**Introduction**

3D printing has been widely used for almost 30 years nearly in the engineering, industry and manufacturing fields. In dentistry, it is used in many fields like oral and maxillofacial surgery, prosthetic dentistry, implantology, endodontics, periodontology, and orthodontics. Due to the rapid development of 3D printing technology and new materials, the application possibilities became more and more widespread. Among the 3D printing technology, light curing is a kind of technique that can be used in the field of dentistry next to powder bed fusion and fused deposition modelling. The applicable materials in light curing technology are resins and ceramics. Advantages of this technique are good mechanical resistance, reduced construction time, and the printed object has higher surface quality [15]. Working on the digital light processing (DLP), photo jet (PJ) and stereolithography (SLA) principles belong to light curing technology [15]. The stereolithographic (SLA) technology is the most frequently used and most investigated technology in dentistry [6]. In this technique, the applied model materials are photopolymerizable resins in which a mixture of mono and multifunctional (meth) acrylate monomers is used. The formed structure after the photopolymerization cross-linked network, that mechanical properties are influenced by the structure and functionality of initial monomers [1]. The most frequently used model materials give a stiff and rigid printed object. The flexible and elastic model materials or shape memory polymers have recently appeared. Elastic and flexible model materials for 3D printing were presented by Formlabs Inc. two years before [7]. The difference between the flexible and elastic properties is the recovery time. The recovery time means the time required for the specimen to return to its original (before deformation) state. The recovery time of elastic materials is shorter than the flexible version. The flexible material withstands the effect of bending, flexing, and compression force even through repeated cycles. The most commonly examined mechanical properties of these materials are tensile and tear strength [12]. These stiff soft-touch materials can also open new application areas in the field of dentistry. The above-mentioned flexible Formlabs resin is recommended for the preparation of moulds, masks and studying of the anatomy of cartilage and ligament. Another flexible and biocompatible 3D printable resin from Formlabs is Indirect Bonding Tray (IBT) resin. In the field of orthodontics, the flexible resin (IBT resin) can be used for the preparation of indirect bonding trays and orthodontic bracket placement [8]. Based on the technical data sheet of IBT resin, the tensile strength and Young's modulus are less than 5 MPa and 16 MPa [9].

Next to the above presented physical characterization, the chemical characterization is also important that give information about the formed cross-linked structure. The formed crosslinked network has an effect on physical properties of polymer. Therefore, mechanical and chemical characterization are complementary methods. One possible chemically characterization of a photopolymer is the measuring of degree of conversion (DC), which express the incorporation rate of the monomers into the polymer chain. This ratio can be measured by
Fourier transformation infrared spectroscopy (FT-IR). The polymerization can continue for up to 24 hours after irradiation, which is called a post-polymerization process [14].

In our study, a flexible 3D printable resin is prepared and characterized chemically and physically. The flexibility of printed objects is achieved by the chemical structure of chosen acrylate monomers and their ratio.

Materials and Methods

3D printable acrylate resin preparation

In this study, the mixture of butyl acrylate (BA; Sigma-Aldrich, USA) and urethane dimethacrylate (UDMA; Sigma-Aldrich, Germany) monomers were used in a 3:7 weight ratio. This monomer ratio was experienced for optimal flexibility. The photoinitiator was phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide (BAPO; Sigma-Aldrich, Italy) that was used in 0.2 %w/w in the resin matrix. The applied coinitiator was ethyl 4-(dimethylamino) benzoate in 0.4 %w/w in the resin matrix. The mixture was stirred one night in dark on a magnetic stirrer before use.

Preparation of specimens for tensile strength measurements

The flexible materials can be well characterized by tensile strength measurements. For tensile strength measurements, dog-bone shaped (or dumbbell-shaped specimens) specimens were prepared (Figure 1). The specimen parameters were 5 mm in width and 2 mm in thickness. The gauge length of specimens was 30 mm. The specimen maker was made from silicone impression material. The surface of the resin inside the mould was covered by polyester foil to prevent the formation of an oxygen inhibition layer. The resin matrix polymerization was performed in LC-6 light oven (Scheu, Germany) for 1 min, 2 min and 5 min.

Tensile strength measurements

Before the tensile strength measurements, the dog-bone shaped specimens were stored at room temperature in dry and normal light conditions for 24 hours. This period is the dark phase of polymerization. The tensile strength measurements were performed with a help of a mechanical testing device (Instron 5544, USA). The average thickness and width were calculated at each specimen based on three times measuring of width and thickness at three different places. The crosshead speed was 1 mm/min. The tensile stress (MPa) and Young’s modulus (MPa) were calculated by BlueHill software. The number of tested specimens was 15 (n = 15).

Specimen preparation for the degree of conversion (DC) measurements

For DC measurements 2 mm thick and 10 mm in diameter cylindrical specimens were prepared with a help of a Teflon mould. The surface of the resin inside the mould was covered by polyester foil to prevent the formation of an oxygen inhibition layer.

Degree of conversion measurements

Before the degree of conversion measurements (DC), the samples were stored at room temperature in dry and normal light conditions for 24 hours. The DC was measured by Nicolet 6700 Fourier Transformation Infrared Spectroscopy (Thermo Electron Co. USA) in attenuated total reflectance mode. The DC was calculated by the following formula:

\[
DC (\%) = \frac{A_{\text{polymer aliphatic}}}{A_{\text{polymer internal standard}}} \times 100
\]

where \( A_{\text{polymer aliphatic}} \) means the absorbance of aliphatic groups of polymerized sample; \( A_{\text{polymer internal standard}} \) means the absorbance of carboxyl groups (C = O) in the polymer chain; \( A_{\text{monomer aliphatic}} \) means the absorbance of aliphatic groups of monomer in unpolymerized resin; \( A_{\text{monomer internal standard}} \) means the absorbance of carboxyl groups (C = O) of monomer in unpolymerized resin. The absorbance of the internal standard was unchanged during the polymerization. The resonance wavenumber values of aliphatic groups were 1637 cm\(^{-1}\), of the carboxyl group 1715 cm\(^{-1}\) [4]. The number of the tested specimens was three (n = 3). The top and bottom surfaces of cylindrical specimens were also analysed. The top surface means the upper layer from which the specimen received the light. The bottom surface means the lower layer, close to the mould bottom. The depth of penetration of infrared light is a few micrometres. One spectrum means 16 measurements. Three different places were measured for each specimen.
3D printing trial
A 3D printing trial was performed by Formlabs Form 2 (Formlabs Inc., Sommerville, USA) SLA printer of our prepared photopolymerizable resin in open mode with a resolution of 50 μm. The set printed object parameters are the same as specimens of tensile strength measurements that are 5 mm in width and 2 mm in thickness with 30 mm gauge length. The printed objects were analysed by tensile strength measurements after 24 post-polymerization times. The mechanical analysis of printed objects was performed without post-treatment or post-curing.

Statistical analysis
Student t-tests were used for statistical analysis of data with a help of the Excel Analysis Tool pack (Microsoft, USA). Before the t-test, an f-probe was performed. In the case of equal variance two-sample t-test was performed. In the case of non-equal variance, the Welch test was used. The significance limit was 0.05.

Results

Tensile strength measurements results
The tensile stress (MPa) and Young’s modulus (MPa) data are shown in Figure 2 and Figure 3, respectively. The tensile stress data increased by polymerization time. At 1 min polymerization time the stress was 0.78 MPa, at 2 min was 0.90 MPa and 5 min was 1.15 MPa. There was a significant increment between the 2 min and 5 min (p < 0.05). The difference in stress was significant between the stress at 1 min and the stress at 5 min polymerization time (p < 0.05). There was no significant difference in stress at 1 min and 2 min.

Young’s modulus also increased by polymerization time. The modulus was 14.08 MPa, 15.18 MPa and 17.23 MPa at 1 min, 2 min and 5 min polymerization time, respectively. The differences in modulus at 1 min and 2 min, 2 min and 5 min, and 1 and 5 min were significant.

Degree of conversion (DC) results
The DC data of polymerized specimens was shown in Figure 4. The polymerization conversion increased with polymerization time. The DC data were 79.60, 81.21 and 82.58% at the top surface of polymerized specimens. The differences were not significant at the top surface. At the bottom, DC were 61.69, 71.55 and 72.95% for 1, 2 and 5 min polymerization time, respectively. The differences in modulus at 1 min and 2 min, 2 min and 5 min, and 1 and 5 min were significant. The conversion data of the bottom showed a significantly lower value than on the top surface (p < 0.05) in 2 mm thickness.
3D printing trial results
The prepared resin matrix was successfully printed out in 3 dimensions. The 3D printed dog-bone shaped specimens are shown in Figure 5. The parameters of 3D printed specimens were 0.81 ± 0.12 mm in thickness and 5.09 ± 0.08 mm in width. The thickness of the 3D printed object did not reach the set value of 2 mm. The tensile strength and modulus of tested materials \((n = 12)\) were 9.19 ± 1.3 MPa and 315.19 ± 40.78 MPa, respectively.

Overall, it was concluded from present study that BA:UDMA = 7:3 ratio is suitable for preparation of flexible polymer. The measured tensile strength data confirmed that the polymerized specimens remain flexible after curing. The results of this study showed that the tensile strength and DC value increased by polymerization time. The favourable physical and chemical changes are based on the fact that longer illumination gives the opportunity for the formation of more reactive compounds, which can facilitate the incorporation of more monomers into the polymer chains. It is well-known from the literature that the prolongation of the polymerization time increases the polymerization conversion \([5]\), similarly to our results. By more monomer reaction, the formed polymer structure become stronger and tough therefore it can be concluded that there is a linear relationship between the DC and tensile strength. Higher DC means higher strength of resin \([3]\).

Discussion
Light-sensitive polymers and their composites are used in the group of 3D printing technologies with photopolymerization techniques. The matrix consists of a mixture of several components, which are produced by manufacturers in such a way that its viscosity, reactivity, mechanical properties and structure formed by polymerization are suitable for the purpose. In this study, a 3D printable, photopolymerizable resin was prepared and characterized that showed flexibility after the curing process. One possible application of flexible polymer is as 3D printable impression materials. The first step of digital workflow in orthopaedics is printing out of positive model based on the computer tomography (CT) recording. Thereafter the impression was taken from this positive form with flexible silicone material then the impression was used as a mould for different scaffold materials after the sterilization of the impression \([10]\). This digital workflow can be reduced if the negative or impression is printed out from a flexible acrylate system based on CT recording. This way the printing and taking an impression of a positive model can be eliminated from the workflow. Thus the procedure becomes faster and cost-efficient. During the application of impression material, a tensile force act on the interfaces upon separation. Therefore, tensile strength was investigated in the experimental resin.

The tensile stress and Young’s modulus increased with polymerization time increasing. When the polymer chain growth is initiated, its length is independent of the curing time. The reaction time increases the number of polymer chains opposing to increasing the length of the chain, which increases the material’s resistance to tensile forces \([2]\). Along with this, the modulus also increases with polymerization time.

The degree of conversion expresses the number of incorporating monomers into the polymer chain, which gives information about the polymerization efficiency. The FT-IR measuring revealed that the specimens showed higher DC at the top surface of the specimens. This surface is the upper surface in the Teflon mould in which the specimens were prepared. The specimens got more light intensity from this direction. The bottom surface of the specimens got less light from the bottom direction because of the non-transparency of the Teflon mould. The differences in DC at the upper and bottom surfaces are well known in connection with dental photopolymers \([11]\). The differences in DC between the top and bottom surfaces were 17.90, 10.17 and 9.63% at 1, 2 and 5 min polymerization time, respectively. However, the differences in DC between the top and bottom surfaces were significant but the difference decreased continuously with polymerization time increasing.

The 3D printing trial was implemented successfully with experimental resin in Formlabs 3D printer. The thickness of the 3D printed object did not reach the set parameters. The set thickness was 2 mm; the printed object was 0.81 ± 0.12 mm thick. Behind this, there can be many reasons among other non-optimal viscosity of the resin, and the non-optimal concentration of the photoinitiator system.
It is important to note that the polymerization depth is the difference in mould in the light chamber and at 3D printing, which can influence the polymerization, conversion thereby the mechanical properties. Moreover, the light source of the chamber also differs from the laser operating the 3D printer. The working wavelengths of the light chamber are between approximately 350 and 450 nm, the maximums are approximately 370 nm (UV-A) and approximately 450 nm (blue light). The Form 2 Formlabs printer works at 405 nm wavelength. Therefore, the comparison of 3D printed and light chamber polymerized specimens cannot make.

Based on the measured data, the mechanical properties were compared with commercial products. The tensile stress of flexible 80A resin and elastic 50A of Formlabs were 3.7 and 1.61 MPa, respectively. The experimental resin after light oven polymerized form produced 1.15 MPa tensile stress and after 3D printing 9.19 MPa. The IBT resin of Formlabs showed under 5 MPa tensile stress data based on its technical data sheet. Young’s modulus of IBT resin is under 16 MPa. The experimental resin showed 14.08 MPa, 15.18 MPa and 17.23 MPa at 1 min, 2 min and 5 min polymerization time. In the case of 3D printing, the modulus was 315.19 ± 40.78 MPa. 3D printable impression materials showed 62 and 83% (Figure 4). The reason for higher mechanical properties were compared with commercial products. The reason for higher mechanical properties were compared with commercial products. The reason for higher mechanical properties were compared with commercial products. The reason for higher mechanical properties were compared with commercial products. The reason for higher mechanical properties were compared with commercial products.

The conversion data was different at the top and bottom surface at 2 mm thickness. However, the polymerization layer thickness can be much smaller during 3D printing which can influence the DC and properties of the printed objects [3]. DC of the resin-based composite was between 43 and 70%. After photopolymerization of experimental resin in the light chamber, the DC showed 62 and 83% (Figure 4). The reason for higher DC in tested materials is the absence of inorganic filler and transparency of the liquid resin. In the case of 3D printed object, the average DC of 3D printed objects was 34.78 ± 1.23 MPa at the top and bottom surface. This value is under the DC of the light chamber polymerized object, which can be explained by the different light sources and exposure time at the light chamber and laser diode of the 3D printer [13].

The conversion data was different at the top and bottom surface at 2 mm thickness. However, the polymerization layer thickness can be much smaller during 3D printing which can influence the DC and properties of the printed objects [3]. DC of the resin-based composite was between 43 and 70%. After photopolymerization of experimental resin in the light chamber, the DC showed 62 and 83% (Figure 4). The reason for higher DC in tested materials is the absence of inorganic filler and transparency of the liquid resin. In the case of 3D printed object, the average DC of 3D printed objects was 34.78 ± 1.23 MPa at the top and bottom surface. This value is under the DC of the light chamber polymerized object, which can be explained by the different light sources and exposure times.

**Conclusion**

Based on our measurements it can be concluded that the mixture of butyl acrylate and urethane dimethacrylate is suitable for flexible photopolymer preparation. The flexible properties are confirmed by strength measurements. The trial printing study showed that this matrix can be applied in an SLA 3D printer.

**Acknowledgement:** Project no. TKP2021-EGA-20 (Biotechnology) has been implemented with the support provided from the National Research, Development and Innovation Fund of Hungary, financed under the TKP2021-EGA funding scheme.

**References**

7. https://formlabs.com/materials/flexible-elastic/ (2022.08.01.)
8. https://dental.formlabs.com/store/materials/ibt-resin/ (2022.08.01.)
SZÁLÓKI M, A KHATAR KABLI, HEGEDŰS CS

3D nyomtható flexibilis akrilát alapú gyanta előállítása és jellemzése

Jelen munka célja 3D nyomtható gyanta előállítása, amely a polimerizáció után flexibilis tulajdonságokat mutat, valamint mechanikai és fizikokémiai jellemzése a polimerizált objektumoknak. A kísérleti gyanta butil-akrilát (BA) és uretan-dimetakrilát monomereket tartalmazott 7:3 tömeg arányú keverékben, valamint fenil bis (2,4,6-trimetilbenzoil) foszfin oxid fotoiniciátor (BAPO) 0,2 m/m%-ban és etil 4-(dimetilamino) benzoát koiniciátor 0,4 m/m%-ban. Szakítószilárdsági vizsgálat (Instron 5544) elvégzéséhez a próbatestek 1, 2 és 5 percig polimerizálódtak fogászati fénykályhában. A polimerizációs konverzió (DC) meghatározása céljából FT-IR spektroszkóppal mérések készültek a próbatestek tetején és alján. A polimer szakítószilárdsági értékei növekedtek a polimerizációs idővel. Ennek hátterében a magasabb DC értékek állnak, amelyeket a mért DC adatok alátámasztanak. A kísérleti gyanta próbanyomtatása sikeres volt, így a gyanta használható SLA 3D nyomtatókban.

Kulcsszavak: 3D nyomtatás, SLA technika, flexibilis akrilát polimer, fotopolimer, szakítószilárdság, polimerizációs konverzió.