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Influence of microwave irradiation on a polyesterification reaction

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ABSTRACT

The paper focuses on selective microwave heating and its influence on a polyesterification process. As a model reaction, the polyesterification reaction of adipic acid with neopentyl glycol is investigated. Non-catalyzed and tin (II) chloride catalyzed reaction experiments have been performed with microwave and conventional heating in an open, stirred vessel under a nitrogen atmosphere. Except faster heating times obtained under microwave heating, no different effects on the polyesterification reaction were found between the two heating modes. After 3-h experiments the conversion of the acid groups was similar under microwave heating and conventional heating. Particular emphasis was given on elucidating the important, though scarcely reported in the microwave literature, issues of energy consumption and efficiency. Approximately 20–30% of the electric energy consumed by the microwave oven is converted to thermal energy in the vessel during (non-reactive) heating of the individual components of the polyesterification process. This fraction drops to ~5% in the event of isothermal reaction experiments. A vast amount of energy is lost in the magnetron and the multimode cavity; these losses do not hamper conventional (conductive) heating, which is currently more economical. Finally, different ways of improving the thermal efficiency and thus the economic prospects of microwave technology are discussed.

1. Introduction

Polyesterification is one of the most important reactions in the chemical industry. Although the fundamental production technology of polyesters is well established, many efforts are being put into the intensification of these processes. Since polyesterification is an equilibrium reaction, one of the possibilities to maximize conversion and to obtain a product with high molecular weight is using an open reaction system with a continuous removal of water (by-product) from the reaction mixture.

In recent years considerable research efforts have been devoted towards the application of microwave heating in polymer synthesis. There are many studies on the applications of microwave irradiation in polymerization reactions under different process conditions, which have been already reviewed elsewhere [1–3].

Proper temperature monitoring and agitation in microwave reactors is of paramount importance for obtaining valid results [4,5]. The possible types of temperature sensors used under microwave conditions and their advantages and disadvantages were examined in [6,7]. The influence of using different microwave sources on heating efficiency, reproducibility of results and microwave cavity design were investigated in [8–10]. Variations of parameters such as the reaction vessel size, the volume of heated materials and the microwave power output have also been examined in [9,11]. Several attempts have been made to synthesize the polyesters under microwave heating. Jermolovicius and coworkers [12] carried out a polyesterification reaction in microwaves with removal of the generated water by azeotropic distillation. Velmathi and coworkers have investigated the polymerization of succinic acid with 1,4-butanediol with different catalysts in a monomode microwave reactor under N_2 atmosphere or under vacuum [13–15]. Reduced time of polymerization has been observed compared to conventional heating. Nonetheless, questions can be raised on the validity of the infra-red based temperature measurement applied on the reactor wall [4] due to potential temperature gradients between the reactor interior and the glass surface temperature.

This paper presents experimental results for a non-catalyzed and tin (II) chloride catalyzed polyesterification reaction between an aliphatic dicarboxylic acid (adipic acid) and an aliphatic diol (neopentyl glycol). The influence of reaction temperature and different heating modes (i.e. conventional heating using a heating mantle (HM) vs. microwave heating (MW)) on the formation of the by-product and its removal from the reactor has been investigated. Specific attention was paid to the accuracy of temperature measurements and the similarity of glass set-up in both heating

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systems for a fair comparison between the two heating systems. The impact of microwave heating of individual components (polymer product, water and ethylene glycol (EG)) is also examined along with the effect of the applied microwave power. Finally, the energy consumption and energy efficiency in both heating systems are compared and discussed.

Nomenclature

AV	acid value (number) [mg KOH/g of polymer]
c_p	specific heat capacity [J/kg/K]
m	mass [kg]
M_n	number-average molecular weight [kg/kmol]
MW	microwave
HM	heating mantle
N	normality of potassium hydroxide solution [mol/dm^3]
P_{loss}	electric power consumed [W]
$P_{mw,gen}$	the part of electric power, which is converted into microwave power by the magnetron [W]
$P_{loss,magn}$	the part of electric power, which is not converted to microwave power [W]
$P_{refl,cavity}$	microwave power, which is lost in the cavity by reflection and cavity loss [W]
$P_{abs,sample}$	the electromagnetic power, which is converted into heat in the heated sample [W]
$P_{loss,sample}$	power loss from the liquid sample to the surroundings due to heat conduction [W]
Q_{cons}	total electric energy consumed [kJ]
$Q_{loss,sample}$	total thermal energy losses from the liquid sample via conduction [kJ]
$Q_{thermal,sample}$	total microwave energy that is converted into thermal energy in the liquid sample [kJ]
$Q_{mw,gen}$	total microwave energy generated by the magnetron [kJ]
$Q_{abs,sample}$	total thermal energy that is absorbed by the sample as sensible enthalpy or converted into chemical energy (via the polycondensation reaction) and vapor heat [kJ]
$Q_{reaction}$	total heat of reaction [kJ]
Q_{vap}	total heat of vaporization [kJ]
t	time [s] [min] [h]
T	temperature [K]
U	overall lumped heat transfer coefficient [W/K]
V	volume [m^3]
V_1	volume of potassium hydroxide solution used for titration of the polymer sample [ml]
V_2	volume of potassium hydroxide solution used for titration of the blank sample [ml]
W	sample weight [g] or Watts

Greeks symbols

η_{TE}	thermal efficiency coefficient: represents the fraction of electric energy converted into thermal energy in the liquid mixture
η_{PE}	process efficiency coefficient: represents the fraction of electric energy absorbed as sensible heat or converted into chemical energy (via the polycondensation reaction) and vapor heat
η_{magn}	magnetron efficiency: the fraction of electric energy converted into electromagnetic energy

2. Experimental

2.1. Materials

The chemicals *for the reactive system* were purchased from Aldrich Chemical Co. and include the following: 1,4-butanedicarboxylic acid (commonly called adipic acid (AD)) (99.6+ % of purity, CAS 124-04-9); 2,2-dimethyl-1,3-propanediol (commonly called neopentyl glycol (NPG)) (99+ % of purity, CAS nr 126-30-7); tin (II) chloride (98% of purity, CAS nr 7772-99-8). *For the non-reactive experiments*, 1,2-ethanediol (commonly called ethylene glycol (EG)) (99+ % of purity, CAS nr 107-21-1) was purchased from Aldrich Chemical Co. In this series of experiments, tap water and the end-polymer product (actually oligomer due to the low conversion, ~73%, of COOH groups) obtained from the polyesterification reaction have been used as well.

For analysis of the end-polymer product the following chemicals have been used: ethanol (99.9+ % of purity, CAS 64-17-5), which was obtained from Chemproha Chemical Distributions; tetrahydrofuran (THF) containing 250 ppm BHT as stabilizer (99+ % of purity, CAS 109-99-9), potassium hydroxide pellets (KOH) (purity of 85+ %, CAS 1310-58-3) and potassium hydrogen phthalate (99.95+ % of purity, CAS 877-24-7), which were purchased from Sigma–Aldrich Chemical Co.

2.2. Experimental procedures

2.2.1. Set-up and chemical systems description

Non-reactive and isothermal reactive experiments have been performed with microwave and conventional heating. Microwave heating was performed in a microwave multimode cavity (MARS CEM Corp.) of 1600 W maximum power output and an inboard power control system based on temperature measurements (details in the next section). Conventional (conductive) heating was performed with an electric heating mantle (LabHeat, type KM-ME) with electronic laboratory controller and a maximum power output of 150 W. Both microwave and conventional heating experiments have been performed in a 250 ml three-neck round-bottomed glass reactor equipped with an overhead stirrer operated at 140 rpm. The size of the microwave cavity is reasonably big (48.14 l); in order to obtain comparable results in both heating systems the distance between the reactor and the condenser was minimized by positioning the reactor in the upper part of the cavity. A standard distillation kit was placed above the upper cavity wall and was connected to a graduated cylinder in order to collect the distillate.

In the non-reactive system, a series of experiments was performed to estimate the microwave power absorbed by the liquid while ramping up the temperature. Pure substances, like EG, tap water, and the end-polymer have been heated, in both the microwave and conventional heating systems. EG was used for this dynamic experiment due to being liquid as opposed to neopentyl glycol which is solid at room temperature. Each of the experiments has been repeated at least twice.

In the reactive system, the polyesterification reaction of adipic acid with neopentyl glycol has been performed in slight excess of glycol. The molar ratio of reagents was 1–1.1. The reaction was carried out isothermally at two temperatures (140 °C or 165 °C) with a maximum generated power of 800 W in the microwave cavity and 150 W in the heating mantle. Both reagents, i.e. adipic acid and neopentyl glycol are solids at room temperature; therefore, melting of the reagents is necessary in order to start the reaction. The melting points of the reagents are 153 °C and 124 °C, respectively. The polyesterification reaction occurs in the liquid phase, hence only melted or dissolved particles can react with each other. In the case of the tin (II) chloride catalyzed polyesterification reaction, the solid catalyst has been placed in the reactor before starting to heat-up towards the set temperature. At the beginning of the reaction, the evaporation of the formed water from the mixture of diol, dicarboxylic acid and polymer occurs vigorously while after a certain time further removal of water is only possible by increasing the temperature in the reactor or by applying vacuum. Except for a nitrogen flow of 35–40 ml/min to help the removal of the by-product, the above measures were not applied in this investigation, as it was not the aim of this investigation to achieve complete conversion.

2.2.2. *Temperature measurement*

During both types of experiments (conventional and microwave heating), the temperatures in the glass reactor and at the top of the distillation set-up were measured by fiber-optic (FO) sensors mounted inside the experimental system in direct contact with the reaction mixture and the vapor by-product, respectively. The FO sensors have thoroughly been discussed in the literature and are considered to be a state-of-the-art temperature measurement technique under microwave conditions [5]. The FO sensor for temperature measurement in the microwave reactor was provided by the supplier of the microwave equipment, whereas the one for temperature measurement at the top of the distillation kit was a FOT-L-BA Model from FISO. Both thermometers were protected by a glass capillary against potential damage. The FO sensors exhibit short response times (1.5 s in the reactor and 0.5 s at the top of the distillation set-up). Small delays in temperature measurements could be caused by the glass protection, although, this was not considered to be significant [16]. The measured temperatures were registered with PC software. In case of the conventional heating experiments with the electric HM, the temperature control was based on a Pt100 thermometer (provided along with the HM) immersed in the reaction mixture. In addition, temperature was also monitored by a FO sensor. The temperature measurements with the two methods differed by 1 °C at most during the entire conventional heating experiment.

2.2.3. *Power control system and power consumption*

Since the reaction experiments were performed isothermally, the power control system of the microwave oven was adjusting the amount of power generated by the magnetron based on the temperature measured by the FO sensor immersed in the reaction mixture. Therefore, the power control system controlled the power input upon reaching the set temperature. It is remarked that in the reactive system, the power varied between 250 and 800 W in order to keep the temperature at the set-point (140 °C or 165 °C). On the contrary, in the non-reactive system the power was set to 800 W (half of the maximum power that could be generated by the magnetron).

For the measurement of the total energy consumption a commercially available domestic power meter (Energy Logger 3500, Voltcraft) has been used. This power meter determined the amount of power consumed (P_{cons}) by the microwave apparatus or the heating mantle device. Since electric devices consume power for the period of idle mode, the power consumption has been measured only for a period when the devices were in the “on-mode”.

2.3. *Products analysis*

To monitor conversion, several samples were taken from the reactor during the course of an experiment. Conversion was estimated from the acid group content in the sample, which was measured by the acid number or acid value (*AV*). The latter was determined by titration, immediately after sampling, according to the method for testing powder coating resins provided by DSM [17]. First, the samples were weighed (±0.0001 g) and dissolved in 60 ml tetrahydrofuran (THF) at room temperature. A solution of 1% of phenolphthalein in ethanol was used as an indicator. The standard 0.1 M ethanol solution of potassium hydroxide was used to react with COOH groups in the polymer. The end point was obtained when the solution turned red. Standardization of the potassium hydroxide solution was performed by potassium hydrogen phthalate titration [17]. *AV* is expressed in mg of potassium hydroxide per g of polymer as follows:

$$AV = \frac{56.1 \cdot (V_1 - V_2) \cdot N}{W} \tag{1}$$

The number-average molecular weight (M_n) of the polymer product was determined by Gel Permeation Chromatography (Waters GPC, with Breeze software) equipped with a refractive index (RI) detector and styragel column set (HT2 and HT6E). THF was used as effluent at a flow rate of 1 ml/min. The detector and the column were kept at 37.5 °C. Calibration of the system has been done with polystyrene standards with a narrow molecular weight distribution. The polymer was dissolved in THF at a 1:1 ratio of mg of polymer to ml of THF. The specific heat capacity of the end-polymer mixture (required to calculate the energy absorbed by the sample) has been measured by a Differential Scanning Calorimeter DSC-7 (PerkinElmer) in N_2 atmosphere with sensitivity of 0.4 μW and calorimetric accuracy of ±1%, with temperature accuracy of ±0.1 °C.

3. Results and discussion

3.1. *Distribution of energy in the microwave unit*

The energy distribution in the microwave apparatus is given by the following equation:

$$\begin{aligned} P_{cons} &= P_{loss,magn} + P_{mw,gen} \\ &= P_{loss,magn} + P_{refl,cavity} + P_{loss,sample} + P_{abs,sample} \end{aligned} \tag{2}$$

Eq. (2) simply states that the total amount of electric power consumed P_{cons} by the microwave device is only partially converted by the magnetron into microwave irradiation ($P_{mw,gen}$) that is subsequently delivered to the microwave cavity. The rest is lost at the magnetron ($P_{loss,magn}$). $P_{mw,gen}$ is further analyzed into three constituents: (1) the power effectively absorbed by the sample ($P_{abs,sample}$), (2) the power that is lost in the microwave cavity due to reflection at the cavity walls ($P_{refl,cavity}$), and (3) the power that is lost in the microwave cavity via heat conduction from the heated sample to the air outside the glass reactor $P_{loss,sample}$. A significant amount of power consumed during the operation of the microwave device is lost at the magnetron itself. The power efficiency of the magnetron (η_{magn}) has been estimated experimentally for the non-reactive and reactive system. In the non-isothermal, non-reactive experiments, power efficiencies of 43–50% and 56–63% were estimated when operating the MW unit using 25% and 50% of the maximum power of the magnetron (1600 W), respectively. In the isothermal reactive experiments, η_{magn} were somewhat lower (40–44%) due to the magnetron operation at lower power levels (oscillating in the range 250–800 W); as explained in Section 2.2.3, the MW oven was adjusting the amount of power generated to maintain a constant reactor temperature. Despite the big energy losses in the magnetron, its power efficiency and consequently the power efficiency of the process itself can be substantially improved when operating the microwave unit at higher power levels. A crucial issue in microwave technology that is scarcely reported in the literature is the energy efficiency of the process. To shed light on this issue, two efficiency metrics are defined below:

(1) The thermal efficiency of the glass reactor, η_{TE}, which represents the amount of electric energy consumed by the MW oven

(Q_{cons}) that is eventually converted into thermal energy in the glass reactor ($Q_{thermal,sample}$):

$$\eta_{TE} = \frac{Q_{thermal,sample}}{Q_{cons}} = \eta_{magn} \frac{Q_{thermal,sample}}{Q_{mw,gen}} \tag{3}$$

$$Q_{thermal,sample} = Q_{abs,sample} + Q_{loss,sample} \tag{4}$$

(2) The process efficiency, η_{PE}, which is defined under the generic convention of “what we get” over “what we pay for” and represents the “useful” amount of thermal energy that is actually absorbed by the sample ($Q_{abs,sample}$) during the experiment over Q_{cons}:

$$\eta_{PE} = \frac{Q_{abs,sample}}{Q_{cons}} = \eta_{magn} \frac{Q_{abs,sample}}{Q_{mw,gen}} \tag{5}$$

The efficiencies above are defined on total energy (Q) basis. Total energies are obtained by integrating power (P) over the time course of experiments. In the case of non-reactive experiments (described in Section 3.2), where a liquid sample is simply heated up, $Q_{abs,sample}$ increases the sensible heat of the sample; in the case of isothermal reactive experiments (described in Section 3.3), part of $Q_{abs,sample}$ enables the polyesterification process and is converted to chemical energy, while the rest is converted to vapor heat. The difference between η_{TE} and η_{PE} in a MW oven represents the fraction of thermal energy generated in the sample that is lost to the surroundings of the glass reactor via heat conduction. The efficiency values reported hereafter have been calculated, according to Eqs. (3)–(5), via multiplying the average magnetron efficiency ($\bar{\eta}_{magn}$) by the efficiency values on $Q_{mw,gen}$ basis. $\bar{\eta}_{magn} = 0.6$ and $\bar{\eta}_{magn} = 0.42$ are considered for the non-reactive experiments with constant $Q_{mw,gen}$ (800 W) and reactive experiments with variable $Q_{mw,gen}$ (250–800 W), respectively.

3.2. Non-reactive system

A series of non-reactive heating experiments (with MW and HM) have been performed with the individual components of the actual polyesterification process in order to calculate heating times and efficiencies. EG (liquid phase at room temperature), tap water and the end-polymer product have been exposed to microwave irradiation and heated to two target temperatures of 80 °C or 145 °C (except water, which vaporizes). Fig. 1 shows the temperature increase of the different substances mentioned above with time using microwaves. These experiments have been performed at a constant generated microwave power of 800 W. Fig. 1 shows that from the three substances, EG is heated up the fastest; the polymer and EG have comparable heating rates, whereas water is heated up significantly slower. In Table 1, the heating rates of the polymer as well as Q_{cons} are presented at two operation powers of 800 and 400 W. In the last column of Table 1, the respective values with HM are quoted. It is shown that when doubling the applied power from 400 to 800 W (MW), the heating time is approximately halved, whereas Q_{cons} increases a little (<10%). In comparison of the two heating modes, operating the microwave oven at 800 W results in ~1 order of magnitude faster heating at the expense of Q_{cons} being, approximately, twice as high. The power applied with HM, though, is only 150 W (limited by the equipment itself). A more straightforward comparison can be done by linear extrapolation (in case of MW) of the “electric energy consumption” and “heating time” to “power applied” slopes, based on the data at 400 and 800 W, down to the power level of 150 W used in HM. This yields 5.6 min of heating time (vs. 21.4 in HM) and 216 kJ electric energy consumption (vs. 130 in HM). Albeit this linear extrapolation to a lower power level for HM should be seen as a rough approximation, it gives a feeling of the different heating times and electric energy requirements with the two heating modes on equal generated power level basis. All in all, use of MW results in sample heating several times faster than the conventional heating at the expense of higher electric energy consumption. Nonetheless, if it was not for the rather low magnetron efficiency (40–60% as discussed above), the heating process would be energetically comparable for the two heating modes or even favorable under MW.

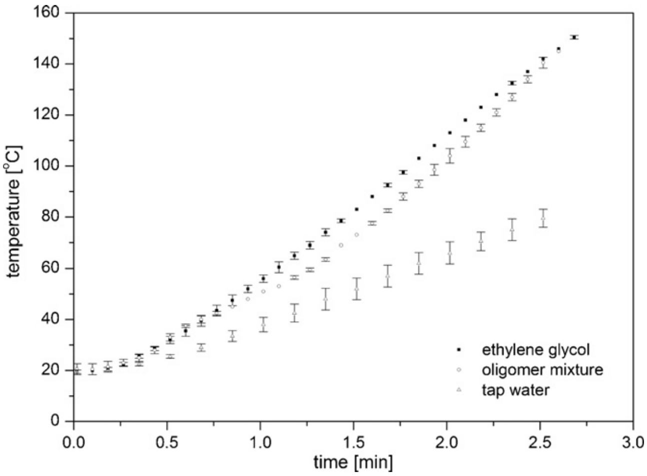

Fig. 1. Sample temperature vs. heating time of water, EG, and the polymer product (~75% of conversion of COOH groups). A constant volume (175 ml) is used for all samples. The magnetron is operated at 800 W.

As mentioned in the previous section, the electromagnetic energy converted into heat in the sample is partially absorbed by the sample itself increasing its temperature and thus, its sensible heat ($Q_{abs,sample}$) and partially lost to the surroundings via heat conduction. $Q_{abs,sample}$ is calculated by:

$$Q_{abs,sample} = \int_{T_0}^{T_{final}} mc_p \, dT \tag{6}$$

In Eq. (6), T_0 is the initial temperature. The specific heat capacities (c_p) for ethylene glycol and water are known [18], whereas that for the polymer sample has been measured. The total heat transferred from the liquid to the surroundings (only for MW experiments) can be calculated from:

$$Q_{loss,sample} = \int_{t_0}^{t_{final}} U(T(t) - T_o)dt \tag{7}$$

U [in W/K] is an average lumped heat transfer coefficient accounting for conduction heat transfer from the liquid to the sur-

Table 1
Electric energy consumption and heating time of a polymer product sample (~75% conversion, 175 ml sample volume) heated up to 145 °C in duplicate experiments.

Type of heating	Heating of liquid polymer from room temperature up to 145 °C		
	MW	MW	HM
Power applied [W]	800	400	150 (pulsed)
Heating time to set temperature [min]	2.5	4.4	21.4
Electric energy consumption (Q_{cons}) [kJ]	245	227	130

Table 2
Thermal and process efficiencies (η_{TE} and η_{PE}, respectively) for MW heating, and η_{PE} for HM in the event of EG, water and the polymer product. The liquid samples (175 ml) are heated up to 80 °C and 145 °C. Heat losses from the sample (in case of MW heating) are calculated based on a lumped heat transfer coefficient of 0.2 W/K. The magnetron is operated at 800 W.

	MW		HM
	η_{TE} (%)	η_{PE} (%)	η_{PE} (%)
80 °C			
EG	24.6	24.0	44
Water	20.4	20.4	41
Polymer	19.8	19.2	38
145 °C			
EG	31.8	30.6	47
Polymer	26.4	25.2	45

roundings of the glass reactor via the glass wall and to the gas phase above the liquid via the gas–liquid interphase. In the microwave cavity, U has been determined, first, by fitting the exponential decrease in the sample temperature when the microwave power is off (cooling curve). It was found to be ~0.17–0.22 W/K depending on the temperature range and the compound examined. These values are in good agreement with those obtained via heat transfer correlations. Table 2 shows, in the second and third columns, the thermal and process efficiencies calculated from Eqs. (3) to (7) for MW heating of EG, water and the polymer product. It is remarked that these values hold for a round-bottomed glass reactor with 175 ml of liquid. The highest efficiencies are obtained for EG and the lowest ones for the polymer mixture. The process efficiencies are up to 2% lower than the thermal efficiencies signifying that the heat losses from the glass reactor during fast sample heating up to the target temperature are low. The process efficiencies in HM (defined as in Eq. (5)) are higher compared to MW at both temperatures. Thermal efficiencies for the HM experiments are not reported as the definition of Eq. (3) does not have an equivalent counterpart for HM. In fact, 100% of the electric energy consumed is converted to thermal energy via electric resistances outside the reactor and is partially conducted into it. Higher efficiencies under MW heating can be attained if (a) a larger reactor volume is used; (b) the position of the glass reactor in the cavity is optimized in that it is placed at a spot of (local or global) maximum electric field strength, and (c) the magnetron is operated at a higher power level.

3.3. Reactive system

3.3.1. Pretreatment time

At the beginning of the process the reagents are in the solid phase at room temperature and need to be melted. In this paper, the above pretreatment time is denoted as delay time and is defined as the time needed by the reaction mixture to reach the temperature of 140 °C starting from switching on the heating device. At this temperature, most of the solids are melted and the stirrer starts to operate. In case of MW experiments, the pretreatment time is on average 5 min for the experiments at both temperatures of 140 °C and 165 °C. In the case of HM, the pretreatment time is ~25 min, both for the experiments at 140 °C and at 165 °C. During the melting phase the power generated by the magnetron is at the maximum level of 800 W, while during the HM experiments, the power is at the maximum level of 150 W for the HM. It can be assumed that the difference in melting time is related to the different energy input. One of the consequences of the difference in pretreatment times is that the temperature at the top of the distillation column reaches its maximum value at later times in case of HM compared to MW (90–100 min vs. 60–70 min at 140 °C and 40–45 min vs. 15–17 min at 165 °C). Furthermore, the maximum temperature reaches 100 °C in MW, whereas only 94.5 °C in HM is obtained (see Figs. 2 and 3).

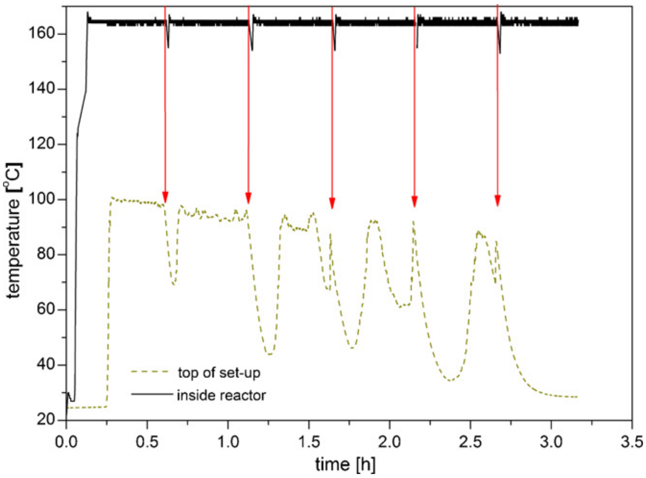

Fig. 2. Temperature inside the reactor and at the top of the set-up vs. time in a MW experiment at 165 °C including pretreatment time.

3.3.2. Sampling procedure

The reaction progress was tracked by taking samples from the reaction mixture at predefined time intervals of ~30 min. In case of MW experiments, the MW equipment was shut down for ~1 min during the sampling (when no sampling was applied, the magnetron was continuously on). As a consequence, the temperature in the reactor and at the top of the separation column decreased significantly (8–12 °C in the reactor and ~30–55 °C at the top of the distillation set-up; see Figs. 2–4). After the sample was taken and the oven was on again, it took less than a minute for the reaction mixture to reach the set temperature, whereas the response at the top of the column was rather slow (7–20 min). The time range of the response depends on the stage of the reaction at which the sampling takes place. In order to check the influence of taking samples, one extra 3-h microwave experiment without sampling was performed and the results are shown in Fig. 4; the temperature trends at the top of the column outside the oven remain similar, except during the sampling period. In case of the experiments with HM, the sampling procedure was much simpler because it was not necessary to switch off power every time a sample was taken.

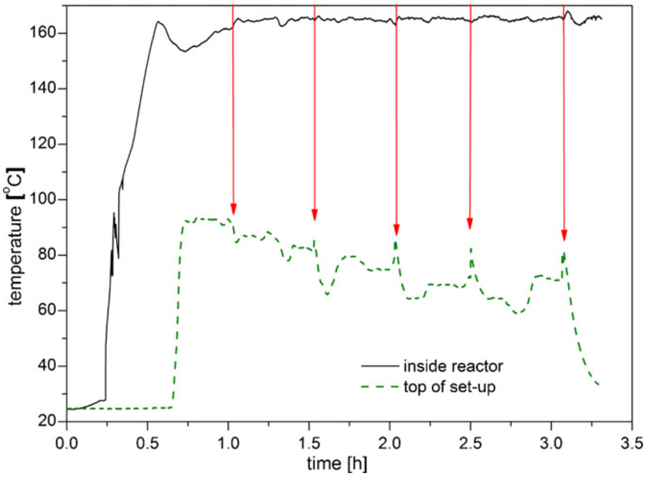

Fig. 3. Temperature inside the reactor and at the top of the set-up vs. time in a HM experiment at 165 °C including pretreatment time.

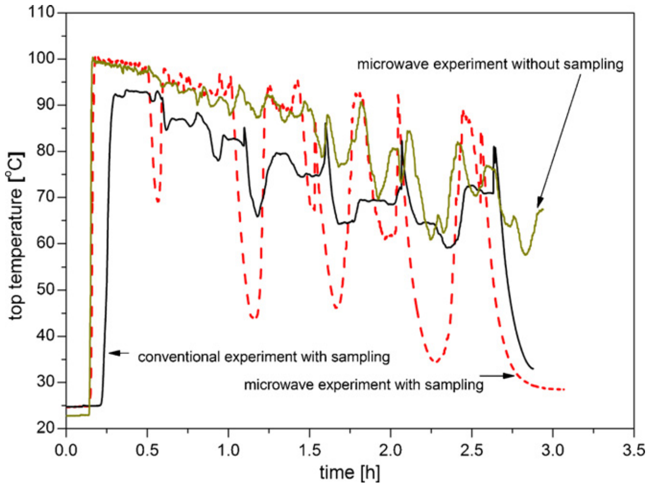

Fig. 4. Temperature at the top of the set-up in the MW and HM experiments performed at 165 °C excluding the pretreatment time.

3.3.3. Conversion in non-catalyzed and catalyzed reaction systems

Acid value measurements were performed to determine the concentration of the free acid groups in the reaction mixture. Then, conversion of COOH groups was calculated based on Eq. (1). Fig. 5 shows conversion of COOH groups vs. time in case of MW and HM at 165 °C. At the beginning of the reaction when the reactants concentration is high and conversion is low, the reaction rate is somewhat higher under microwave conditions. At about 1.5 h (conversion ~65%) the two conversion lines cross and then conversion in MW appears slightly lower than in HM. After 3 h of reaction at 165 °C the conversion of COOH groups in both cases is ~73%. At this point the reaction is close to equilibrium and the trend lines approach their asymptotic values. As it was already discussed above, it was not the aim of these experiments to reach higher conversion. Fig. 5 also presents one experimental point (filled square) representing the MW experiment without taking samples at intermediate intervals (the oven was continuously on); no significant difference in the end-conversion was found. Overall, it appears that the heating mode does not significantly affect conversion.

Fig. 6 shows the data for non-catalyzed and $SnCl_2$-catalyzed reaction experiments with MW and HM at 140 °C. After 3 h of reaction at 140 °C without catalyst (excluding pretreatment time), the conversion of COOH groups is ~53% in HM and ~57% in MW. As expected, these conversions are lower compared to the experiment at 165 °C (Fig. 5). They show, however, that conversion is relatively insensitive to the heating mode irrespective of the reaction temperature (i.e. same finding for 140 °C and 165 °C). When using $SnCl_2$ as catalyst for the polyesterification reaction, the end-conversion (3-h reaction) increases by more than 10% in both heating modes (Fig. 6: ~66% vs. ~53% in HM and ~68% vs. ~57% in MW). Nonetheless, it is again concluded that the presence of catalyst does not affect the coupling of the reaction system under investigation with microwave irradiation.

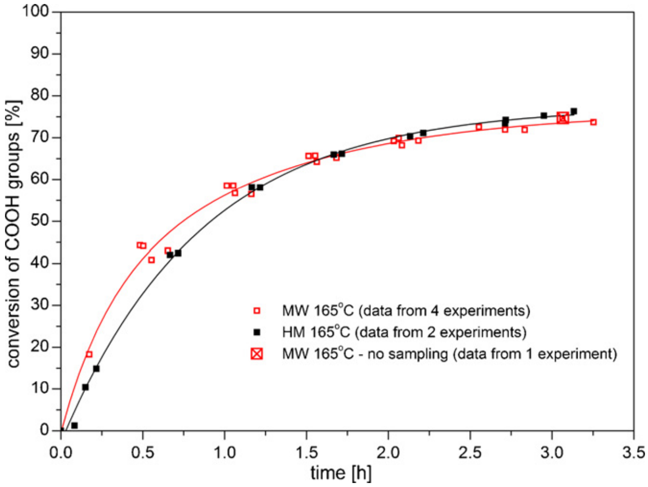

Fig. 5. Conversion of COOH groups vs. time at 165 °C for non-catalyzed reaction experiments in MW and HM (excluding pretreatment time).

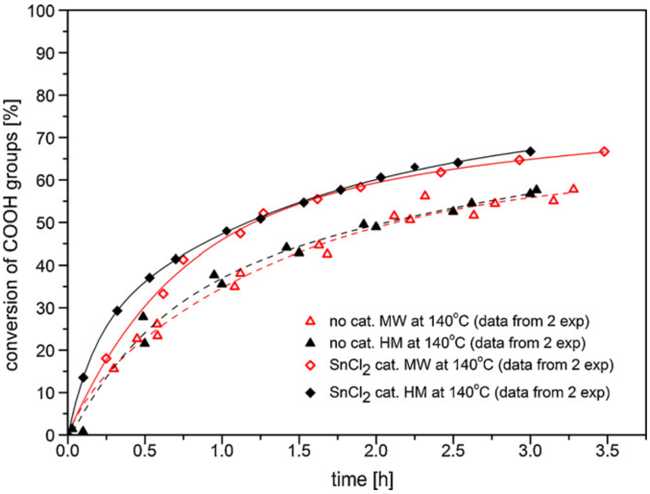

Fig. 6. Conversion of COOH groups vs. time at 140 °C for non-catalyzed and $SnCl_2$-catalyzed reaction experiments in MW and HM (excluding pretreatment time).

The product characteristics (polymer mixtures) were examined by GPC and appeared to be independent of the heating method. There are no significant differences in the product chromatograms between the non-catalyzed experiments carried out at the different temperatures with different sources of heat (data not shown). The molecular weight dependence as a function of AV is shown in Fig. 7. The left set of data represents the molecular weight of the polymer product in the case of experiments at 165 °C, whereas the right one represents the molecular weight of the polymer product at 140 °C. As expected, the molecular weight is higher at the higher temperature due to the higher acid conversion. The molecular weight of the end-polymer product is in the range 700–800 at 140 °C and 900–1000 at 165 °C depending on AV. Overall, Fig. 7 shows that

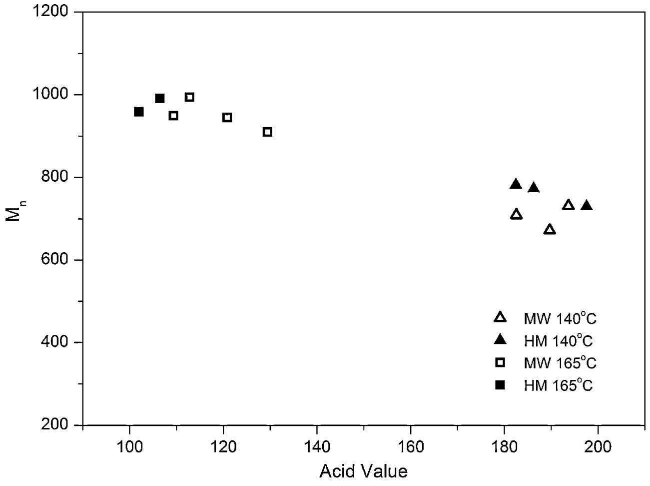

Fig. 7. Number-average molecular weight vs. AV for non-catalyzed reaction experiments at 140 °C and 165 °C in MW and HM.

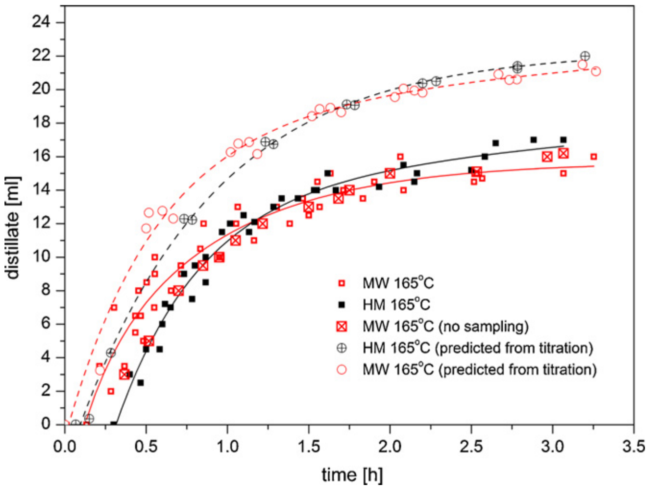

Fig. 8. Comparison of collected amount of distillate during non-catalyzed experiments performed at 165 °C in MW and HM excluding pretreatment time.

Table 3

Contribution of heat of reaction, heat of vaporization and heat losses to thermal and process efficiencies (η_{TE} and η_{PE}, respectively) for MW heating, and to η_{PE} for HM. $Q_{reaction}$ and Q_{vap} have been calculated based on the maximum obtained experimental conversions of 55% and 75% at 140 °C and 165 °C, respectively. $Q_{loss,sample}$ is calculated based on a lumped heat transfer coefficient of 0.2 W/K. Non-catalyzed reaction experiments.

Conversion	MW		HM	
	140 °C 55%	165 °C 75%	140 °C 55%	165 °C 75%
$Q_{loss,sample}$ (kJ)	259	313	–	–
$Q_{reaction}$ (kJ)	126	172	126	172
Q_{vap} (kJ)	34	44	34	44
$Q_{mw,gen}$ (kJ)	4000	4070	–	–
Q_{cons} (kJ)	9524	9691	974	1087
η_{TE} (%)	4.4	5.5	–	–
η_{PE} (%)	1.7	2.2	16.4	19.9

the molecular weight of the polymer is not significantly influenced by the heating method, which is consistent with the conversion profiles of Figs. 5 and 6 that were discussed above.

3.3.4. *Collected distillate*

In this section, the by-product (water) formation and its removal from the reactor are discussed. Fig. 8 shows the distillate volume vs. reaction time in case of MW and HM at 165 °C. The dashed lines represent the estimated amount of water produced based on the stoichiometry and the measured conversion. The solid lines represent the actual amount of distillate in the collector outside the MW oven/HM. The difference between the two sets of lines is the amount of water that remains in the polymer mixture and on the glassware walls. As mentioned in Section 2.2.1, complete removal of water could have been achieved by applying vacuum. It should also be noted here that a significant amount of water is vaporized off the reactor during sampling. The MW experiments show that water is formed slightly earlier compared to HM. More specifically, ~15 min past the reactor temperature has reached 140 °C water is formed and removed from the reaction zone in the MW experiments, whereas in HM the removal of water starts ~35 min past the reactor temperature has reached 140 °C. This is in consistency with the higher acid conversion at the beginning of the reaction under MW heating shown in Fig. 5. The water fraction remaining in the reactor zone was slightly lower in the MW experiments. Furthermore, the glycol content in the distillate was found to be less than 1% (w/w). Collectively, the water distillate trends in Fig. 8 can be seen as an alternative way to track reaction progress in MW and HM. These trends confirm the weak effect of the heating mode on the polyesterification process investigated here.

3.3.5. *Efficiency*

The electromagnetic energy converted into heat in the sample in the reactive MW experiments is partially transformed to chemical energy via the endothermic polycondensation process, partially converted to vapor heat and partially lost via the glass walls to the surroundings due to conduction. To calculate the heat of reaction at the reactor temperature, the required heats of formation of the monomers and the water product are obtained from the ASPEN database. The heat of formation of the polymer product is first computed at 25 °C (based on the repeated unit) according to van Krevelen and Chermin [19] from group contributions and structural corrections based on experimental data, which are sufficiently accurate over the temperature interval of 300–600 K. This is a commonly used method if no experiments or ab initio calculations are performed. It is noted that the group contributions are given to calculate standardized free enthalpies of formation at the ideal gaseous state. It is mostly assumed, though, that they hold in liquid phase as well. Eventually, the polymer heat of formation at 140 °C or 165 °C is computed by adding the sensible enthalpy content at the given temperature to the standard enthalpy of formation. The sensible enthalpy is calculated based on correlations between liquid heat capacities and temperature for linear macromolecules [19].

Table 3 shows the contributions of heat of reaction ($Q_{reaction}$), heat of vaporization (Q_{vap}) and heat losses ($Q_{loss,sample}$) to η_{TE} and η_{PE}, for MW heating, and to η_{PE} for HM. $Q_{loss,sample}$ is calculated based on an average heat transfer coefficient of 0.2 W/K (see also discussion in Section 3.2). The total electrical energy consumed (Q_{cons}) is ~9500–9700 kJ, whereas the total MW energy ($Q_{mw,gen}$) delivered to the cavity during a reactive MW experiment is ~4000 kJ. A significant fraction of the latter is reflected and lost in the cavity. Thermal efficiencies of 4.4% and 5.5% are calculated for MW heating. These values are lower than those reported in Table 2 for the non-reactive (pure heating) experiments. It is stressed here that there is an important sample mass and volume reduction during the experiment, which decreases the efficiency. In particular, 75–80% of the water (containing less than 1% organics) produced in the mixture was collected as distillate but an additional amount escaped from the system as vapor during sampling or remained in the system affixed on the glass walls. In passing, the approximate Q_{vap} in Table 3 is computed assuming that the entire amount of water produced has been vaporized off the liquid phase. Besides, not only water but also an important amount (at least 16 g) of the product mixture (also containing unreacted monomers being good MW absorbers) has been removed from the system during sampling. In total ~17% of the initial mixture volume is estimated to be lost during the experiments. Next to the decreasing absorbing capability of the product mixture caused by the removal of good MW absorbers, the volume reduction is particularly detrimental in MW heating, which is known to be volumetric heating as opposed to conducting surface heating. However, some volume reduction is inevitable during the process, as water must be distilled off to shift equilibrium to nearly complete conversion. The latter is indispensable for production of polymer with high molecular weight. As already explained in Section 3.2 (on the non-reactive experiments), the MW efficiency can further be enhanced by using a larger reactor volume, by optimizing its position in the cavity so that it is placed at the maximum electric field strength position, and by operating the oven at a higher power level. The process efficiencies in MW heating are found to be ~2% (Table 3). Contrary to the non-reactive system, the relative contribution of heat losses from the sample is now bigger due to the higher temperature operation and the much longer duration of the reactive experiments. Besides, similar to the non-reactive system conditions in Table 2, process efficiencies under conventional heating (HM) are higher compared to those in the MW experiments (Table 3).

4. Conclusions

A microwave-assisted polyesterification reaction between neopentyl glycol and adipic acid was investigated in this work and compared to a conventionally heated process in an electric heating mantle. The two heating modes are also contrasted as efficient means of merely heating up the individual substances of the process. A compilation of the most important conclusions is given below:

- MW heating of the individual components of the polyesterification process is several times (>3) faster than conventional heating at the expense of a higher electric energy consumption (~ a factor 2). The latter is primarily attributed to the rather low magnetron efficiency (~40–60% depending on the power level applied in this work).
- The heating mode (MW vs. HM) does not significantly affect conversion and the properties of the end-polymer product. After 3-h reaction experiments (with no catalyst and with $SnCl_2$ catalyst) the conversion of acid groups was similar under MW heating and conventional heating. As expected, the use of catalyst and higher reactor temperatures improves conversion for both heating modes.
- Approximately 20–30% of the electric energy consumed by the MW oven is converted to thermal energy in the reactor during (non-reactive) heating of the individual components of the polyesterification process. This fraction drops to ~5% in the event of isothermal reaction experiments. A vast amount of energy is lost in the magnetron and the multimode cavity; these losses do not hamper conventional (conductive) heating, which is currently more economical.
- From the operational point of view, higher efficiencies under MW heating in multimode cavities can be attained when using larger reactor volumes and when the position of the glass reactor in the cavity is optimized in that it is placed at a spot of (local or global) maximum electric field strength. This suggests that concerted modeling and experimental efforts are required to get the best of the MW technology. In addition, the use of more efficient monomode cavities and microwave transmission antennas placed inside the reactor should be explored. In the long run, microwave ovens powered by renewable energy sources such as solar energy could circumvent the problem of low conversion efficiency of the expensive electric energy to electromagnetic energy by the magnetron.

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