. The numbers in the sample denotations stand for the reaction time.

D. Characterization methods

Fourier transform infrared spectra (FTIR) were recorded on the freeze dried cellulose using a Thermo Scientific spectrophotometer Nicolet iS5, operating in the attenuated total reflectance mode (ATR) with 16 scans and a resolution of 8 cm⁻¹.

The morphology of the MCC particles was observed by a light microscope (Delta Optical SZ-630 T) at magnifications of forty-fold to detect larger particles and to get an overview of the sample sizes on the microscopic level.

Thermogravimetric analysis (TGA) was performed by means of a Netzsch 209F1 Libra thermal analyzer, operating in the dynamic mode at the heating rate of 10 K/min from 30 to 600°C in the atmosphere of synthetic air. The sample mass was ca. 3.6 mg, measured in open α -Al₂O₃ crucibles.

RESULTS AND DISCUSSION

FTIR/ATR analysis

The comparison of the absorbance FTIR spectra of the reference sample and the post-reaction samples evidenced the presence of ester groups and differences in the esterification extent. The full spectrum for modified MCC is shown in Figure 2 (2a - conventional heating, 2c - microwave irradiation). For the sake of better visualization, the spectra are presented in the spectral range of 1800÷1650 cm⁻¹ in Figure 2b and 2c for conventional and microwave heating, respectively.

The FTIR spectra of MCC modified with SA showed a group of new distinctive peaks as compared with the spectrum of MC-REF, which proves partial esterification of MCC. The new peak at 1725 cm⁻¹ may be related to the stretching vibrations of the carbonyl group (ν C = O).

The intensity of that new peak in the spectra of the microwave samples modified with SA initially increased with the reaction time up to 90 min and then leveled at a constant value for the last two samples with the longest reaction time (Fig. 2d). This indicated that the maximum reaction time after which the degree of cellulose substitution does not change further was reached after 90 min. The alterations in the intensity of carbonyl absorption bands of the MCC esters reflect the changes in the substitution degree of cellulose [15]. Increased absorption at 1725 cm⁻¹ was consistent with the increased intensity of absorption at 1240 cm⁻¹, which originates from the stretching vibrations of the C-O bond in the ester group [16].

The carbonyl absorption bands in the MCC modified under conventional heating (Fig. 2b) were significantly weaker as compared to that modified under microwave irradiation (Fig. 2d). A prolonged time of the

reaction did not cause a significant increase in the extent of esterification (Fig. 2b).

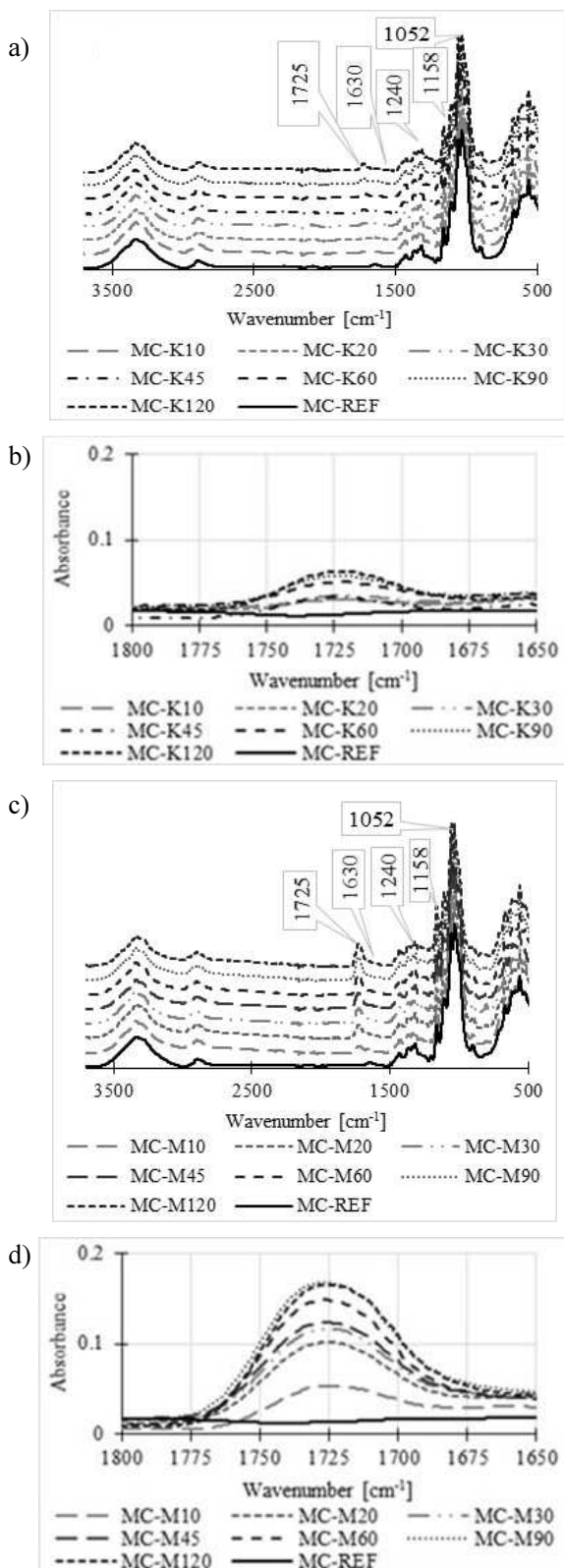


Fig. 2. FTIR spectra of microcrystalline cellulose modified with succinic anhydride under conventional heating (a, b) and microwave irradiation (c, d)

Rys. 2. Widma FTIR mikrokrystalicznej celulozy modyfikowanej bezwodnikiem bursztynowym w warunkach ogrzewania konwencjonalnego (a,b) oraz mikrofalowego (c,d)

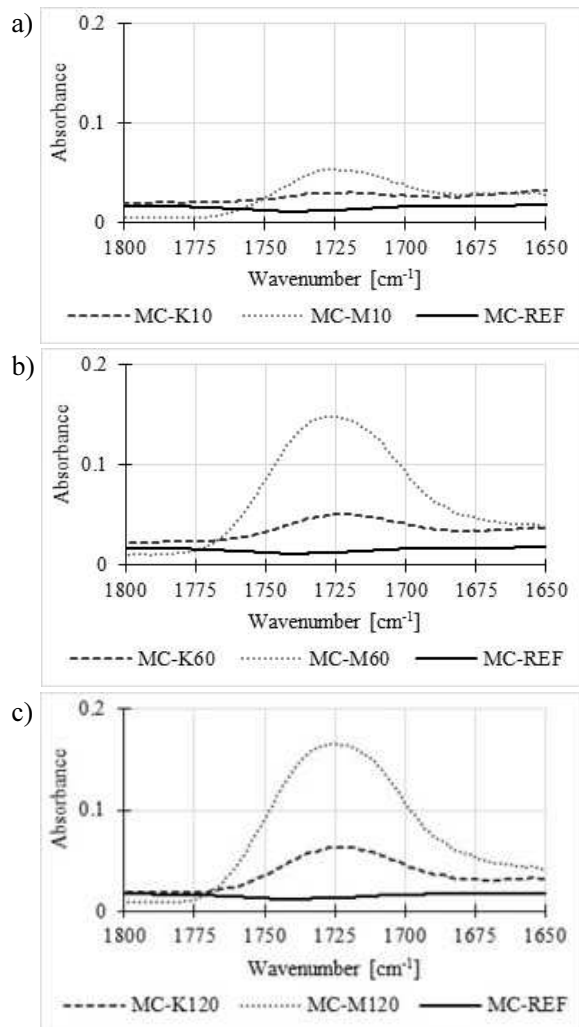


Fig. 3. Comparison of FTIR spectra in carbonyl stretching range of raw microcrystalline cellulose and MCC modified with succinic anhydride under conventional heating and microwave irradiation for selected reaction times: a) 10 minutes, b) 60 minutes, c) 120 minutes

Rys. 3. Porównanie widm FTIR w zakresie spektralnym drgań rozciągających grupy karbonylowej dla referencyjnej mikrokrystalicznej celulozy i MCC modyfikowanej bezwodnikiem bursztynowym w warunkach konwencjonalnego i mikrofalowego ogrzewania odpowiednio dla czasów reakcji: a) 10 minut, b) 60 minut, c) 120 minut

Strong peaks at 1052 and 1158 cm^{-1} were identified as C-O and C-O-C stretching vibration in cellulose, respectively [17, 18], and the broad peak at 1630 cm^{-1} may refer to the bending vibrations of adsorbed water.

Light microscope analysis

The microphotographs shown in Figure 4 were obtained by placing a small amount of cellulose powder on a glass slide. The reduction of the MCC particles after modification is clearly visible in the microphotographs (Fig. 4b, 4c) compared to unmodified MCC (Fig. 4a). The esterification reaction of cellulose may cause a decline in particle size due to partial hydrolysis of amorphous areas [4].

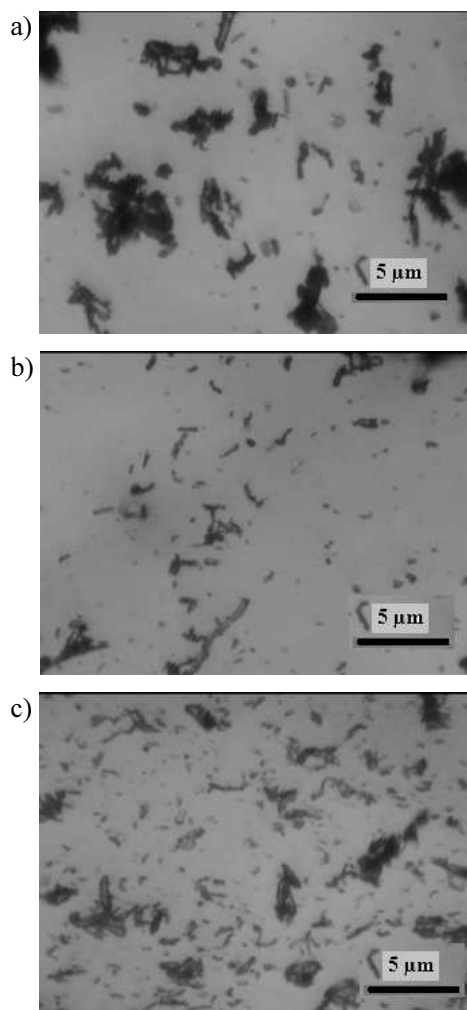


Fig. 4. Light microscopy images of: a) MC-REF, b) MC-K90, and c) MC-M90

Rys. 4. Mikrofotografie mikroskopii optycznej próbek: a) MC-REF, b) MC-K90, and c) MC-M90

TG/DTG analysis

Mass losses and characteristic decomposition temperatures for the MCC samples are given in Table 1 for the samples modified under conventional heating and in Table 2 for the samples obtained under microwave irradiation. The TG and DTG curves recorded during thermooxidative degradation of MCC modified under conventional heating are shown in Figure 5a and 5b, respectively. The TG and DTG curves of MCC modified under microwave irradiation are presented in Figure 5c and 5d. The data showed a decrease in thermal stability with an increasing reaction time for all the samples, regardless of the heating method.

At the beginning of the process as we can see in Figure 6a, thermal stability decreases in relation to the reference sample, but the initial temperature of degradation is still over 220°C (Tables 1 and 2), which allows the application of MCC as a natural filler for numerous biopolymers. However, there was significant deterioration in the thermal stability of the sample modified under microwave irradiation for longer reaction times as compared to the sample from conventional heating,

as we can see in Figure 6c. This closely correlates to the greater degree of modification obtained under microwave irradiation as compared to conventional heating. The decrease in thermal stability may result from a change in the mechanism of thermal degradation associated with the presence of new functional groups. The lowering of the degradation temperature of the modified MCC may partly refer to the development of the specific surface area of the modified material. It was reported that as the surface of the crystals increased, their thermal conductivity increased and the thermal resistance was reduced [19].

The thermogravimetric study allowed the initial temperature of degradation for the samples to be determined, which is important for the further use of this material in composites processing. The dependence of the initial temperature of degradation ($T_{5\%}$) on the reaction time is shown in Figure 7. The graph shows that $T_{5\%}$, after simultaneously dropping for both modified samples, show different trends for longer reaction times. The $T_{5\%}$ for the samples obtained under conventional heating starts to rise at heating times over 30 min, while for samples which were obtained under microwave irradiation, it drops further.

TABLE 1. Mass loss and decomposition temperatures for MCC samples modified under conventional heating

TABELA 1. Ubytki masy i temperatury degradacji próbek MCC modyfikowanych w warunkach ogrzewania konwencjonalnego

	MC-REF	MC-K10	MC-K30	MC-K60	MC-K120
$T_{5\%}$ [°C]	299	265	225	244	280
T_{onset}	311	314	310	273	307
T_{1max} [°C]	325	326	323	292	323
Mass loss [%]	90	89	86	76	88
T_{2max} [°C]	493	468	465	504	509
Mass remaining at 600°C [%]	6	8	12	18	9

TABLE 2. Mass loss and decomposition temperatures for MCC samples modified under microwave irradiation

TABELA 2. Ubytki masy i temperatury degradacji próbek MCC modyfikowanych w warunkach ogrzewania mikrofalowego

	MC-REF	MC-M10	MC-M30	MC-M60	MC-M120
$T_{5\%}$ [°C]	300	262	223	233	205
T_{onset}	311	313	300	306	299
T_{1max} [°C]	326	327	325	324	324
Mass loss [%]	90	83	81	84	83
T_{2max} [°C]	493	486	425	445	421
Mass remaining at 600°C [%]	6	12	15	13	14

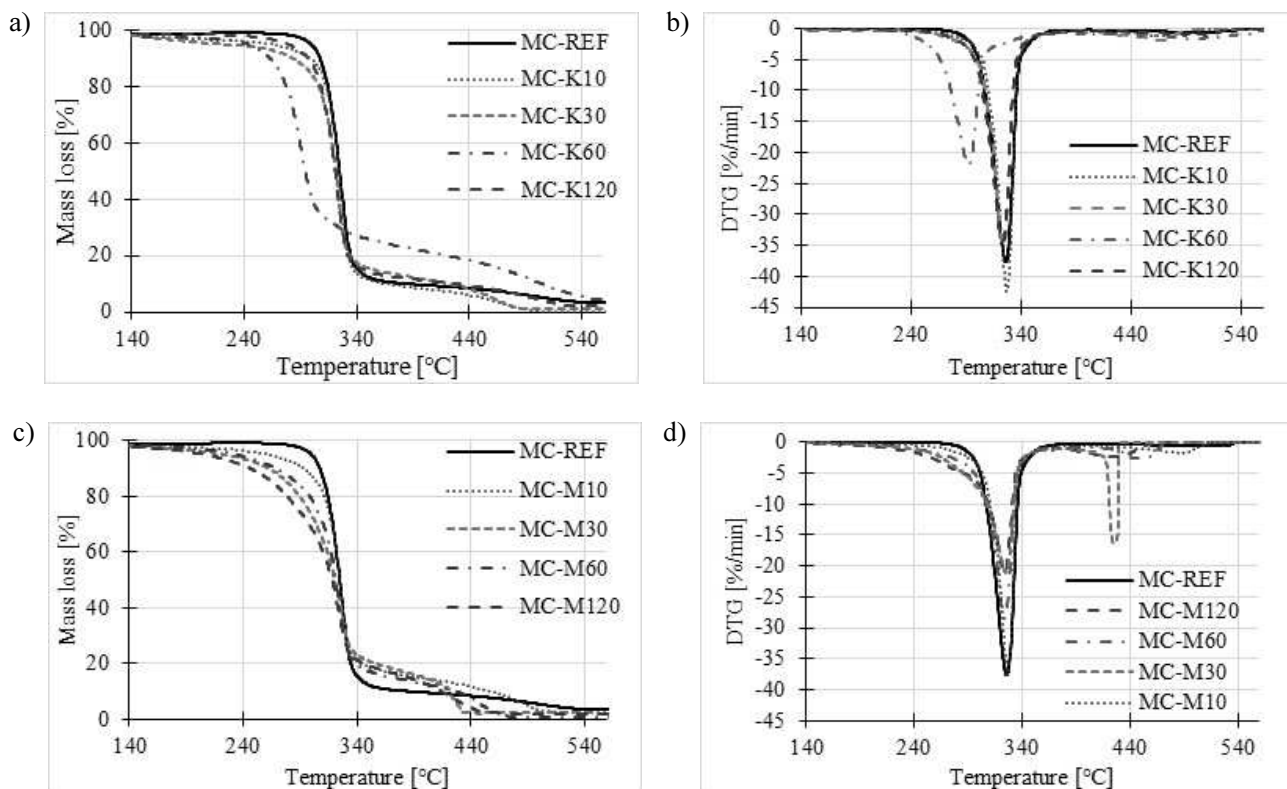


Fig. 5. TG profiles of thermooxidative degradation of MCC modified under: conventional heating (a,b) and microwave irradiation (c,d)

Rys. 5. Krzywe TG degradacji termooksydacyjnej MCC modyfikowanej w warunkach ogrzewania: konwencjonalnego (a,b) oraz mikrofalowego (c,d)

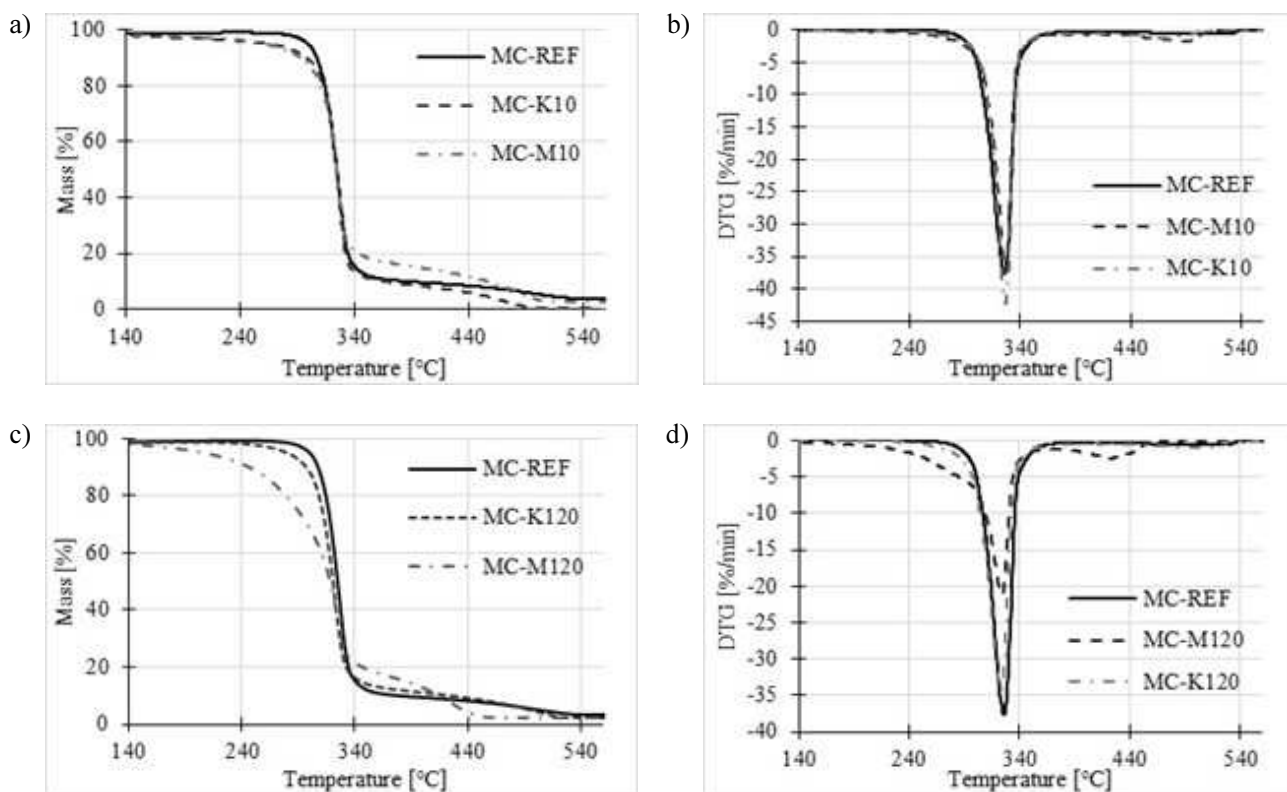


Fig. 6. Comparison of TG curves for thermooxidative degradation of MCC modified under conventional and microwave heating for different reaction times: 10 minutes (a,b) and 120 minutes (c,d)

Rys. 6. Porównanie krzywych TG degradacji termooksydacyjnej MCC modyfikowanej w warunkach ogrzewania konwencjonalnego oraz mikrofalowego po różnych czasach reakcji: 10 minut (a,b) oraz 120 minut (c,d)

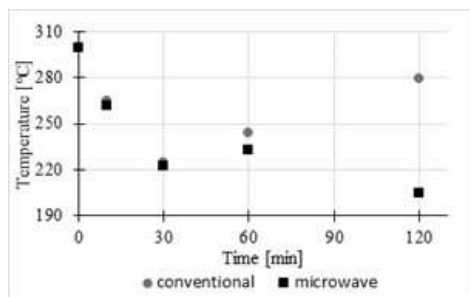


Fig. 7. Dependence of initial temperature of degradation ($T_{5\%}$) on reaction time

Rys. 7. Zależność początkowej temperatury degradacji ($T_{5\%}$) od czasu reakcji

CONCLUSIONS

MCC was successfully modified by esterification with succinic anhydride in the DMF solvent system using pyridine as the catalyst under conventional heating and microwave irradiation, which was proven by the FTIR study.

The FT-IR spectra showed the appearance of a new peak at 1725 cm^{-1} due to the introduction of ester groups in the cellulose structure. The intensity of this new peak in the spectra of microwave samples modified with SA initially increased with the reaction time up to 90 min and then leveled at a constant value for the last two samples with the longest reaction time. Therefore, the surface modification of cellulose gradually increased with an increasing reaction time and was considerably more effective under microwave irradiation.

The TG/DTG analysis showed decreased thermal stability of modified MMC and the initial temperature of degradation followed the extent of chemical modification. There was significant deterioration in the thermal stability of the sample modified under the microwave irradiation for longer reaction times as compared to the sample from conventional heating, which closely correlates with a greater degree of modification obtained under microwave irradiation. Proper selection of the modification conditions with respect to the surface properties and thermal stability of the MCC provides a natural filler for a wide group of biopolymers.

As an environmentally friendly, new bio-based and biodegradable material, MCC can partly replace the currently applied synthetic fillers in polymer composites.

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