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# APPLICATION OF WATER-THINNABLE PHOTOPOLYMERIZABLE RESIN FOR SHAPING OF MICROREACTORS – PRELIMINARY RESULTS

## ZASTOSOWANIE WODOROZCIEŃCZALNYCH, FOTOUTWARDZALNYCH ŻYWIC DO FORMOWANIA MIKROREAKTORÓW – WSTĘPNE WYNIKI

The article presents the preliminary research on application of synthesized water-thinnable polyester resin for shaping of ceramic element by photopolymerization. The ceramic pastes made of alumina (30 vol%) and photocurable resins were used to prepare thin layers (tapes) and then were exposed to UV radiations. The cure depth and König hardness of cured layers were determined as well as the effect of a photoinitiator concentration on polymerization. The density of sintered ceramic samples also were examined. The research showed that the developed pastes with water-thinnable resin might be used to mold the ceramic elements by soft lithography method. The results obtained for polyester resin were compared with results obtained for commercially available photocurable resin.

*Keywords*: water–thinnable polyester resin, alumina, UV curing, microreactor

W artykule przedstawiono wstępne wyniki badań dotyczące zastosowania zsyntezowanej wodorozcieńczalnej żywicy poliestrowej w metodzie formowania elementów ceramicznych z zastosowaniem procesu fotopolimeryzacji. Z otrzymanych z tlenku glinu (30%obj) i ulegającej polimeryzacji żywicy poliestrowej past ceramicznych formowano cienkie warstwy, które następnie poddawano działaniu promieniowania UV powodującemu sieciowanie się żywicy. Następnie badano twardość Königa otrzymanych warstw, wpływ ilości fotoinicjatora oraz głębokość na jaką zachodził proces fotopolimeryzacji. Wyznaczono także gęstość otrzymanych spieków. Przeprowadzone badania wykazały, że otrzymane pasty z wodorozcieńczalnej żywicy poliestrowej mogą być wykorzystane w formowaniu elementów ceramicznych metodą litografii miękkiej. Wyniki otrzymane dla past z żywicą poliestrową zostały porównane do wyników otrzymanych z handlowo dostępną światłoutwardzalną żywicą.

## 1. Introduction

In recent years there has been growing demand for microfluidic devices [1, 2], which can be characterized by the fact that they have one or more structures (e.g channels) with at least one dimension less than 1 mm. Microfluidic devices containing channels, mixers, pumps, sensors or heaters can be used in biochemical analysis, in separation or detection of chemical substances, synthesis etc. The application of microfluidic devices is expected to have a number of advantages like high heat and mass transfer rate reactions. Thus, the reaction can be performed under more aggressive conditions with higher yields than it can be achieved with conventional reactors [3, 4]. The microfluidic devices that are used for synthesis are known as microreactors. Commonly used microreactors are made from various types of polymers, glass or metals, which brings many limitations e.g. lack of resistance to aggressive environment and high temperature. The replacement of polymers and metals with ceramic materials will allow to abolish these kinds of limitations due to their high thermal and chemical resistance. Moreover, it will open new areas previously inaccessible for microtechnology, such as high temperature catalytic processes [5, 6] The ceramic materials are also chemically inert for biological applications, which makes them excellent materials for biochemical analysis systems.

However, application of ceramics for microreactors requires development of new ceramic materials and new processing techniques. The application of ceramic dispersion in UV curable media is one of common methods for direct fabrication of ceramics. Commercially used monomers are usually soluble in organic solvents, which are not healthy for users and harmful for the environment. However, such organic systems are advantageous

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due to the wide choice of monomers that can be use for composite formulation [7,8]. In this work, the application of new environmentally friendly photopolymerizable polyester resin was proposed A possibility of application of this new waterthinnable resin will be compared with application of commercially available photopolymerizable resin.

## 2. Experimental

### 2.1. Materials

The ceramic powder used in this study was an $\alpha$-alumina A 16 SG with a mean particle size of 0.5 $\mu$m, density 3.895 g/cm$^3$ measured on AccuPyc II 1340 Pycnometer (Micromeritics, USA) and specific surface area ($S_{BET}$) 8.28 m$^2$/g. The powder was purchased from Almatis (Germany). A TEM image of this alumina powder is shown in Fig. 1. Two types of photopolymerizable resin were used. The first was a commercially available resin called 80 3017-ME produced by Ferro GmbH (further described as Ferro resin). Ferro resin is polymerizable acrylate compound with density 0.95 g/cm$^3$. Ferro resin is curable by UV irradiation without addition of external photoinitiators. This kind of resin is soluble in such organic solvent as trichloroethylene-ethanol azeotrope. The second was synthesized in Industrial Chemistry Research Institute (Warsaw, Poland). It was water-thinnable polyester resin containing hydrophilic sulfonate groups prepared by polycondensation method. The density of pure resin measured on AccuPyc II 1340 Pycnometer (Micromeritics, USA) is 1.27 g/cm$^3$. The synthesis method of this type of polyesters was described by Jankowski et al. elsewhere [9,10]. In this case polymerization was possible by the use of Irgacure 2959 (BASF) photoinitiator. The differences between used photocurable resins are shown in Table 1. In this study the additional dispersants were not used.
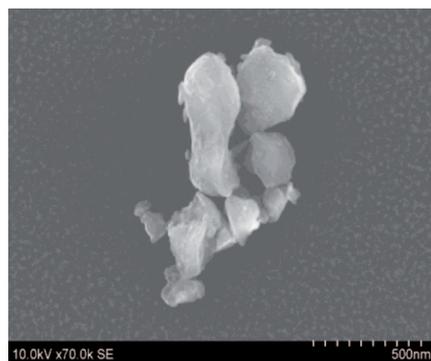


Fig. 1. The TEM image of $\alpha$-alumina A 16 SG (Almatis)

### 2.2. Paste preparation, molding and UV curing

To prepare ceramic paste with good homogeneity the alumina powder was mixed with curable resin and milled for 30 min in planetary ball mill PM100 (Retsch) with speed of 300 RPM. The solid content of alumina in the resin solution varied from 10 to 50 vol.%. In case of synthesized resin, the additional photoinitiator was used. The concentration of photoinitiator varied from 1 to 5 wt% (based on the synthesized resin).

The prepared pastes were casted onto a glass substrate or on a hydrophobic polymer sheet. The process was performed with manual applicators with defined gaps. For cure depth measurements the pastes also were casted into silicone molds having a depth of 5mm and diameter of 15mm.

The UV curing process was achieved by keeping the green sheets (layers) under a lamp which emits the UV radiation ( Lasertex lamp). The wavelength output spectra of the lamp ranged from 320 to 450nm with a radiation intensity 130mW/cm$^2$. The curing time for Ferro resin and synthesized polyester resin was 150s and 285s respectively. The curing time was set experimentally. Longer exposure to UV radiation didn't cause further changes in measured value of cure depth and König hardness (König pendulum: AWS-5, Dozafil, Poland)

TABLE 1

The differences between photocurable resins

| Resin | Used as | Solvent | Photoinitiator | Density [g/cm$^3$] | Curing time [s] | Working temperature [°C] |
|---|---|---|---|---|---|---|
| 80 3017-ME Ferro | received | ethanol-trichloroethylen azeotrope | not required | 0,95 | 150 | < 30 |
| Synthesized | 70wt% water dispersion | water | Irgacure 2959 | 1.2 (dispersion) | 285 | < 70 |

### 2.3. Measurements of green and sintered samples

In order to evaluate the degree of polymerization the hardness of green cured layers was measured by the use of König pendulum. This method evaluates hardness by measuring the damping time of an oscillating pendulum. When the pendulum is set into motion, the pendulum balls roll on the surface and put pressure on the cured layers. Depending on the degree of polymerization, the damping will be stronger or weaker. The hardness of any given coating is given by the number of oscillations made by the pendulum within the specified limits of amplitude related to the damping time on glass.

The depth at which the polymerization occurred (cure depth) was measured with micrometer. After curing by UV radiation the uncured layer was mechanically removed and the samples were washed out in ultrasound bath for 10 minutes in trichloroethylene-ethanol azeotrope (3017 resin) or in water (synthesized resin). Then, the maximum thickness of cured layer was measured.

The obtained layers were also sintered for 1 hour at 1550°C. Due to high amount of polymer in samples the initial heating rate was 1°C/min up to 700°C and then heating rate was increased to 5°C/min. After sintering the relative density and open porosity of sintered layers were measured by Archimedes method.

### 3. Results and discussion

The applied resins differed greatly among each other (Table 1). The commercially available Ferro resin is soluble in organic solvent. For example, in this study trichloroethylene-ethanol azeotrope was used for washing out the uncured paste. What's more, this resin doesn't need the additional photoinitiators and was used as received. The recommended working temperature is below 30°C. On the other hand, the synthesized polyester resin is water thinnable, which means that water can be applied as solvent. In fact, the polyester resin was used as a 70wt% water dispersion with density of 1.2 g/cm$^3$. Unlike Ferro resin, the synthesized resin requires the addition of photoinitiators but in this case the working temperature is up to 70°C. Hence, the influence of photoinitiator concentration was first tested for 70wt% dispersion of polyester resin. Figure 2 shows the variation of König hardness of cured layer on a glass substrate versus the photoinitiator concentration. The curing time for layers with 1 wt% and higher wt% of photoinitiator was 665s and 285s respectively. One can see that the increasing concentration of photoinitiator at the same time increases the König hardness. This effect is due to increasing concentration of photoinitiator that induces the formation of

more radicals, which initiate the photoreaction. It must be noticed that 1 wt% of photoinitiator requires very long curing time to achieve the feeling of dry surface. However, higher concentraor of photoinitiators causes rapid polymerization of the upper layers of the film and because of that the UV radiation cannot penetrate deeply enough in the bottom layers to achieve polymerization. The consequence is the decrease of the König hardness. Based on this measurements the addition of 3wt% of photoinitiator was selected for further investigation. The effect of high photoinitiators concentration was previously reported by Wicks et al. and Chartier et al. [11,12]
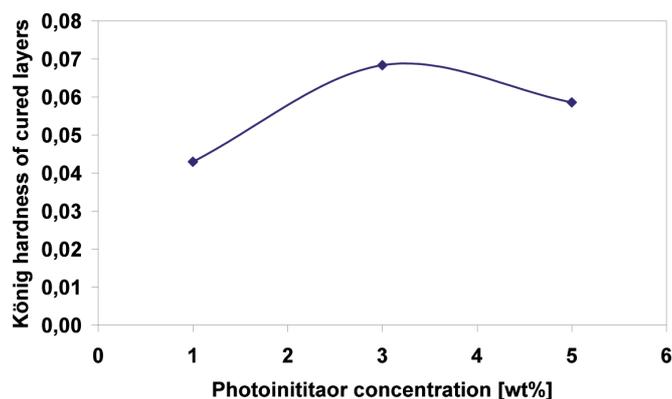


Fig. 2. The effect of photoinitiators concentration on König hardness of cured layer made of 70wt% water dispersion of polyester resin

TABLE 2

The effect of solid loading on maximal cure depth in pastes made of synthesized polyester resin with 3wt% of Irgacure 2959 photoinitiator. Exposure time to UV radiation was 285s

| Alumina [vol. %] | Max. cure depth [mm] |
|---|---|
| 0 | 2.20 |
| 10 | 0.51 |
| 20 | 0.39 |
| 30 | 0.26 |

Due to the scattering effect of UV radiation on the ceramic particles, which limits the light penetration in the layer, the maximal cure depth depends on solid loadings of ceramic powders in monomer (resin) solution as well as on differences in refractive index between monomer and ceramic powder and size of particles [11-16]. Generally, increasing solid loadings decrease the maximal cure depth, what is shown in Table 2. Even such a small amount of alumina as 10vol% radically decreases cure depth. In case of 10 vol% of alumina addition to synthesized monomer the drop of cure depth is greater then 4 times. Increasing the concentration of alumina up to 30% in volume results in a further drop of cure depth. It must be noticed that in case

of synthesized polyester resin 30vol% of solid loading was the highest concentration of alumina in pastes that allowed to tape cast them on the substrate. The pastes with higher concentration of alumina were too viscous.

In case of Ferro resin the maximal concentration of alumina possible to obtain in pastes was 50vol%. This solid content of alumina allowed to obtain the homogeneous pastes with good casting properties. Similarly to pastes with synthesized resin, the increasing concentration of alumina in paste causes decrease of maximal cure depth. The comparison of cure depth between used resin was presented in Table 3. One can see that maximal cure depth for Ferro resin is higher than for synthesized resin. It is worth to note that even for the highest solid loading of alumina in paste made of Ferro resin, which is actually 20vol% much higher than in paste with synthesized resin, the measured maximal cure depth is higher. If we compare the curing time we can see that in case of Ferro resin the exposure time to UV radiation was shorter. As it was mentioned before the curing time was set experimentally and longer exposure to UV radiation than 150 and 285s for Ferro resin and synthesized resin respectively didn't cause further changes in measured value of cure depth and König hardness. It can be due to different nature of used resins. The Ferro resin is based on acrylate compounds that usually polymerize quite fast and easily. Here, one can see that photopolymerization of polyester resin is much slower (requires longer time of curing with addition of 1-5wt% of photoinitiator). It seems that the refractive index of polyester resin differs from refractive index of alumina (about 1.77) much more than refractive index of Ferro resin and that is why the polymerization in Ferro resin goes deeper. To confirm this assumption the measurements of refractive index of alumina and resins will be done in the future.

Apart of that, both pastes might be applied in molding of ceramic elements. The example of cured sample prepared with the use of polyester resin with 3wt% of photoinitiator and 30vol% alumina is presented in Figure 3. Here the authors would only like to demonstrate the possibility of the application of dispersion developed in this work. The paste was shaped by soft lithography method on the alumina substrate and cured to solid by UV radiation. The stamp with patterned relief structures on its surface was made of PDMS (Sylgard 184, Dow Corning). Due to such properties as low interfacial free energy of surface, good chemical stability or an optical transparency down to 300nm, PDMS is the most popular elastomer used in soft lithography [1, 17]. The obtained samples have no cracks or deformations and the surface structures have sharp edges. It shows that application of synthesized water-thinnable polyester resin is reasonable and might be used for shaping microreactors in the future.
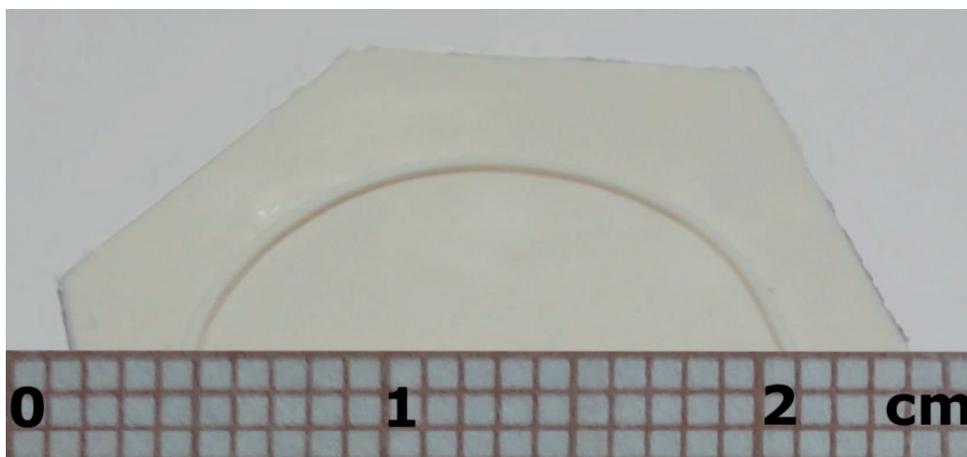


Fig. 3. Sample (water-thinnable polyester resin with 3wt% of photoinitiator and 30vol% of alumina) mould by soft lithography method on the alumina substrate and cured to solid by UV radiation

TABLE 3

The comparison of maximal cure depth for pure resins and pastes with high solid loading of alumina

| Resin | Concentration of alumina [vol%] | Photoinitiator | Exposure time to UV radiation [s] | Max. cure depth [mm] |
|---|---|---|---|---|
| 3017 Ferro | | not required | 150 | 2.48 |
| 3017 Ferro | 50 | not required | 150 | 0.90 |
| Synthesized polyester resin | | 3wt% of Irgacure 2959 | 285 | 20 |
| Synthesized polyester resin | 30 | 3wt% of Irgacure 2959 | 285 | 0.26 |

The effect of applied resins on König hardness of cured layers was also measured and the selected results are presented in Table 4. The measurements were done for two thicknesses of cured layer with application of pastes with 30vol% solid loading. Generally, the thicker cured layer, the lower König hardness. Such results are not surprising because the penetration of light in the layered is attenuated by light scattering on the powder particles and the absorption of the UV radiation. Therefore, the deepest parts of layers (for large thicknesses) are either not polymerized or weakly polymerized, which decreases the König hardness. Because of this limitation photopolymerization is usually conducted for thin layers (below 100$\mu$m) 18-20. The hardness of layers made of Ferro resin is lower than of the layers that have the same thickness but are made of synthesized resin These results are surprising because it was expected that due to higher value of maximal cure depth, König hardness of layer made of paste with Ferro resin would be higher. Higher König hardness of layer made of polyester resin means that the elements shaped by lithography method (e.g. soft lithography) will be less susceptible to deformation during molding and reproduction of pattern will be more precise. It was also found that the synthesized polyester resin is more sensitive to the change thickness of layers. It shows that despite lower König hardness of layers made of Ferro resin, the polymerization goes more efficiently and deeper.

TABLE 4

The effect of applied resins on König hardness of cured layers

| Resin | Concentration of alumina [vol%] | Photo-initiators | Thickness of layer [$\mu$m] | König hardness of cured layers |
|---|---|---|---|---|
| 3017 Ferro | 30 | not required | 150 | 0.70 |
| 3017 Ferro | 30 | not required | 400 | 0.63 |
| Synthesized polyester resin | 30 | 3wt% of Irgacure 2959 | 150 | 0.083 |
| Synthesized polyester resin | 30 | 3wt% of Irgacure 2959 | 400 | 0.061 |

The samples made of Ferro resin and synthesized polyester resin with 50vol% and 30vol% were sintered for 1 hour at 1550°C. Due to high amount of polymer the sintering proceeded in two stages. In the first stage up to 700°C the initial heating rate was 1°C/min. In the second stage the heating rate was increased to 5°C/min. After densification process the relative density and open porosity were measured. The obtained values are summarized in Table 5. In both cases the densification hasn't been carried out to the end and the measured relative densities

were lower than 90%. The relative density of samples that were prepared with the usage of water thinnable polyester is about 5% lower. However, it must be noticed that in this case the solid loading was only 30vol% and in the presence of high amount of organic phase that separates alumina particles between one another it was even more difficult to achieve the densification which was in case of samples prepared with Ferro resin. Due to low value of relative densities the sintered samples show high open porosity. Figure 4 shows the image of sintered samples made of paste with Ferro resin from an light microscope. It can be seen that the pores are quite large, up to 10-20 $\mu$m. The application of such porous material in microreactors proves to be both advantageous and disadvantageous. Too high porosity can make liquid or gaseous substrates penetrate the walls and be trapped there during flow through the microreactors channel. This will influence the yield of the final products or in case of sensor - cause measurement errors. On the other hand, the porosity might be useful in case of deposition of catalyst onto microchannel walls The catalyst will either fill the pores and this way more catalyst will be deposited or thanks to roughness generated by porosity catalyst might be bonded to the surface in a stronger way. However, a great problem might be caused by very high shrinkage. The differences in shrinkage between ceramic paste and substrate during sintering might cause cracks and defects in sintered sample. It means that the substrate should be made form the same ceramic powder as applied paste and have the similar density in green state. Thanks to that the shrinkage in both cases should also be similar during sintering and there shouldn not be any cracks and deformation in final product.

TABLE 5

Relative density open porosity and shrinkage of samples made of paste with photopolymerizable resin after sintering for 1 hour at 1550°C

| Resin | Concentration of alumina [vol%] | Relative density [%] | Open porosity [%] | Shrinkage [%] |
|---|---|---|---|---|
| 3017 Ferro | 50 | 89.4 | 7.2 | ~ 30 |
| Synthesized polyester resin | 30 | 84.8 | 6 | ~ 35 |
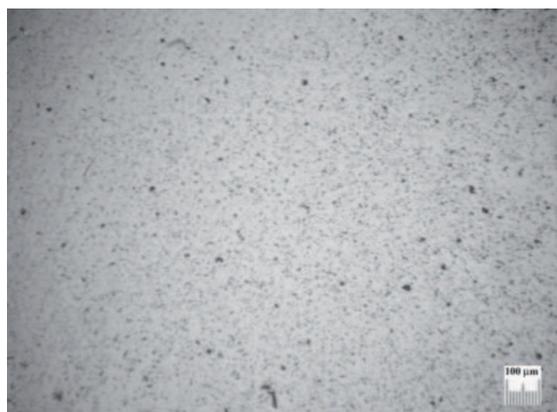
Fig. 4. The image of sintered sample made of paste with Ferro resin from the light microscope (magnification x100)

## 4. Summary

In this work the possibility of application of new water-thinnable resin was compared with application of commercially available photopolymerizable resin. The synthesized polyester photocurable resin requires the addition of photoinitiators. The research showed that to achieve the best degree of polymerization, the proper photoinitiator concentration must be carefully selected. Due to high viscosity the solid loading of alumina in pastes made of polyester is 20vol% lower than in pastes made of Ferro resin and reaches only 30vol%. In this preliminary research on application of polyester resin any additional dispersants were used. It is expected that in further work an application of dispersing agents will allow to increase the concentration of alumina in pastes. What's more, due to dispersibility in water the polyester resin might be use to prepare aqueous slurry with high volume fraction of alumina (0.5-0.6) where the addition of polyester will be varied in range 10-20wt% based on alumina. In contrast to the Ferro resin, the water-thinnable polyester can be processed up to 70°C. The increase of temperature might decrease the viscosity of resin, which will also make it possible to increase the solid loading.

Despite significant differences in concentration of solid loading, in both cases the sintered samples have low relative density and open porosity, which is disadvantageous.

It was also presented that developed pastes with water-thinnable resin might be used to mold the ceramic elements by soft lithography method.

It must be noticed that synthesized resin has another big advantage that is not presented in this paper and concerns handling of the resin. Commercially available Ferro resin requires such organic solvents as above mentioned azeotrope. The organic solvents are usually quite expensive, not very healthy or even toxic. Besides, the cleaning of the equipments was still not easy and took a long time. On the other hand, the polyester resin is a water-thinnable compound, which means that it is possible to use cheaper and nontoxic water for cleaning. Thanks to that the cleaning process was much easier and faster. What is more, the wastes after cleaning are easy to concentrate by simple water evaporation.

It seems that application of synthesized water-thinnable polyester resin is reasonable and might be used for shaping of microreactors or other ceramic elements in the future. However, the further research must be done.

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