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## EFFECT OF SOLVENTS ON CURING PROCESS OF PHOTOPOLYMERIZABLE CERAMIC SUSPENSIONS

### WPLYW ROZPUSZCZALNIKA NA PROCES FOTOPOLIMERYZACJI ŚWIATŁOUTWARDZALNYCH ZAWIESIN CERAMICZNYCH

The effect of solvent on rheological properties and way of preparation of ceramic suspensions or dispersions was presented. The research showed that in case of applied polyester resin the water cannot be used in preparation of UV curable suspensions. However, the highly loaded ceramic dispersion in UV curable media can be prepared if the water is replaced by PEG. Thus, the dispersions with good homogeneity and solids content up to 45-50vol.% of alumina can be obtained. The dispersion prepared in this way can be tape casted and UV cured.

*Keywords:* water-thinnable polyester resin, alumina, UV curing, photopolymerization

W pracy przedstawiono wyniki badań nad wpływem rozpuszczalnika na właściwości reologiczne i sposób przygotowania zawiesin ceramicznych. Pokazano, że w przypadku zastosowanej żywicy poliestrowej woda nie może być użyta do przygotowania światłoutwardzalnej zawiesiny ceramicznej. Jednakże stężona zawiesina ceramiczna może być otrzymana jeżeli woda zostanie zastąpiona glikolem polietylenowym. W ten sposób możliwe jest przygotowanie zawiesiny o stężeniu fazy stałym dochodzącym do 45-50%obj. i dobrej jednorodności oraz lepkości, pozwalającej na jej formowanie metodą odlewania cienkiej folii ceramicznej i utwardzenie promieniowaniem UV.

#### 1. Introduction

In recent years there has been a fast development in rapid prototyping technology that makes it possible to obtain complex ceramic parts in direct fabrication and in consequence reduces the fabrication cost and time. The rapid prototyping methods such as stereolithography require a dispersion of ceramic powders in UV curable monomer or aqueous suspension of ceramic powder with addition of monomers. Exposure to the ultraviolet laser or UV lamp light cures and solidifies the ceramic suspension [1-8].

Nowadays, commercially available, acrylic based monomers, such as 1,6-hexanediol diacrylate, are preferable due to low viscosity and fast curing [7]. Such monomers are usually toxic and mostly soluble in organic solvents. In this work, we proposed the application of environmentally friendly, water-thinnable photopolymerizable unsaturated polyester resin. The effect of solvent on preparation of photopolimerizable ceramic suspension, rheological properties and UV curing was investigated.

#### 2. Experimental

##### 2.1. Materials

An alumina Almatix A16SG, with an average particle size of  $700\pm 64$  nm, measured by DLS method, was pur-

chased from Almatix GmbH (Germany). The powder was an  $\alpha$ -alumina with a density of  $3.895$  g/cm<sup>3</sup>, measured on AccuPyc II 1340 Pycnometer (Micromeritics, USA) and had specific surface area (SBET)  $8.28$  m<sup>2</sup>/g, measured on ASAP 2020 (Micromeritics, USA). As a photopolymerizable monomer an unsaturated polyester resin, synthesized in Industrial Chemistry Research Institute (Warsaw, Poland), was used. It was water-thinnable polyester resin, containing hydrophilic sulfonate groups, prepared by polycondensation method. The synthesis method of this type of polyesters was described by Jankowski et al. [9,10]. A density of pure resin, measured on AccuPyc II 1340 Pycnometer (Micromeritics, USA), was  $1.27$  g/cm<sup>3</sup>, a glass temperature was  $2.5^\circ\text{C}$ . A size of particles in aqueous dispersion, measured on Zetasizer NanoZS (Malvern, England), was  $435\pm 75$  nm. Irgacure 500 (BASF) was used as a photoinitiator. Water and polyethylene glycol (PEG), with a molecular mass  $600$  g/mol, were used as solvents. Dispex A40 (BASF) was used as a dispersing agent for aqueous ceramic suspensions.

##### 2.2. Preparation of UV curable ceramic slurry

**UV curable alumina aqueous suspension.** The unsaturated polyester resin (PR) was used as a 60-70wt.% aqueous dispersion. Such high concentration of PR in water was possible to obtain due to the presence of hydrophilic sulfonate

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groups in molecule structure, that give the water-thinnable properties. The dispersion was stable and it could be stored for a long time. The alumina aqueous suspensions with PR were prepared in redistilled water at room temperature. The solids content in the suspensions varied from 20 to 50vol.%. The concentration of pure PR varied from 5 to 20wt.% (based on the alumina powder). The concentration of photoinitiator was 3wt.% (based on the synthesized resin) [11]. The amount of dispersing agent, Dispex A40, varied between 0.4 and 1.2wt.%. Suspensions were mixed in alumina jar, in a planetary ball mill PM100 (Retsch, Germany), for 60 min with a speed of 300 RPM.

**UV curable dispersion of alumina in PR dispersion.** The UV curable dispersions of alumina in 60-70wt.% aqueous polyester resin dispersion were mixed in alumina jar, in a planetary ball mill PM100 (Retsch, Germany), for 30 min with a speed of 300-400 RPM. The solids content in the dispersion varied from 10 to 30vol.%. The concentration of photoinitiator was 3wt.% (based on the synthesized resin).

**UV curable dispersion of alumina in glycol-polyester mixture.** The UV curable dispersions of alumina in mixture of polyethylene glycol (PEG) with a molecular mass 600 g/mol, and PR were mixed in alumina jar, in a planetary ball mill PM100 (Retsch, Germany), for 30 min with a speed of 300-400 RPM. Polyester resin to PEG ratio was 1:1. The solids content in the dispersion varied from 10 to 50vol.%. The concentration of photoinitiator was 5wt.% (based on the synthesized resin).

### 2.3. Rheological measurements

A rheometer Kinexus Pro (Malvern, England) with plate-plate geometry was used for viscosity measurements. During measurements the shear rate was ramping up from 0.1 to 500  $s^{-1}$  and down to 0.1  $s^{-1}$ . The measurements were carried out at 25°C. All measurements were repeated two times.

### 2.4. Zeta potential measurements

Zeta potential measurements in this study for all suspensions were conducted on a Zetasizer Nano ZS (Malvern, England). The concentration of NaCl electrolyte in the solution was  $10^{-3}$  mol/dm<sup>3</sup>. The solution was ultrasonicated for 5 min before the measurements. The pH of the suspension was adjusted using 0.15 mol/dm<sup>3</sup> HCl or NaOH solution and varied from 3 to 11.

### 2.5. UV curing and cure depth measurements

The UV curing process was achieved by keeping the UV curable ceramic slurries under a UV lamp (iron doped metal halide) Lasertex (Poland). The wavelength output spectra of the lamp ranged from 320 to 450 nm with a radiation intensity 130 mW/cm<sup>2</sup>. The curing time was 280 s.

## 3. Results and discussion

Photopolymerizable ceramic suspensions can be prepared by addition of monomer and photoinitiator into a stable ceramic suspension. Thus, we can combine the principles of

colloidal processing with a technology of photocuring. That is why, Dispex A40 was used to prepare the stable and highly loaded ceramic suspension. Figure 1 shows an effect of dispersing agents on viscosity of 54vol.% alumina aqueous suspensions, at shear rate 100  $s^{-1}$ , as a function of Dispex A40 concentration. This research revealed that the lowest viscosity of ceramic suspensions can be obtained by addition of 0.8wt.% (based on the alumina powder) of Dispex A40. The lower or higher concentration of dispersant in suspension increases the viscosity. Therefore, for further research the concentration of 0.8wt.% was selected.

As it was mentioned before, in colloidal processing the stable suspension is required. The stability of ceramic suspension can be determined by the values of zeta potential. It is believed that zeta potential higher than 25-30 mV is high enough to create a barrier that prevents coagulation of ceramic particles and to stabilize the suspension. The results of zeta potential measurements as a function of pH are presented in Figure 2. A curve of zeta potential for pure alumina is typical for this powder. Between pH 3 and 5 the values of zeta potential are higher than 50 mV. Above pH 5 the zeta potential steadily decreases until pH 8.5, where the curve passes through the isoelectric point (IEP). In the range of 9 to 11 pH, the values of zeta potential are highly negative. The small addition of Dispex A40 shifts the IEP to pH around 4. What is important, above pH 5 the values of zeta potential are higher than 60 mV (the absolute value). It means that the suspension with pH >5 should be stable. The addition of polyester resin to the suspensions shifts the IEP to pH = 3 and decreases a little values of zeta potentials. However, in the range of pH from 5 to 11 the measured potential is still over 40 mV (the absolute value), what is enough to keep stability of suspensions.

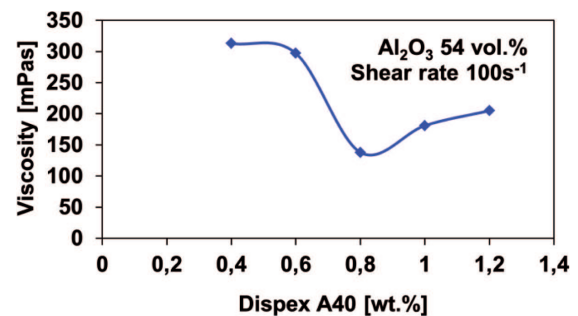


Fig. 1. Effect of dispersing agents on viscosity of 54vol.% alumina aqueous suspensions at shear rate 100  $s^{-1}$  as a function of Dispex A40 concentration

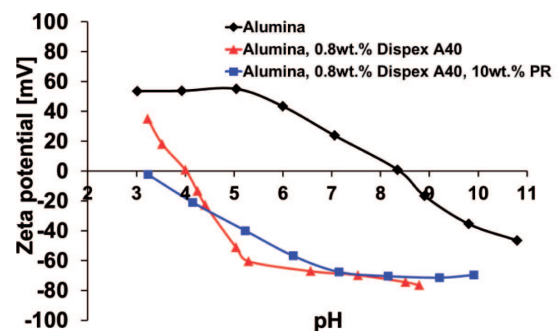


Fig. 2. Zeta potential curves of alumina suspensions without any addition, with addition of 0.8wt.% of Dispex A40 and with addition of 0.8wt.% Dispex A40 and 10wt.% polyester resin

In gelcasting process, which is similar in the nature to the photopolymerization of ceramic suspensions (photo-gelcasting), the amount of monomer in the suspensions is not higher than 5wt.%. However, the preparation of thin ceramic tapes by photo-gelcasting required much higher concentration of monomers. Due to the application of Dispex A40 it was possible to prepare the alumina aqueous suspensions with polyester resin up to 25wt.% and with viscosity low enough to apply them in tape casting method. Figure 3 shows the viscosity of alumina suspensions as a function of a concentration of polyester resin at shear rate  $100\text{ s}^{-1}$ . Applied polyester resin was characterized by very high viscosity, about 300 Pas at shear rate  $100\text{ s}^{-1}$  (see Figure 5). It was expected that the addition of polyester increased the viscosity of suspensions. However, up to 20wt.% of PR the suspensions maintained their flow properties. Higher concentration of PR drastically increased the viscosity and above addition of 25wt.% of PR the suspensions start to be uncastable by tape casting.

Further research reveals that irrespective of the concentration of polyester resin in the suspensions, the casted thin ceramic tapes cannot be cured by UV irradiation without cracks and defects. The UV curing process was achieved by keeping the casted suspensions under a UV lamp. During operation, the UV lamp heated the samples up to  $55^{\circ}\text{C}$ . Thus, due to high surface area in respect to volume in casted thin ceramic layers, in addition to the curing process, a drying effect occurred. In this way, shrinkage related to fast drying and polymerization was responsible for cracks formations. An example of cracked layers is presented in Figure 4.

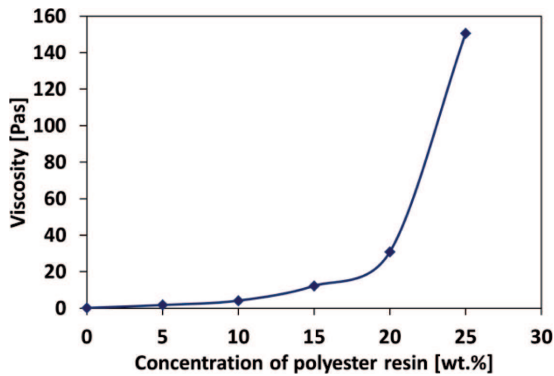


Fig. 3. Viscosity of 54vol.% alumina suspensions as a function of concentration of polyester resin at shear rate  $100\text{ s}^{-1}$



Fig. 4. An image of thin layer made of 54vol.% alumina suspensions with addition of 25wt.% polyester resin, obtained by tape casting method and cured by UV irradiation

Due to the problems with fabrication of crack-free thin ceramic tapes by photo-gelcasting of aqueous suspensions, the UV curable dispersions of alumina in 60-70wt.% aqueous polyester resin dispersions were prepared. In such a way, amount of water in photocurable ceramic suspension could be reduced and thus, during UV curing, it was possible to avoid cracking of cured layers. Although the pure polyester resin was a very viscous medium, the aqueous dispersions of polyester resin show quite low viscosity. That is why, the dispersions with solids content up to 30vol.% were possible to prepare. A comparison of viscosity of pure resin to aqueous dispersion is presented in Figure 5. Although the preliminary results presented somewhere else [11] were very promising, there was a lot of problems with homogenization of such ceramic dispersions. Very often during mixing in planetary ball mill with speed 180-300 RPM the ceramic dispersions were separated into two phases: water and glue-like mixture of PR and alumina. The more detailed rheological measurements confirmed that the aqueous dispersions of polyester resin as well as the ceramic dispersion exhibit tendency to separation into two phases. The effect of shear rates on rheological behavior of 60 and 70wt.% aqueous dispersions of PR is presented in Figure 6. One can see a sudden drop of viscosity around shear rate  $80\text{--}100\text{ s}^{-1}$ , related to the separation of dispersion into two phases. It means that the homogenization process cannot be realized with high mixing speed, what makes it rather ineffective.

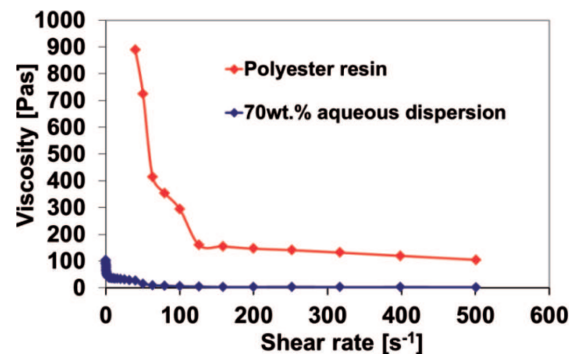


Fig. 5. Viscosity of pure polyester resin and 70wt.% aqueous dispersion as a function of shear rate

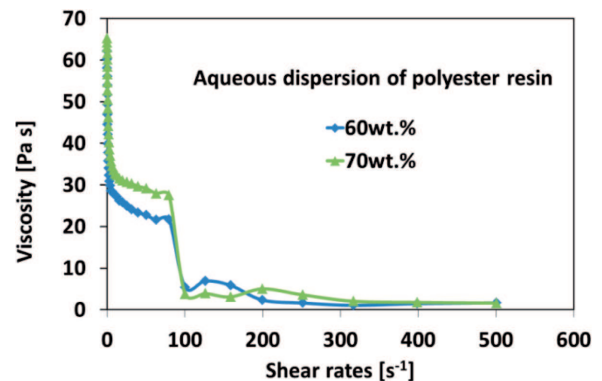


Fig. 6. Viscosity of aqueous dispersions of polyester resin as a function of shear rate

Therefore, it was decided to replace water with another solvent. Due to compatibility with molecular structure of resin, the polyethylene glycol (PEG) was selected. The mixture of PEG with PR (ratio 1:1) is very stable in time, and doesn't separate during mixing. The used PEG-PR mixture shows low viscosity around 2Pas in whole range of shear rates (almost Newtonian-like liquid). That is why, it was possible to prepare UV curable ceramic dispersion with high solids loading up to 50vol.%. Figure 7 shows the viscosity of dispersions in PEG-PR mixture as a function of solids content of alumina. Such dispersions were mixed in planetary ball mill at speed up to 400 RPM, what ensured good homogeneity. In general, increase of solids content of alumina increases the viscosity. Although the homogenization of 50vol.% dispersion was possible, the viscosity was too high for casting of thin layers. Therefore, the dispersion of 45vol.% was selected for tape casting. Figure 8 shows an image of thin ceramic tape made of selected dispersion and cured by UV irradiation. Obtained tape showed good mechanical properties. The tape was smooth, elastic and strong enough to be cut by scissors.

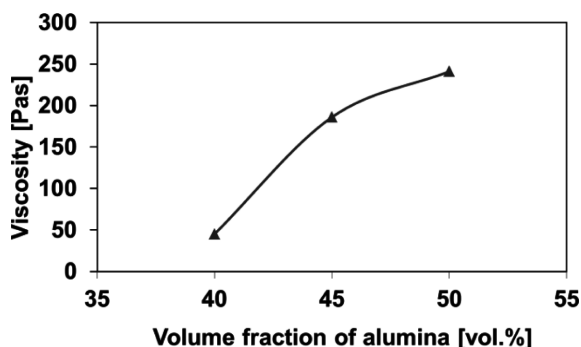


Fig. 7. Viscosity of dispersions in PEG-PR mixture as a function of volume fraction of alumina at shear rate  $100 \text{ s}^{-1}$

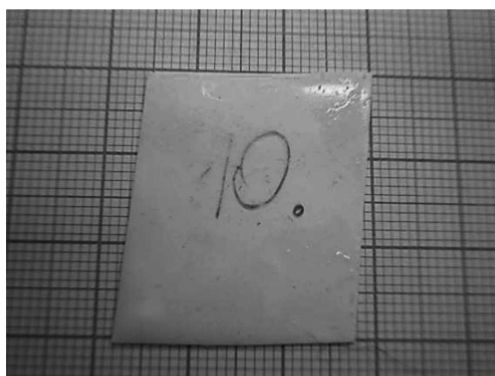


Fig. 8. An image of thin ceramic tape made of 45vol.% dispersion of alumina in glycol-polyester and cured by UV irradiation

#### 4. Conclusions

In this work the water-thinnable polyester resin was used for preparation of photopolymerizable ceramic suspensions.

Although the polyester resin was designed to be dispersible in water, which is cheap and environmentally friendly solvent, due to evaporation during UV curing and separation during mixing, water cannot be applied in UV curable suspensions. However, the highly loaded ceramic dispersion in UV curable media can be prepared if the water is replaced by PEG. Thus, the dispersions with good homogeneity and solids content up to 45-50vol.% alumina can be obtained. The dispersion prepared in this way can be tape casted and easily UV cured. What is more, after UV curing the tapes show good mechanical properties.

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