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Ultrasonication as a Method for Examination of Glasses Derived from UV Curable Nanosilica Pastes

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Abstract

Ceramics and glasses are well suited as materials for chemical microreactors working at high temperatures and chemically aggressive environments. Such microreactors are conveniently produced by rapid prototyping of UV curable dispersions. Ultrasonic methods can provide information on the mechanical properties by the detection of defects and discontinuity of such materials. The technique is used here to study the effect of the paste composition on the properties of the final glasses. The effects of the base monomer type, crosslinker concentration and photoinitiators were examined. The results of ultrasonic measurements were applied to determine both the materials constants and dependences of ultrasonic wave speeds on the original paste composition. It was shown that ultrasonic tests can be useful for optimization of compositions of UV curable ceramic pastes, used in rapid prototyping.
Keywords: Ultrasonication, Chemical microreactors, Rapid prototyping, Nanosilica, Ultrasonic wave velocity

BADANIA ULTRADŹWIĘKOWE SZKIEŁ OTRZYMANYCH Z NANOKRZEMIONKOWYCH PAST SIECIOWANYCH PROMIENIOWANIEM NADFIOLETOWYM

Ceramika i szkło dobrze nadają się na chemiczne mikroreaktory pracujące w wysokich temperaturach i chemicznie agresywnych środowiskach. Takie reaktory dogodnie wytwarzane są metodą szybkiego prototypowania z użyciem zawiesin sieciowanych promieniowaniem nadfioletowym. Metody ultradźwiękowe mogą dostarczać informacji o właściwościach mechanicznych materiałów poprzez wykrywanie wad i nieciągłości ich budowy. W prezentowanej pracy wykorzystano metodę ultradźwiekową do badania wpływu składu pasty na właściwości otrzymanych szkieł. Badano wpływ rodzaju podstawowego monomeru, stężenia cząsteczek wiążących krzyżowo i fotoinicjatorów. Wyniki pomiarów ultradźwiękowych zastosowano do oznaczenia zarówno stałych materiałowych, jak i związków pomiędzy prędkościami fali ultradźwiękowej a składem wyjściowych past. Pokazano, że badania ultradźwiękowe mogą być użyteczne w przypadku optymalizacji składu past ceramicznych sieciowanych promieniowaniem ultrafioletowym, przeznaczonych do szybkiego prototypowania.
Słowa kluczowe: badania ultradźwiękowe, mikroreaktory chemiczne, szybkie prototypowanie, nanokrzemionka, prędkość fali ultradźwiękowej

1. Introduction

Stereolitography (SL) was the first developed rapid prototyping (RP) technique. It allows three dimensional elements to be produced by laser beam irradiation based on the previously designed digital model [1]. The first idea, appeared in the eighties of the last century, used to obtain such devices, was the curing of pure monomers leading to local polymerization. The interest in UV curable systems has grown since then and now also other methods of rapid prototyping are known; enabling the application of different suspensions, also containing ceramic particles dispersed in acrylic monomers [2], as in the presented paper. Stereolithography as a modern tool can be also applied to the formation of microreactors.

Microreactors are microchannel devices in which chemical reactions take place. Two or more fluids are injected separately into the apparatus and mixed by diffusion, without turbulence. Microreactors are very suitable for the chemical or pharmaceutical applications because of several advantages compared to their macroscale counterparts. The high surface-area to the volume ratio is several orders of magnitude larger than for a conventional batch reactor. This enhances heat and mass transfer. Temperature control of strongly exothermic chemical reactions is improved due to the small hold up, high heat transfer rates to the channel walls and by the relatively high heat capacity of the channel walls compared to the heat supplied by the reaction mixture. Due to that, the reactions are very safe and fully controllable.

The small volume of reactants needed for each experiment is an additional advantage [3]. In commercially available microreactors for high temperature applications ceramic or glass can replace polymers or metals (used in corrosive enviroments) [4]. The unique transparency of silica deep into the UV range can be exploited for photochemical microreactors. However, in the case of ceramic based systems, RP requires the use of UV-resin based and transparent ceramic slurries if at all possible. The development of the slurries that have an extremely high amount of solids loading is urgently needed and will provide an important benefit for developing ceramic microtechnology. Ceramic bodies produced from nanoparticles usually show an excellent sintering behaviour [5, 6] and provide a sufficient resolution for the fine microstructures [7].

Furthermore, nanoparticles can reduce UV light scattering in the highly particle loaded resin since scattering processes may significantly reduce the intrusion depth of UV radiation into the slurry and prevent bulk curing of the resin.

The ultrasonic method belongs to the group of non-destructive methods of analysis, being commonly used for testing of materials properties, it is also used for quality control purposes [8]. The method provides opportunity for direct determination of the elastic properties of isotropic materials, but first of all, it is the only method, which simultaneously allows all materials and elasticity constants of the anisotropic bodies to be determined.

The ultrasonic method is based on the measurement of propagation velocity of ultrasonic waves in elastic media, where the velocity is a function of microstructure, elastic constants, density as well as geometrical dimensions of the tested material [9-11]. The ultrasonic tests are repeatable and they can be performed on products of different shapes, sizes and compositions (phase and volume), in different directions and places of the studied object [11].

The individual investigations require choosing a suitable type of measuring device and instrumentation, otherwise it can be the reason of inequivalences of data derived from the measurement of impulses with regard to the occurrence of the strong suppression and the dispersion of ultrasonic waves in porous ceramic materials [9, 12].

In this work we present the results of application of the ultrasonic method for testing nanosilica samples, obtained from dispersions prepared by using UV curable acrylates mixtures, and we show usefulness of the ultrasounds method for the non-destructive analysis, performed during the process of optimization of the materials composition.

The optimization consisted in choosing the composition of samples, which were characterized by the highest values of elastic constants. A type of the main monomer (4-HBA (BDMA) or HEA), a content of the additional monomer (M282), a content of nanosilica (OX50) in the range of 30–40 %, a type of photoinitiator used for hardening the samples (TPO or LTM) and its content were changed during the optimization. The materials constants depend directly on the velocity of ultrasonic waves (1, 2, 3), that is why every change of the value of longitudinal, V_L, and transverce, V_T, velocity registered due to changing the composition of samples, delivers the information about the better or worse elastic properties of the material.

2. Experimental

Amorphous silicon dioxide nanopowder (OX50) from Evonik, (Germany) was mechanically dispersed by a laboratory dissolver Ultra Turrax T 50 (USA) in UV curable mixtures of monomers. The concentration of nanopowder was 30, 35 or 40 vol.%. The main monomer of mixtures was 4-HBA (4-hydroxybutylacrylate, BASF, Germany) or HEA (2-hydroxyethylacrylate, BASF, Germany). These two monomers have one acrylic group and are ended with OH groups. The polar group makes them superficially similar to silica. The second monomer used in all mixtures was M282 (polyethyleneglycol 200 diacrylate, RAHN, Switzerland). The addition of M282 was necessary in order to strengthen the cured samples. The content of M282 was 7 or 25 vol.%. All monomers were chosen due to their refractive indices similar to silica, which provide a high curing depth and a decrease of van der Waals forces. TPO (2,4,6-trimethylbenzoyldiphenylphosphine oxide, Rahn, Switzerland) and LTM photoinitiators were used for UV hardening. The dispersions were cast on the polystyrene molds and cured in the curing chamber (Uvacube100 Honle, UV Technology) with the iron bulb which gives the intensity of 120 mW/cm^2. The UV spectrum was most intensive in the range of UVA. All dispersions were divided into eight groups and their acronyms are presented in Table 1. The cured samples were debound and sintered in air. The sintering program is presented in Table 2.

The non-destructive method using the measurement of the propagation velocity of longitudinal ultrasonic waves was used in the test. The MT-541 device equipped with 0.5 MHz transducers was used. The sticking-plaster was used as

Table 1. Dispersions and their acronyms.

Dispersion	Acronym
30, 35 or 40 vol.% OX50, 25 vol.% M282, HEA*, 3 wt% TPO	3H3T
30, 35 or 40 vol.% OX50, 25 vol.% M282, HEA*, 3 wt% LTM	3H3L
30, 35 or 40 vol.% OX50, 25 vol.% M282, 4-HBA*, 3 wt% TPO	3B3T
30, 35 or 40 vol.% OX50, 25 vol.% M282, 4-HBA*, 3 wt% LTM	3B3L
30, 35 or 40 vol.% OX50, 7 vol.% M282, 4-HBA*, 3 wt% LTM	14B3L
30, 35 or 40 vol.% OX50, 7 vol.% M282, HEA*, 3 wt% LTM	14H3L
30, 35 or 40 vol.% OX50, 7 vol.% M282, 4-HBA*, 5 wt% TPO	14B5T
30, 35 or 40 vol.% OX50, 7 vol.% M282, HEA*, 5 wt% TPO	14H5T

* The HEA and 4-HBA contents are a balance to 100 vol.%.

a coupling medium providing the protection from the additional interferences of the medium coupling the sample.

Each group of dispersions was divided into three subgroups: 30, 35 and 40 in dependence on the content of nanosilica OX50. The analysis was performed on 24 subunits and at least three samples were selected from each subgroup for ultrasonic investigations (Table 1).

The measurements of the velocity of longitudinal ultrasonic wave propagation were performed on at least 72 samples of the following dimensions: height, *h*, from 5.5 to 17 mm and diameter, Φ, from 3.3 to 7.4 mm.

The measurements were performed along the diameter of each sample in two mutually perpendicular directions (the ΦX and the Φ⊥ directions) as well as along the thickness of samples (the *h* direction) (Fig. 1). At least six independent measurements were carried out for each direction and each sample, and the average values of velocity and standard deviations were calculated.

Table 2. Sintering program.

Segment	1	2	3	4	5	6
Ramp [°C·h^{-1}]	60	-	150	-	300	-
Temperature [°C]	500	500	750	750	1250	1250
Holding time [h]	none	2	none	2	none	2

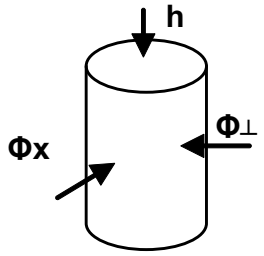

Fig. 1. Directions of measurement.

3. Results and discussion

3.1. Velocities of longitudinal ultrasonic waves

The results of measurements of the propagation velocity of ultrasonic wave for the samples containing 40 % nanosilica OX50 and 3 % LTM photoinitiator but differing in the content of the basic monomer BDMA and HEA, were shown in Fig. 2.

The largest average velocities (V_L = 4705.0 ± 308.7 m/s) were determined for the 3B3L group. The velocities lower by about 16.8 % were registered for 14H3L. For the 14B3L group, the velocities lower by ~29.6 % were measured than for the group 3B3L while the lowest values of velocity (V_L = 2250.0 ± 160.1 m/s) were registered for the group 3H3L. They are smaller values by up to 52.2 % in relation to the 3B3L group.

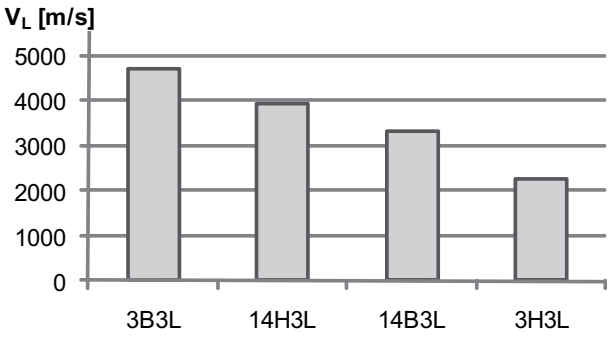

Fig. 2. Groups of 40 % OX50 with the 3 LTM photoinitiator.

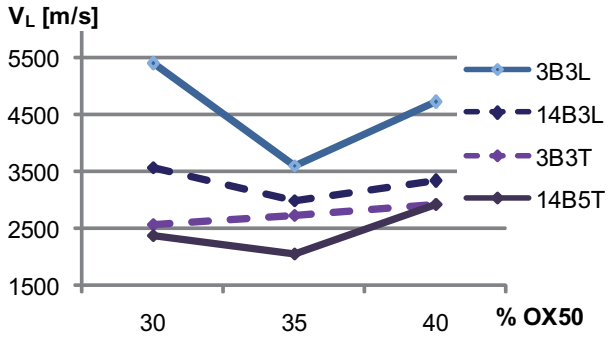

Fig. 3. Velocities of longitudinal ultrasonic waves for BDMA groups.

The influence of changes in the nanosilica content in the samples on the value of longitudinal wave was presented in Fig. 3. The highest velocity (V_L = 5377.9 ± 133.9 m/s) was measured for the group containing 30 % nanosilica in 3B3L. In the groups of samples containing the BDMA monomer, the lowest value of velocity was determined for the 35 % content of OX50 in 14B5T. The changes of V_L can be seen in every group studied (Fig. 3).

By changing the proportion and kind of the applied photoinitiators while keeping equal the proportions of the BDMA or HEA monomer and additional M282 monomer, a change of the velocity of longitudinal ultrasonic wave was observed. For the group of samples with the constant content of the HEA and M282 monomers and at 3 % of the LTM photoinitiator, the largest value V_L was measured in the case of 14H3L with 40 % OX50 (Fig. 4). This value of velocity was V_L = 3914.5 ± 396.2 m/s. For comparison, for the 14H5T group containing 40 % OX50 and 5 % TPO, the value of wave velocity of V_L = 2335.8 ± 63.7 m/s was received and it was lower by about 40 %.

The values of wave velocity are presented in Fig. 5 for the groups with a constant content of the BDMA and M282 monomers but differing in the photoinitiator used (LTM or TPO). Not only the content of nanosilica OX50 in this case influences the registered values of V_L, which are directly connected with the values of materials constants of the samples, but also the kind of photoinitiator which was used. The highest velocity values were measured for the 30 % OX50 3B3L samples.

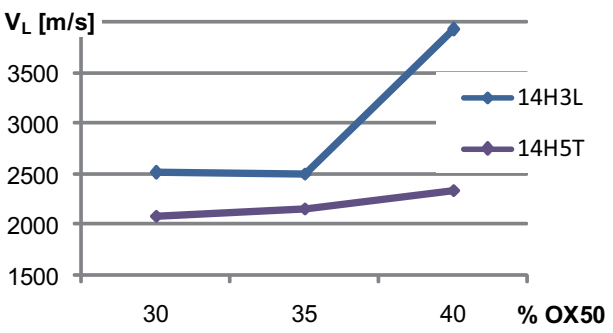

Fig. 4. Velocities of longitudinal ultrasonic waves for the 14H groups.

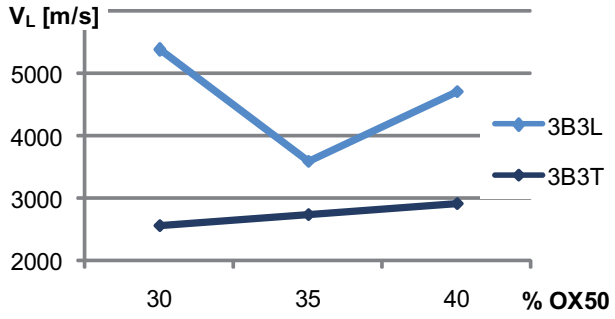

Fig. 5. Velocities of longitudinal ultrasonic waves for 3B groups.

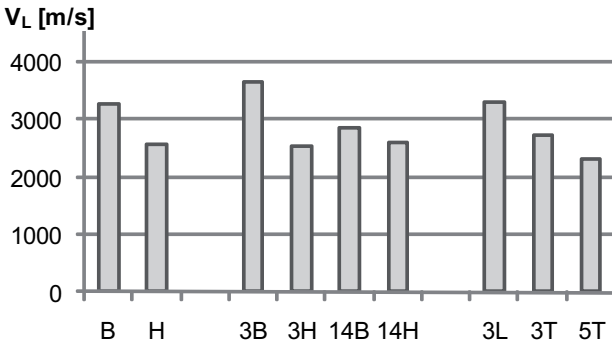

Fig. 6. Average velocities of longitudinal ultrasonic waves for particular groups.

The highest average values of V_L were determined for the groups with the basic BDMA monomer (Fig. 6), inducing as a result the highest values of corresponding materials constants, which is described in the next section. Lower average velocities were shown by the groups with the basic monomer of HEA, suggesting worse elastic properties. The value of velocity for the individual contents of main monomers, *i.e.* the 7 or 25 % admixture of the M282 monomer, was similarly introduced. The higher values characterized the groups containing BDMA as the main monomer (3B and 14B), when compared to their equivalents containing HEA (3H and 14H).

The highest average value of velocity of the longitudinal ultrasonic wave (V_L = 3612.4 m/s) was measured for the groups containing the 3 % LTM photoinitiator. The lower value by ~17 % was obtained for the groups containing the 3 % TPO photoinitiator. The lowest value of velocity by ~29.5 % was obtained for the groups containing the 5 % TPO photoinitiator. Fig. 6 presents schedules of the velocity values for the individual photoinitiator groups.

It has been stated above how the measured values of the velocity of longitudinal ultrasonic waves are influenced by the change of type and content of the basic monomer (BDMA or HEA), the change of nanosilica content as well as the change of the photoinitiator used.

Table 3. Results for individual group.

Group name	Contents of OX50	Density [g·cm^{-3}]	Velocity of longitudinal ultrasonic wave [m·s^{-1}]		Materials constants	
			mean	σ	E [GPa]	G [GPa]
3B3T	30	2.17	2562.0	328.5	13.36	5.76
	35	2.17	2728.8	449.5	15.15	6.53
	40	2.17	2902.9	161.8	17.15	7.39
14H3L	30	2.00	2506.4	119.7	11.78	5.08
	35	2.00	2502.5	164.3	11.74	5.06
	40	2.00	3914.5	396.2	28.73	12.38
3B3L	30	2.00	5377.9	133.9	54.23	23.37
	35	2.00	3583.7	158.7	24.08	10.38
	40	2.00	4705.0	308.7	41.51	17.89
14B3L	30	1.99	3560.6	243.1	23.72	10.22
	35	1.99	2980.5	313.1	16.62	7.16
	40	1.99	3310.9	273.8	20.51	8.84
3H3T	30	1.98	2674.4	112.8	13.32	5.74
	35	1.98	2643.9	149.3	13.02	5.61
	40	2.17	2837.2	133.8	16.42	7.08
3H3L	30	1.95	2490.6	616.4	11.39	4.91
	35	1.95	2255.2	190.2	9.34	4.02
	40	1.95	2250.0	160.1	9.29	4.01
14H5T	30	2.16	2078.8	72.3	8.76	3.77
	35	2.16	2159.8	54.3	9.45	4.07
	40	2.16	2335.8	63.7	11.06	4.77
14B5T	30	2.15	2364.1	240.6	11.27	4.86
	35	2.15	2043.6	215.1	8.42	3.63
	40	2.15	2913.3	195.2	17.11	7.37

3.2. Materials constants

In order to estimate the elastic properties of the studied samples it was necessary to performe measurements of the velocity of transversal wave. A UZP-1 device equppied with 2 MHz converters for the velocities of transversal waves was used to measure elastic properties of the chosen compact samples. The average value of the velocity of transverse ultrasonic wave was estimated to be V_T = 1334.8 m/s.

The measured velocity of transverse wave in the samples was used to determine the Poisson's coefficient according to the following formula:

$$\mu = \frac{\left(V_L^2 - 2 \cdot V_T^2\right)}{2 \cdot \left(V_L^2 - V_T^2\right)}, \qquad (1)$$

where V_L is the velocity of longitudinal wave, V_T is the velocity of transverse wave.

The estimated value of Poisson's coefficient of μ = 0.160 was accepted for all the remaining samples for calculation of the Young modulus and the shear modulus.

If the real value of Poisson's ratio in different samples was different from the assumed μ = 0.160, for example 0.1 or 0.2, then the *E* and *G* calculated error did not exceed 5 %.

The apparent density for calculations of the *E* and *G* materials constants was indispensable estimated on the basis of sample mass measurements and their geometrical dimensions. The estimated apparent densities are presented in Table 3. The values of apparent density are in the range of 1.95 to 2.17 g/cm^3 and they are imperceptibly lower than the theoretical density 2.2 g/cm^3 [13]. The lower density values could be the effect of cracking of samples and therefore an error of the volume measurements.

The average values of the velocity of longitudinal waves along the sample diameter and height for individual samples are presented in Table 3, and they were used to calculate the materials constants according to the following formule:

$$E = \frac{V_L^2 \cdot \rho \cdot (1+\mu) \cdot (1-2\mu)}{(1-\mu)}, \qquad (2)$$

$$G = \frac{E}{2 \cdot (\mu + 1)}, \qquad (3)$$

where:
E – Young modulus,
G – shear modulus,
μ – Poisson's coefficient,
ρ – apparent density of samples.

For all 24 tested subgroups of the samples, the highest values *E* and *G* of materials constants (*E* = 54.23 GPa and *G* = 21.37 GPa) were determined for the samples of composition 30 % 3B3L *i.e.* 30 vol.% OX50, 25 vol.% M282, 4-HBA, 3 wt% LTM. The lowest values of materials constant, (seven times smaller) were measured for the samples of composition 35 % 14B5T, *i.e.* 35 vol.% OX50, 7 vol.% M282 4-HBA, 5 wt% TPO.

All the values of Young modulus, shear modulus, density and velocity for individual groups of the samples are presented in Table 3.

4. Conclusions

Individual groups of the studied materials show differences of the propagation velocity of ultrasonic wave depending upon the amount and kind of main monomer, the content of nanosilica, and also the quantity and kind of photoinitiator used.

The highest values of longitudinal wave velocity and as a result the largest values of materials constants were obtained for the BDMA group samples of the 3B3L composition. The highest values were measured for the samples containing 30 % nanosilica OX50. Somewhat lower values V_L, *E* and *G* were obtained for the groups derived from the 40 % OX50 admixture. The lowest for groups with the 35 % admixture of OX50.

For the group containing the HEA monomer, the highest values of longitudinal ultrasonic wave, Young modulus and shear modulus were obtained for the samples containing 40 % of OX50 (14H3L). While lower values were determined for the samples from the 3H3T group, containing 30 and 35 % of OX50. However, the difference of velocity was comprised within the margin of measurement error.

The group of samples obtained with the BDMA main monomer are characterized by higher average values than the HEA group. Larger average values of materials constants were also obtained for the samples containing 40 % of OX50, lower for 30 %, and the lowest for the groups with the 35 % admixture of OX50.

The highest average value of the velocity of longitudinal ultrasonic wave (V_L = 3612.4 m/s) was measured for the groups containing the 3 % LTM photoinitiator. The average value lower by ~17 % was obtained for the groups containing the 3 % TPO photoinitiator. The lowest value of velocity by ~29.5 % was obtained for the groups containing the 5 % TPO photoinitiator.

The highest values of Young's modulus (*E* = 54.23 GPa) and shear modulus (*G* = 23.37 GPa) were determined for the group composed of 30 vol.% OX50, 25 vol.% M282, 3 wt% LTM and the rest of 4-HBA. The lowest *E* = 8.42 GPa, *G* = 3.63 GPa showed the group with the composition 35 vol.% of OX50, 7 vol.% of M282, 5 wt% of TPO and the rest of 4-HBA. These values are seven times lower than mentioned for the best materials.

The described changes of the velocity of longitudinal ultrasonic wave and connected changes of the materials constants, due to the dependance on selection of individual components of the original paste, can be useful for optimization of the composition of UV curable ceramic pastes, exploited in rapid prototyping.

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