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Light-curable urethane(meth)acrylates materials for vat photopolymerization technology

Abstract

Vat photopolymerization is one of the most significant additive manufacturing technologies, enabling the production of complex-geometry parts with high accuracy and good reproducibility. This has led to the widespread application of the technology in prototyping, dentistry, medicine, the jewelry industry, and other fields.

The most widely used resins for resin-based 3D printing are light-curable formulations exhibiting rigid and impact-resistant properties. These formulations are used for functional prototyping and the manufacture of medical devices, where high biocompatibility, compositional stability, and predictable properties after printing and post-processing are of particular importance.

At the same time, the development of this technology requires an expansion of the range of available resins, including flexible, elastic, and soft systems. Of particular interest is the development of light-curable formulations for producing soft parts that simultaneously possess low hardness, high tensile strength, and self-healing capability. Despite existing examples of flexible parts manufactured by vat photopolymerization, the challenge of creating truly soft resins has not yet been fully resolved.

As resin systems develop, technological approaches aimed at increasing the productivity of vat photopolymerization are also being improved. These include increasing the power of radiation sources, changing the spectral range of curing, increasing the mechanical speed of platform movement, and optimizing layer thickness and exposure modes. All these technological approaches are aimed at increasing printing speed. However, higher printing speeds may be accompanied by incomplete curing, increased internal stresses, deterioration of interlayer adhesion, and changes in the final mechanical properties of the printed part.

Oligomers play a key role in the formulation of light-curable compositions for 3D printing. Their functionality and molecular weight determine the fundamental

physicochemical and rheological properties of the liquid formulation, as well as the overall performance characteristics of the final part formed during 3D printing. Targeted oligomer synthesis makes it possible to obtain light-curable formulations with a predefined set of properties.

In this regard, optimization of the composition of light-curable formulations for vat photopolymerization should be considered in combination with printing and post-processing parameters. Thus, the synthesis of new oligomers for the development of light-curable formulations for resin-based 3D printing, as well as the optimization of both technological properties, including rheological behavior and reactivity, and performance properties of light-curable compositions based on these oligomers, represent highly relevant areas of research.

The aim of this study was to develop a methodology for obtaining light-curable resins that combine reduced viscosity, a high photopolymerization rate, and high accuracy, as well as the required level of physicomechanical properties necessary for implementing the 3D printing process.

Objectives:

1. To develop new approaches for obtaining strong and elastic resins for resin-based 3D printing;
2. To determine the relationships between the structure of oligourethane (meth)acrylates and oligourethane-urea methacrylates and the properties of light-curable formulations and printed parts based on them;
3. To determine the relationships between the parameters of the radiation source and the vat photopolymerization process, as well as the accuracy of the printed parts;
4. To determine the relationships between the components of light-curable formulations and the biocompatibility of the resulting printed parts.

Scientific Novelty

The scientific novelty of the PhD thesis lies in establishing the relationships between the chemical structure of urethane (meth)acrylic and urethane-urea methacrylic oligomers, photoinitiating systems, and photopolymerization parameters, and the properties of light-curable formulations intended for vat photopolymerization, including physicomechanical properties, cytotoxicity, and accuracy.

It has been shown that targeted modification of the structure of urethane acrylate oligomers through variation of acrylic functionality, incorporation of inert low-molecular-weight fragments, and the use of different isocyanates makes it possible to purposefully regulate viscosity, oligomer reactivity, double-bond conversion, glass transition temperature, and the physicomechanical characteristics of the cured resin based on these oligomers.

The possibility of using *tert*-butylaminoethyl methacrylate (*t*-BAEMA) as an effective blocking agent for isocyanate groups has been demonstrated. The role of *t*-BAEMA in the formation of resins with a pronounced self-healing effect has been revealed, which is associated with the ability of sterically hindered urea derivatives to undergo a retro-reaction.

It has been established that the formation of interpenetrating polymer networks through the interaction of isocyanate groups with chain extenders is an effective method for increasing strength and controlling the physicomechanical characteristics of elastic resins.

It has been established that the critical energy of photopolymerization, E_c, and the penetration depth, D_p, depend on radiation intensity. It has been shown that changing the wavelength of the light source from 385 to 405 nm leads to changes in E_c and D_p due to differences in the spectral overlap between the emission of the light source and the absorption of photoinitiators, pigments, and other components.

For the first time, the influence of radiation intensity and photopolymerization process temperature on the conversion of double bonds present in the oligomer structure and on the strength properties of printed parts based on urethane acrylate light-curable resins has been systematically demonstrated.

It has been established that an increase in light intensity at a constant energy dose may lead to a decrease in double-bond conversion, whereas an increase in temperature promotes its increase.

For the first time, a broad range of commercially available acylphosphine oxide photoinitiators used for vat photopolymerization has been studied. It has been shown that the structure and concentration of the photoinitiator affect cytotoxicity, printing accuracy, and the reactivity of the formulations.

Practical Significance

Comprehensive approaches have been developed for designing light-curable formulations for vat photopolymerization (VPP) with tunable technological and performance properties. It has been shown that variation of the structure and functionality of urethane acrylate oligomers, as well as the incorporation of inert fragments, makes it possible to control the viscosity and reactivity of the initial light-curable formulation and the physicomechanical properties of the printed parts. These findings can be used in the development of new resins for 3D printing.

Formulations based on oligourethane-urea methacrylates have been developed, enabling the production of elastic resins that are promising for the manufacture of soft functional parts by VPP and are characterized by increased strength, high elongation at break, and a self-healing effect.

The data obtained on the influence of radiation intensity and temperature can be used to optimize printing and post-processing modes, improve the accuracy of the resulting parts and the conversion of double bonds, and enhance the mechanical properties of 3D-printed parts. In addition, an express method for assessing the accuracy of printed parts has been developed.

The results of the study of a series of photoinitiators make it possible to select a photoinitiating system in a scientifically justified manner, taking into account the requirements for printing accuracy, biocompatibility, and reactivity. This is important for the development of light-curable resins for medical and engineering applications.

The HARZ Labs Dental Model Light Grey was developed based on the obtained results and has been implemented in production.

The main provisions for the defense

1. Investigation of the influence of the oligourethane (meth)acrylate structure on the properties of light-curable resins;

2. Development of approaches for obtaining elastic resins with high tensile strength and high elongation at break;

3. Evaluation of the influence of the nature of the chain extender on the characteristics of light-curable resins;

4. Influence of radiation source parameters on the key parameters of vat photopolymerization;

5. Influence of radiation source power on the double-bond conversion of a light-curable resin;

6. Investigation of printing accuracy and development of a method for its assessment;

7. Investigation of the influence of photoinitiator structure on printing accuracy and cytotoxicity.