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J. REDUTKO[1*], A. KALWIK[1], A. SZAREK[1]

INFLUENCE OF CURING TIME ON PROPERTIES OF DENTAL PHOTOSENSITIVE RESIN APPLIED IN DLP TECHNIQUE OF 3D PRINTING

The article has presented the method of 3D Digital Light Processing printing as one of the technologies used for rapid prototyping of dental models and making elements of dentures. In this work the research was presented, which the aim was to determine the effect of additional exposure time on the properties of the obtained printouts. Dynamic Mechanical Analysis test showed significant differences in stiffness between uncured specimens as well as specimens cured for 10, 20 and 30 minutes. In turn the obtained TG and DTG curves allowed to determine the most optimal curing time for DLP printouts. These studies provide the basis for determining the most appropriate method for handling printouts after the process of printing from liquid resin, so that they are the best possible quality for dentists and prosthodontists.

Keywords: Digital Light Processing, dental models, light-cured resin, DMA, STA

1. Introduction

Rapid prototyping technologies connected with scanning and 3D printing have dramatically changed dental prosthetics, orthodontics and implantology. In maxillofacial surgery and implantation, the use of anatomical models, made with any number of printing techniques, has become common and necessary to facilitate the planning of complex procedures [1]. Modern methods of manufacturing dental models allow to omit several steps of the traditional process of their creation, significantly reducing production time. At the same time, the additive technologies used in dentistry are extremely accurate and convenient for both patients and dentists using them in clinical practice [2-4]. When choosing the appropriate 3D printing method, it is important to consider the availability of materials and their properties in terms of medical applications as well as the desired resolution of the printed objects [5].

Today, many dental and prosthetic laboratories are increasingly using DLP (Digital Light Processing) method of 3D printing based on curing liquid material with a UV light beam. It is a method thanks to which the resulting printouts are very accurate [2,6], with no visible printed layers, and the time of the element production is much shorter compared to the FDM method. Moreover the elements obtained using the DLP technique are characterized by higher precision in comparison with FDM [3]. In this technology, a single layer of photosensitive resin is cured by the light emitted by the projector placed under the plastic tank (where the bottom of the tank is made of a material permeable to UV radiation) [7]. In this case, the layer is not cured point by point as in SLA technology, but as a whole, thanks to which the printing time is much shorter and the resulting layers are between 25 and 100 μm thick range [2-3,8].

Dentistry has been using photosetting materials extensively for a long time, therefore their use for printing implants and denture components was obvious. Methods of producing dental components by 3D printing are based on methacrylic resins, as they show much better biocompatibility compared to acrylic resins. Parts printed with DLP technology are characterized by to some extent anisotropic structure [9], because photopolymerization makes each new printed layer closely connected to the previous one [10,11]. These issues are concerned about e.g. the paper [12], which presents the influence of printing parameters on the accuracy of stereolithographic resin printouts. Moreover, 3D printing in dentistry is becoming increasingly popular due to the speed and efficiency of production and the possibility of adapting it to the specific needs of the patient [13].

Printing of photosensitive resin elements that can be implanted in the human body is not limited to dentistry. Research

[1] CZESTOCHOWA UNIVERSITY OF TECHNOLOGY, FACULTY OF MECHANICAL ENGINEERING AND COMPUTER SCIENCE, DEPARTMENT OF TECHNOLOGY AND AUTOMATION, 21 ARMII KRAJOWEJ AV., 42-201 CZESTOCHOWA, POLAND

* Corresponding author: jredutko@iop.pcz.pl

has been underway to produce microscaffolds for partially printed vascularised tissues and to use them as positioners for precise implant application [14-15].

The aim of this study was to determine the additional curing time of models printed with DLP technology from photosensitive resin, intended for dental applications. The study focused on dynamic mechanical and thermogravimetric analysis of samples cured at different times.

2. Methods and methodology

The tests were carried out on samples made using the incremental method, whose shape was adapted to the holder of the measuring device. The samples were additionally cured after the printing process for 0, 2, 10, 20 and 30 minutes. The test consisted of the determination of the storage modulus, tangent of the loss angle using the Dynamic Mechanical Analysis. Additionally, thermogravimetric curves and first derivatives of thermogravimetric curves were determined during STA. These values were assessed for all additionally cured and uncured samples.

In Autodesk Inventor 2016 program there were designed rectangular specimens measuring 10×56×4 mm for this test. The models were converted from .ipt format to .stl format in high resolution, with an area deviation of 0,004046, a normal deviation of 10, a maximum edge length of 80,72 and an aspect ratio of 21,5. Then, in slicer program - Autodesk Netfabb, the models were split into 50 micron thick layers and saved in the .rshapebuild extension.

2.1. 3D printer and auxiliaries

Samples for testing were printed on a Rapid Shape D20 II printer, which is based on DLP printing technology and is used primarily to produce high-quality dental models. This printer works with using biocompatible methacrylic resins, cured by light having wavelength of 385 nm emitted by a UV LED projector. In turn, the print resolution of the device is 34 μm. The working chamber is small (130×75×110 mm), but it can print even several dental models at the same time, which is why this printer is often used by small prosthetic laboratories.

For DMA test, 5 rectangular specimens measuring 4×10 ×56 mm were printed and then cured in a Sirio Sibari Sr620 lamp emitting light UVA and white light with wavelength of 320÷550 nm. The curing time was equal 2, 10, 20 and 30 minutes. Two samples remained uncured and were cleaned only with isopropanol from the resin residues left on them after the printing process.

2.2. DMA

Dynamic Mechanical Analysis (DMA) is a method of recording changes in the characteristics of the polymeric sample being tested, subjected to periodically changing mechanical loads (e.g. sinusoidal) as a function of temperature. Tests performed with this method allow to determine dynamic modulus of elasticity E'', loss modulus E', as well as tangent of mechanical loss angle tgσ. The purpose of the test is to determine the occurrence of anisotropy of mechanical properties of printed samples. When the sample is exposed to periodically variable vibrations (e.g. sinusoidal), deformation takes values Eq. (1).

$$\sigma = \sigma_0 \sin \omega t \tag{1}$$

where:

ω – angular frequency; $\omega = 2\,\pi f = 2\,\pi/T0$,
f – frequency,
σ_0 – stress amplitude.

Then stresses occur, periodically variable, offset by an angle of $0 < \delta < (\pi/2)$ in relation to the deformation [16]. The value of the complex modulus E^* can then be determined by the sum of the loss modulus E' and the modulus of elasticity E'' Eq. (2).

$$E^* = E' + i \cdot E'' \tag{2}$$

where:

E^* – complex modulus,
E' – the real part of the dynamic modulus,
E'' – the imaginary part of the dynamic modulus.

The ratio of the modulus of elasticity and the modulus of behaviour and elastic energy emission during deformations is called the mechanical loss factor [16] tgδ Eq. (3).

$$\mathrm{tg}\delta = \frac{E''}{E'} \tag{3}$$

For conducting research NETZSCH's DMA 242 (Fig. 1) device was used, which enables to test specimens in a temperature range from –170ºC to 600ºC for any kind of dynamic load (depending on the grip used). In the presented test, a three-point bending fixture in the form of a beam was used [17].

Measurements were carried out according to the following parameters:

- Sample cooling in nitrogen atmosphere,
- Amplitude of 80 μm,
- Frequency of 10 Hz,
- Temperature range from –80 to 250ºC,
- Samples with dimensions of 10×4×50 mm,
- Sample heating speed 2ºC/min.

2.3. STA

Another study conducted within the work was thermogravimetric analysis carried out on the STA 449 F5 Jupiter by NETZSCH (Fig. 2) [18]. This apparatus is used for simultaneous thermal analysis of sample, which is a combination of thermogravimetry (TG) and differential scanning calorimetry (DSC). Hence this study simplifies the evaluation of the changes that take place in the sample because the obtained curves complement each one another. The measuring device can perform measurements

in the temperature range from room temperature to 1200ºC, with the rate of temperature changes from 1 to 25ºC [19].

Static thermogravimetric analysis has been used primarily in the study of kinetics and reaction mechanism. The result of the test is a thermogravimetric TG graph and a parallel DTG analysis, which is the first derivative of the TG curve with respect to time [20,21]. The TG curve is a function Eq. (4):

$$G = f(T) \tag{4}$$

where:

G – mass

T – temperature.

Whereas DTG is:

$$\frac{dG}{dt} = f\left(T\right) \tag{5}$$

where: t – time.

In which:

$$T = \beta \cdot t \tag{6}$$

Where: β – sample heating rate.

In this study thermogravimetric curves (TG) and first derivatives of thermogravimetric curves (DTG) were analysed. The TG curves were analysed to assess the percentage loss in mass in the test specimens. In turn, DTG curves made it possible to determine the temperatures at which the transformations of the tested material took place.

Testing parameters are following:

- Test conducted in nitrogen atmosphere,
- Sample heating speed of 20 K/min,
- Temperature range from room temperature to 800ºC,
- Sample weight is approx. 10 mg.

Fig. 1. Device used in research DMA 242 by NETZSCH [17]

Fig. 2. Device used in research STA 449 F5 Jupiter by NETZSCH [18]

3. Results and discussion

Firstly, the analysis of the curves obtained during the DMA tests, i.e. showing the dependence of the storage modulus and the tangent of the mechanical loss angle as a function of temperature was carried out. The analysis included the results obtained by studying the uncured sample after the printing process and samples cured for 2, 10, 20 and 30 minutes. The collection of the aforementioned curves for all tested samples are shown in Fig. 3 and Fig. 4. This test determines whether the longer curing time of DLP-printed components affects their properties.

Analysing the dependence of the storage modulus of printouts E' on temperature, one can see that in the temperature range from –80ºC to –20ºC, all tested samples do not show significant changes in the storage modulus relative to each other. Within this temperature range the module E' for both cured and uncured samples is between 4400 MPa and 4600 MPa. Differences appeared when the temperature in the measuring chamber exceeded –20ºC. Then one can observe a rapid drop in the value of the storage modulus, especially for the sample not subjected to additional curing after the printing process, as well as for the sample cured for 2 minutes. For an uncured sample, the drop in E' value progresses until it reaches about 45ºC in the chamber. The mildest drop is observed for samples cured for 10, 20 and 30 minutes, whereby the curves of cured samples 20 and 30 minutes practically overlap. The curve corresponding to a specimen cured for 10 minutes shows a slightly smaller loss of stiffness compared to specimens cured for longer. The values of the storage modulus and the tangent of the loss angle that the printed samples achieved at 50ºC and 100ºC are shown in Table 1.

The curves of the storage modulus as a function of time for all five samples correspond to the curves of the tangent of loss angle tgδ. The uncured sample has very good damping properties, reaching its maximum tgδ value of approximately 0,37 at 60ºC. The sample cured for two minutes and the other printed samples reach a similar tgδ value in the range of 0,25-0,27. Differences in glass transition temperatures (represented by the tgδ peaks) are noticeable between an uncured, cured for 2 minutes sample and a cured for 10, 20 and 30 minutes sample. The three longest-cured printed specimens have a glass transition temperature between 135ºC and 140ºC, while a cured in the shortest time sample has a glass transition temperature below 100ºC.

TABLE 1

The values of the storage modulus and the tangent of the loss angle achieved by printed samples at different curing times at 50°C and 100°C

Curing time, minutes	Value of the storage modulus at 50ºC, MPa	Value of the storage modulus at 100ºC, MPa	tgδ of loss angle at 50ºC	tgδ of loss angle at 100ºC
0	469	60	0,314	0,069
2	1927	348	0,153	0,238
10	2500	970	0,099	0,156
20	2649	1352	0,089	0,141
30	2788	1363	0,066	0,135

The next step in the presented work was the analysis of thermogravimetric curves (TG), which represent the mass changes that occurred in the sample as a function of temperature. The loss of mass in the sample may be caused by dehydration or dehydroxylation, combustion of organic substances, as well as thermal decomposition and dissociation of salts [19,20].

The TG and DTG curves were compared in the study, analysing the loss of mass in individual samples. It was determined whether there is a correlation between the curing time and weight changes in printed samples. For an uncured sample (Fig. 3), both the TG and DTG curve remains constant until a temperature of 280ºC is reached. Then, a rapid drop in weight of about 90% in the temperature range from 280ºC to 470ºC is recorded. Three distinct peaks can be seen on the DTG curve showing changes in the rate of decomposition of the components of the tested resin. The first peak at 395,5ºC, the next when the sample reached 435,0ºC and the last at 598ºC. For the sample cured additionally for 2 minutes one can observe a very similar course of curves, differing from the original sample by only a few tenths of a degree.

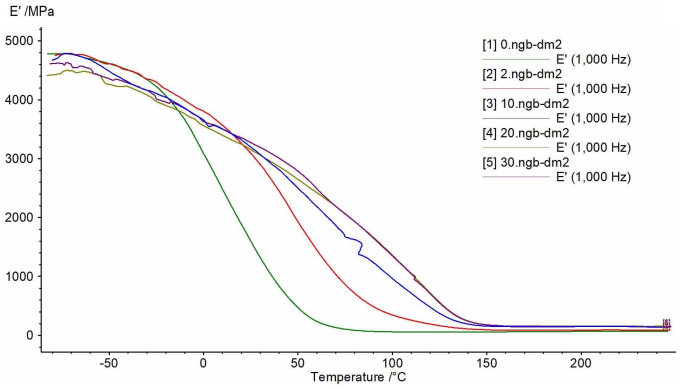

Fig. 3. Storage modulus *E'* dependence on temperature of all tested printouts

The 10-minute cured sample graph shows (Fig. 4) an even more rapid drop in mass than the two previous samples, as it is almost 93% (TG curve) at 300ºC to 470ºC. The DTG curve shows in turn two mass changes: the first at 435,4ºC, the second at 643,9ºC.

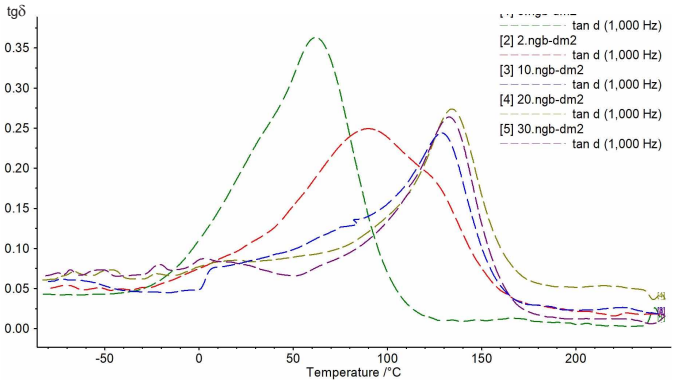

Fig. 4. Course of change of tangent values of the mechanical loss angle tgδ for all printouts tested

The sample cured for 20 minutes in thermogravimetry, largely coincides with the sample cured 10 minutes longer (Fig. 5). The curves representing changes in the cured specimen for the longest time represent a weight drop of more than 93% at 320ºC to 475ºC according to the thermogravimetric curve. In contrast, a derivative of this curve shows a single, rapid transformation at 435,4ºC, similar to the same curve for a sample exposed in a UV lamp for 20 minutes.

Studies carried out by other authors, who determined the impact of curing on samples made by SLA and DLP 3D printing technology, primarily focus on the assessment of mechanical properties before and after curing by UV radiation. All authors

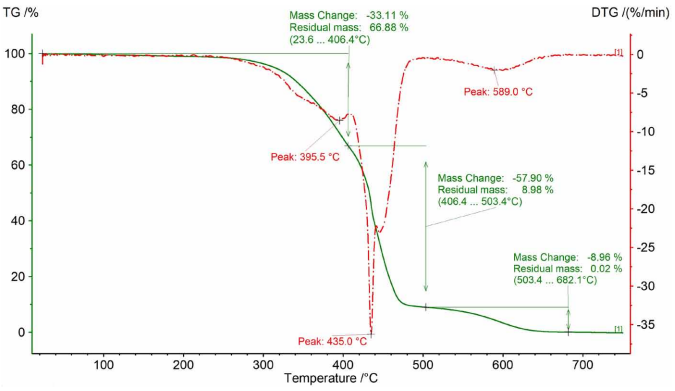

Fig. 5. TG and DTG curves of uncured sample

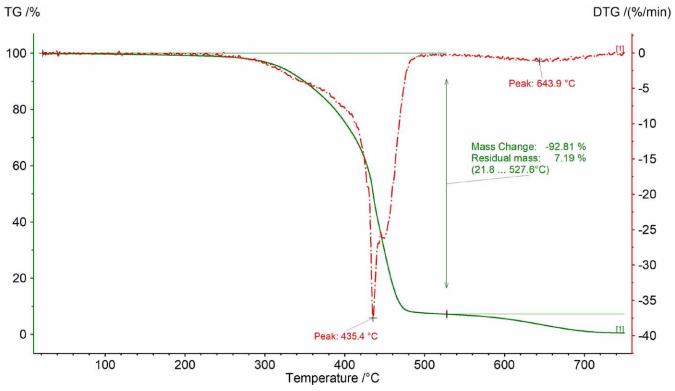

Fig. 6. TG and DTG curves of cured samples for 10 minutes

have agreed that the process of additional curing of samples is necessary to improve the mechanical properties of photopolymer resin elements. Additional exposure of the printouts improves their hardness, but also slightly reduces their tensile strength. However, there is a lack of research to clearly determine the curing time of the models in a UV lamp that would be optimal to achieve the best material properties [22-26].

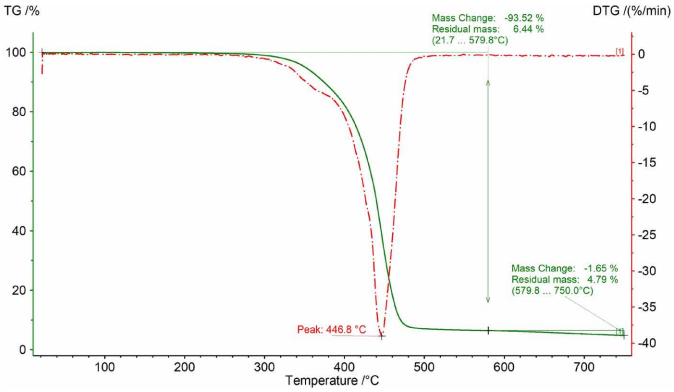

Fig. 7. TG and DTG curves of cured samples for 30 minutes

4. Conclusion

3D printing using a liquid light-cured resin technique is a manufacturing method that requires a deeper understanding, due to the significant improvement in the work comfort of dentists and prosthodontists. While the printing process itself can be described as refined, the selection of appropriate finishing operations seems to cause some problems. In the presented work it was checked whether the curing time of printouts from resin used for dental elements has an influence on their properties. It was also analysed at what temperatures degradation of the tested material occurs.

It was noted that during the DMA test, there are significant differences in printouts stiffness between uncured or very briefly cured samples and samples subjected to additional UV exposure for 10, 20 and 30 minutes. It should be emphasized that a curing time of 10 minutes is sufficient, as longer exposure does not significantly improve the damping properties of the specimens. Printouts cured for 20 and 30 minutes had very similar courses for both the storage modulus and the tangent of loss angle. The longest cured samples show a glass transition temperature above 130ºC, but when this temperature is exceeded, the tgδ curve drops rapidly, which may indicate the start of the material degradation. This process may also be indicated by the fact that after removing from the device chamber, all tested samples looked burnt, changing their colour to amber.

By analysing the STA test and the curves obtained in this test, it can be concluded that the most optimal curing time is 10 minutes. This can be inferred from the weight loss results of the samples. The transformations taking place in the tested samples occur at very similar temperatures (from 435,0ºC to 446,2ºC), however, these differences are more noticeable between uncured samples and samples cured for 20 minutes and longer. For an uncured sample, one can observe three peaks indicating the occurrence of decomposition, for a sample cured for 10 and 20 minutes two mass changes, while for a sample exposed for 30 minutes only one.

In summary, samples cured within 10 minutes have the most favourable properties. A shorter curing time is not sufficient to achieve the desired properties, while a 20 or 30 minute curing does not significantly improve the properties of the printouts compared to samples that are in a UV lamp for 10 minutes. The presented analyses are an introduction to further research enabling to determine the effect of printouts curing time on strength and tribological properties.

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