SYNTHESIS AND PROPERTIES OF POLYSILOXANE COPOLYMERS WITH UREA FRAGMENTS FOR 3D PRINTING

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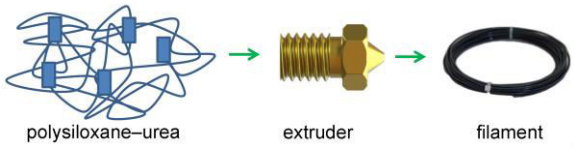
Abstract

3D printing by the fused deposition modeling (FDM) method has become widespread nowadays. Soft materials, which are suitable for FDM printing, can be utilized to print soft robots capable of deformation under various stimuli (such as magnetic, electric fields, or light). In this study, a polysiloxane copolymer with urea fragments with sufficient softness was synthesized and filaments based on it were produced for 3D printing.

Key words: 3D printing, polysiloxane with urea segments.



Introduction

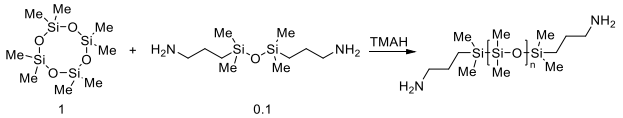
3D printing is a rapidly evolving technology that enables the creation of physical objects from digital models. It finds applications in various fields, including medicine and manufacturing, facilitating rapid prototyping and part restoration [1]. Of particular interest is the printing of soft robots, where special materials are used that change their shape under the influence of various forces. The term originates from the field of robotics, where researchers, inspired by natural systems, attempt to replicate them under laboratory conditions. When printing soft robots, a soft material is used as a base and combined with various fillers capable of responding to control inputs, thereby changing their geometry. The inputs can be magnetic, electrical, optical, *etc.* This technology requires materials that are soft enough while maintaining a stable shape [2].

Popular 3D printing technologies include fused deposition modeling (FDM), selective laser sintering (SLS), and stereolithography (SLA). Different requirements for polymer materials used in printing are dictated by each method. The most widely used technology is FDM. To print a model, a thermoplastic polymer filament is heated in a nozzle to a semi-liquid state and then extruded onto a platform or previously printed layers. The primary criterion for choosing a material is its thermoplasticity, allowing layers to fuse together and solidify models at room temperature. Advantages of this method include its low cost, high speed, and printing simplicity [3].

Traditional materials are not always suitable for 3D printing soft robots, so new options are being explored, such as thermoplastic polyurethanes (TPUs) and polyamides [4]. Other promising materials for 3D printing soft robots, which are beginning to be developed, are polysiloxane copolymers that contain some rigid fragments. It is known that polysiloxanes have highly flexible chains and, as a result, represent very soft materials. Polysiloxanes are ideal for smart composites but unsuitable for basic 3D printing. By incorporating rigid fragments to form physical bonds, a thermoplastic material suitable for FDM 3D printing can be achieved [5–7]. Compared to TPU and polyamide, they can exhibit enhanced flexibility, which can be controlled by the copolymer composition. These properties are of particular interest for 3D printing of multifunctional soft robots. Therefore, the goal of this work was to synthesize polysiloxane copolymers and to prepare filaments for FDM printing based on these materials.

Results and discussion

Polydimethylsiloxane (NH_2-PDMS-NH_2) with aminopropyl terminal groups was synthesized by the published method [8]. For this purpose, the ring-opening polymerization of octamethylcyclotetrasiloxane in the presence of 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane and tetramethylammonium hydroxide used as a catalyst was conducted (Scheme 1).



Scheme 1. Synthesis of α,ω-bis(3-aminopropyl)oligodimethylsiloxane (NH_2-PDMS-NH_2).

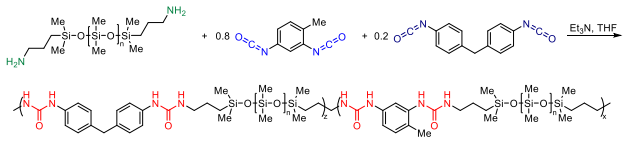
The synthesis was carried out until the reaction reached equilibrium, which was monitored by gel permeation chromatography. The molecular weight characteristics of the resulting product are presented in Table 1.

Table 1. Molecular weight characteristics of NH_2-PDMS-NH_2 and polysiloxane–urea

Sample	M_N	M_w	M_N[a]	D
NH_2-PDMS-NH_2	4600	11000	3800	2.37
polysiloxane–urea	21200	52800	–	2.49

[a] calculated based on the ^{1}H NMR data.

Then, according to Scheme 2, a copolymer of polydimethylsiloxane with urea fragments was obtained from the aminosiloxane (NH_2-PDMS-NH_2) and commercially available isocyanates (toluene-2,4-diisocyanate and methylene diphenyl diisocyanate).



Scheme 2. Synthesis of the polysiloxane–urea.

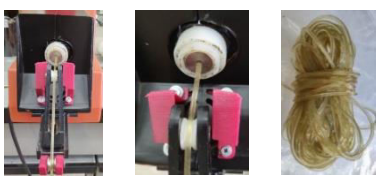
The structure of the polymer obtained was confirmed by ^{1}H NMR spectroscopy, and its molecular weight characteristics were measured by gel permeation chromatography. The synthesis process was optimized, and a batch of 30 g of material was prepared for further filament production.

According to the results of the rheological studies, the shear storage modulus G' of the obtained material is about 200 kPa in the linear viscoelastic range at a shear frequency of 10 rad/s. The melting temperature of the material is ~135 °C.

The material was shredded and then fed through a WellZoom desktop filament extruder. The extrusion temperature was set at 160 °C with a nozzle diameter of 3.0 mm. A soft thermoplastic filament with a diameter of 1.75 ± 0.05 mm was obtained, which is suitable for printing by the FDM method (Figs. 1, 2).

a ***b*** ***c***

Figure 1. Polysiloxane–urea after separation from the reaction products (***a***), ground polysiloxane–urea (***b***), polysiloxane–urea which was loaded into the extruder hopper (***c***).



a ***b*** ***c***

Figure 2. Extrusion of the filament (***a***), view of the filament flow at the exit from the extruder nozzle (***b***), a skein of the resulting filament (***c***).

Conclusions

A polysiloxane–urea was synthesized using commercially available starting reagents. The resulting material is sufficiently soft, with a melting temperature of ~135°C, which is a suitable criterion for filament preparation for FDM printing and subsequent 3D printing. The material was extruded and a soft thermoplastic filament was obtained.

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Electronic supplementary information

Electronic supplementary information (ESI) available online: the experimental section, the NMR spectra, GPC curves, and rheological properties of the compounds obtained. For ESI, see DOI: 10.32931/io2442a.

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