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Microwave assisted synthesis of unsaturated polyester resins

Summary — A novel method of synthesis of unsaturated polyester (UP) resins, based on the catalytic (*i.e.*, with lithium chloride) copolymerization of alkylene oxides (*i.e.*, epichlorohydrin) with acid anhydrides (*i.e.*, maleic, phthalic ones) under microwave irradiation is described. In comparison with condensations of acid anhydrides with diols, this reaction proceeds without emission of any volatile product. All the syntheses were performed under both either conventional heating or microwave irradiation (two variants: mono- and multimode). In general, the application of microwave irradiation allows to reduce the reaction time.

Key words: microwave irradiation, unsaturated polyesters resins, acid anhydrides, epichlorohydrin, reaction time.

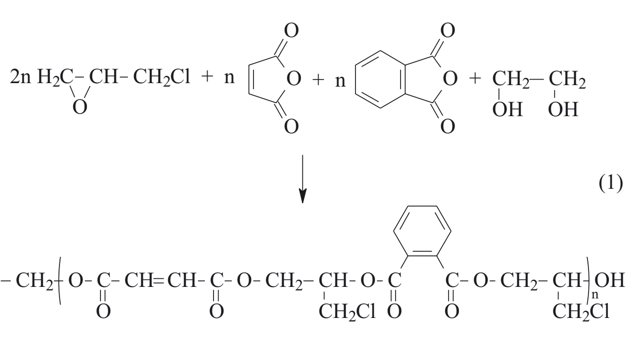
From early 30 th to the 60 th industrial production of unsaturated polyester (UP) resins included solely two methods:

— heteropolycondensation of dicarboxylic acids and/or acid anhydrides with glycols,

— homopolycondensation of hydroxyacids.

Both reactions proceed at high temperature (about 200 °C) with emission of condensation water, which involves large production of industrially effluent water, contaminated with organic side products [1, 2].

Nowadays, the environment protection requires the limitation of liquid industrial wastes. In relation to this problem, the novel technology of UP resins production that based on the copolymerization of acid anhydrides with alkylene oxides has been developed [3—13]. In comparison with the former condensation methods, the reaction is carried out at lower temperature within the range of 100—150 °C without any emission of condensation by-products [equation (1)].


(1)

It was estimated that the production of UP resins could be ten times less energy-consuming because of elimination the distilling-off processes, and decrease in the reaction time and temperature [3]. However, a disadvantage of this process is low degree of *cis* → *trans* isomerization of carbon-carbon double bonds since *cis* bond exhibits lower reactivity than *trans* bond during final crosslinking reactions with styrene. Therefore, during production of UP resins additional step of *cis* → *trans* isomerization is needed in the presence of a catalyst [13].

Recently, novel methods that apply microwave irradiation have been developed to carry out chemical reactions. It is well known that microwave irradiation can accelerate a great number of chemical processes, and, in particular, the reaction time and energy input are supposed to be mostly reduced in the reactions that are run for a long time at a high temperature under conventional conditions [14—20].

In general, microwaves interact with molecules demonstrating a dipole moment. Inability to instant reorientation of the molecules according to changes in the electric field component of electromagnetic (*i.e.*, microwave) irradiation causes that their kinetic energy is converted directly into heat inside a substance. This effect allows to employ microwave irradiation as a source of extremely rapid heating of different materials, and, more recently, it was also successfully applied to synthesis, crosslinking, and processing of polymeric materials [18].

In the present study, we decided to apply microwave irradiation to the synthesis of UP resins in order to ob-

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[*)] Author to whom all correspondence should be addressed; e-mail: pcbogdal@cyf-kr.edu.pl serve whether it is possible to reduce reaction time and compare their properties [*i.e.*, acid number (*AN*), molecular weight distribution and colour] with properties of UP resins obtained under conventional conditions.

EXPERIMENTAL

Materials

Maleic and phthalic anhydrides (Nitrogen Works Kędzierzyn SA, Kędzierzyn-Koźle, Poland), epichlorohydrin — EPI (Aldrich), ethylene glycol — EG (POCh SA, Gliwice, Poland) and lithium chloride — catalyst (Fluka) were used without further purification.

Syntheses of UP resins under microwave conditions

Phthalic anhydride (14 g, 0.10 mole), maleic anhydride (9.0 g, 0.10 mole), ethylene glycol (1.0 g, 0.010 mole), epichlorohydrin (18 g, 0.20 mole) and LiCl (0.1 wt. %) were mixed thoroughly in a three-necked round-bottom flask. Then the flask was placed in multimode microwave reactor Plazmatronika (Poland) equipped with temperature IR-sensor, magnetic stirrer and upright condenser. The range of microwaves power was set from 75 to 105 W, so that the reaction temperature was maintained at three different levels — 120, 130 and 140 °C. The mixture was stirred vigorously under inert atmosphere, and the reaction was continued for time indicated in Table 1 (*i.e.*, until *AN* value of polyester resin dropped below 50 mg KOH/g).

Some reactions under microwave irradiation were performed in a monomode reactor Synthwave 402 (Prolabo) to compare the efficiency of both types of microwave field distribution inside a microwave cavity during the synthesis of UP resin.

Syntheses of UP resins under conventional conditions

The conventional reactions were carried out at the same temperature range in a three-necked round-bottom flask equipped with a mechanical stirrer and thermometer under inert atmosphere, too. The source of heating was an electric mantle.

In some experiments, there were also prepared mixtures with 10 wt. % excess of epichlorohydrin since, according to our experience, it can easily evaporate from the reaction mixture and thus decrease the molecular weight of UP resin.

Methods

All the gel permeation chromatography (GPC) analyses were performed using GPC chromatograph (Knauer). A system of three columns was used: 2xPL-gel (300x7.5 mm; dimension of grains 3 mm and type of pore Mixed-E) with a pre-column. Flow rate of solvent was 0.8 mL/min and temperature of measurement was set to 30 °C. The calibration curve was obtained by using polystyrene standards, while tetrahydrofuran (THF) was used as the solvent.

Acid numbers (*AN*) of UP resins were determined according to Polish Standard PN-87/C-89082/11.

Colour of synthesized polyester was determined according to the Polish Standard PN-86/C-04534/05 (Gardner scale).

RESULTS AND DISCUSSION

The properties of UP resins obtained under microwave irradiation and conventional conditions are presented in Table 1 and Table 2, respectively. As we could observe in our previous investigations on the synthesis of polymers under microwave conditions [21—25], the application of microwaves irradiation for the synthesis of UP resins also resulted in shorter reaction time that was necessary to obtained resins with designed properties. Over twofold reduction of reaction time was observed at temperature of 120 °C, whereas at temperature of 130 °C and 140 °C the reaction time was shortened by about 40 %.

Reaction of EPI with acid anhydrides is exothermic. Thus, the temperature is an important factor during the synthesis of UP resin and should be controlled carefully to avoid an overheating. It was found that the temperature increase up to 130—140 °C resulted in a higher possibility of side reactions that increased $\overline{M}_w$, and, in consequence, $\overline{M}_w / \overline{M}_n$ ratio. The polymers obtained at 130 and 140 °C under both conventional and microwave condi-

Table 1. Characteristics of UP resins obtained under microwave irradiation (multimode microwave reactor)

Temperature, °C	Time, min	EPI/anhydrides/ EG, molar ratio	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w / \overline{M}_n$	*AN*, mg KOH/g	Gardner scale colour
120	120	2.0/2.0/0.1	1541	3274	2.13	43	3
120	120	2.2/2.0/0.1	1954	3685	1.89	20	3
130	100	2.0/2.0/0.1	2197	5524	2.51	28	3
130	90	2.2/2.0/0.1	1566	5795	3.70	14	3
140	60	2.0/2.0/0.1	2019	8513	4.22	27	4
140	45	2.2/2.0/0.1	2179	5386	2.47	47	4

tions were characterized by the higher $\overline{M}_n$, $\overline{M}_w$ and $\overline{M}_w/\overline{M}_n$ values, which was probably caused by side reactions of hydroxyl groups with maleic double bond (Ordelt saturation) that in turn created chain branches. Generally, UP resins synthesized under microwave conditions had slightly lower molecular weight but similar molecular weight distribution. The use of 10 % excess of EPI during the synthesis of UP resin increased the molecular weight.

Table 2. Characteristics of UP resins obtained under conventional conditions

Temperature, °C	Time, min	EPI/anhydrides/ EG, molar ratio	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w / \overline{M}_n$	AN, mg KOH/g	Gardner scale colour
120	300	2.0/2.0/0.1	2104	4021	1.91	17	2
120	300	2.2/2.0/0.1	2156	3969	1.84	19	2
130	180	2.0/2.0/0.1	3125	10 900	3.49	12	4
130	180	2.2/2.0/0.1	3645	14 000	3.84	2	4
140	120	2.0/2.0/0.1	1931	7413	3.84	34	4
140	90	2.2/2.0/0.1	2267	6445	2.84	8	3

Table 3. Comparison of UP resins obtained in multimode and monomode microwave system

Microwave system	Temperature, °C	Time, min	EPI/anhydrides/ EG, molar ratio	AN, mg KOH/g	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w / \overline{M}_n$
Multimode	130	100	2.0/2.0/0.1	28	2197	5524	2.51
Monomode	130	120	2.0/2.0/0.1	30	1200	3000	2.50
Multimode	120	120	2.2/2.0/0.1	20	1954	3685	1.89
Monomode	120	120	2.2/2.0/0.1	9	1580	3360	2.32

Another important factor of the synthesis of UP resin was viscosity of the reaction mixture. During microwave experiments, in which a magnetic stirrer was applied, an increase in the mixture viscosity resulted in difficulties with stirring and, then, in overheating and gelation of the reaction mixtures. As a consequence, such a process had to be stopped to give higher *AN* value and lower molecular weight of a resin. These unsuccessful experiments were useless and their results are presented in this paper. The gelation effect was also observed in conventional reactions, but only at the temperature above 140 °C. Products that were obtained at higher temperature both under microwave or conventional conditions were characterized by darker colour, despite the inert atmosphere used all along the reaction.

The comparison of the products obtained in multimode (Plazmatronika) and monomode (Prolabo) microwave reactors is presented in Table 3. It can be seen that the choice of microwave cavity influences molecular weight of UP resins; *AN* values in case of both reactors reached the desired level <45 mg KOH/g. In general, UP resins obtained in multimode system exhibit higher molecular weight. Moreover, multimode system offers more flexibility during design of microwave experiments.

CONCLUSIONS

Microwave-assisted synthesis is an effective method of preparation of unsaturated polyester resins. In our experiments under microwave irradiation, we observed a reduction in reaction time that was twofold in comparison with conventional processes. However, the most important is the possibility to control the temperature during the microwave experiments to avoid overheating and gelation of the reaction mixtures.

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W kolejnym zeszycie ukażą się m.in. następujące artykuły:

— Wybrane zagadnienia modyfikowania materiałów polimerowych za pomocą promieniowania elektronowego o dużej energii
— Niekonwencjonalne metody wtryskiwania
— Synteza poliimidów z poli(kwasów amowych) i ich estrów
— Badania rozkładu przestrzennego reagentów polimerowych w reakcjach sonochemicznych. Zastosowanie kinetyki konkurencyjnej (*j. ang.*)
— Inicjowana dinadjodanomiedzianem(III) potasu kopolimeryzacja szczepiona akrylanu metylu na alginianie sodu (*j. ang.*)
— Technologiczne aspekty oddziaływania przeciwutleniaczy fenolowych z nadtlenkiem dikumylu w procesach sieciowania poliolefin
— Wpływ grzania strefowego na strukturę włókien PET i dynamikę procesu przędzenia ze stanu stopionego. Cz. I. Krystaliczność i orientacja molekularna