Advancing Digital Dentistry with High Strength, High Toughness 3D Printable Urethane Denture Base and Tooth Formulations

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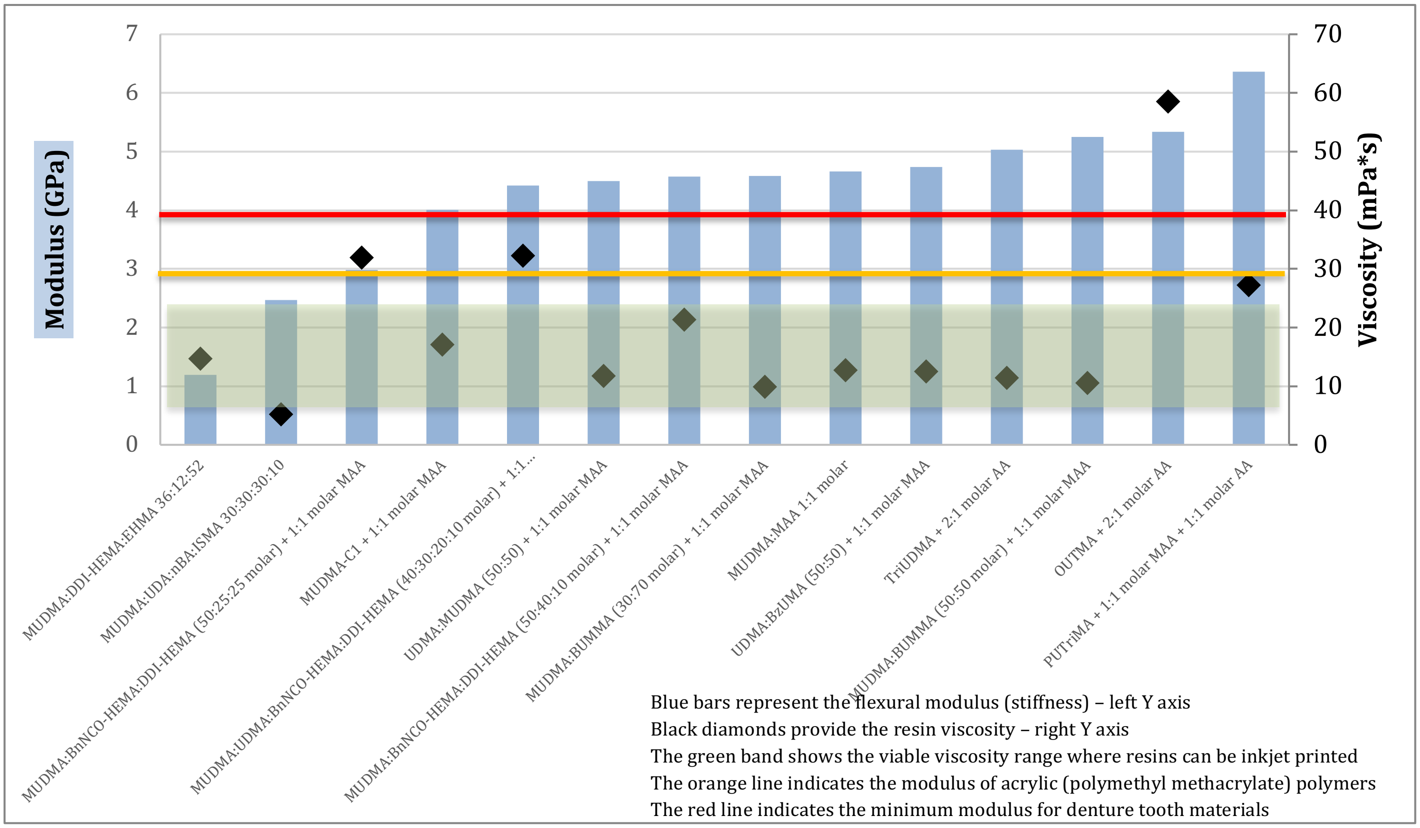
The American Dental Association underlines the impact of oral health on general health with more than 60 adverse health conditions, including diabetes and heart disease linked to poor oral health. Full or partial dentures can restore function and aesthetics of whole arch or single/multiple missing teeth, and >44M people in the US rely on dental prosthetics with many more in need due to access and affordability limitations. Interest in 3D printed denture technology has risen rapidly as it can greatly reduce costs for patient-specific devices, yet 3D printed denture base/tooth resins used today share the limitations in flexibility and fracture toughness as conventional acrylics. We synthesized low to moderate viscosity urethane resins and combined them with coordinating diluent comonomers to maximize the non-covalent interactions known to enhance polymer strength and toughness.

Resins containing a monourethane dimethacrylate (MUDMA) were 3D printed using conventional vat-based digital light processing technology in combination with comonomers such as diurethane dimethacrylate (UDMA) or methacrylic acid (MAA). Samples were 3D printed, post-cured and underwent 3-point bending to test flexural strength (MPa), modulus (GPa), and toughness (MPa). Conversion was obtained via FT-IR spectroscopy and viscosity was measured by viscometer. Samples were tested dry with selected polymers evaluated under wet conditions. Certain formulations displayed sufficiently low viscosity to permit inkjet 3D printing, which allows denture base and tooth formulations to be simultaneously printed for even greater savings of production time and expense.

Formulations containing 1:1 and 2:1 ratios of MUDMA/UDMA were vat-printable without addition of any reactive diluent. Flexural strength under wet conditions for 1:1 (157.5±8.5 MPa) and 2:1 (155.3±5.2MPa) MUDMA/UDMA polymers are clearly greater than conventional heat-cured poly(methyl methacrylate) PMMA teeth or denture base (93.3±3.5MPa). Elastic modulus (stiffness) for 1:1 (2.8±0.1GPa) and 2:1 (3.1±0.1GPa) MUDMA/UDMA formulations were at or below that of dental acrylics (~3GPa), which is expected to facilitate patient comfort. For denture tooth materials, polymers with modulus and strength significantly greater than denture base are desired. For both vat and inkjet applications, multiple formulations were able to achieve modulus and strength results well above that of acrylic denture teeth. Formulations outside of MUDMA and UDMA utilized novel urethane monomers such as TriUDMA or PUTriMA that can reach polymer moduli of 5-6 GPa and flexural strength >200 MPa, which highlights the potential for high-performing urethane-based monomers for both denture tooth and denture base applications using either a two-step vat-based DLP 3D print platform or a single-step inkjet print process. This allows for fabrication of thinner, more deformation-tolerant printed dentures, likely leading to fewer pre-prosthetic surgeries and broken dentures.


Modulus (GPa)
0
1
2
3
4
5
6
7
Viscosity (mPa*s)
0
10
20
30
40
50
60
70
MUDMA:DDI-HEMA:EHMA 36:12:52
MUDMA:UDA:nBA:ISMA 30:30:30:10
MUDMA:BnNCO-HEMA:DDI-HEMA (50:25:25 molar) + 1:1 molar MAA
MUDMA-C1 + 1:1 molar MAA
MUDMA:UDMA:BnNCO-HEMA:DDI-HEMA (40:30:20:10 molar) + 1:1...
UDMA:MUDMA (50:50) + 1:1 molar MAA
MUDMA:BnNCO-HEMA:DDI-HEMA (50:40:10 molar) + 1:1 molar MAA
MUDMA:BUMMA (30:70 molar) + 1:1 molar MAA
MUDMA:MAA 1:1 molar
UDMA:BzUMA (50:50) + 1:1 molar MAA
TriUDMA + 2:1 molar AA
MUDMA:BUMMA (50:50 molar) + 1:1 molar MAA
OUTMA + 2:1 molar AA
PUTriMA + 1:1 molar MAA + 1:1 molar AA
Blue bars represent the flexural modulus (stiffness) – left Y axis
Black diamonds provide the resin viscosity – right Y axis
The green band shows the viable viscosity range where resins can be inkjet printed
The orange line indicates the modulus of acrylic (polymethyl methacrylate) polymers
The red line indicates the minimum modulus for denture tooth materials