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Mendeleev Commun., 2022, **32**, 231–233

Mendeleev Communications

Photosensitive thiol–ene composition for DLP 3D printing of thermally stable polymer materials

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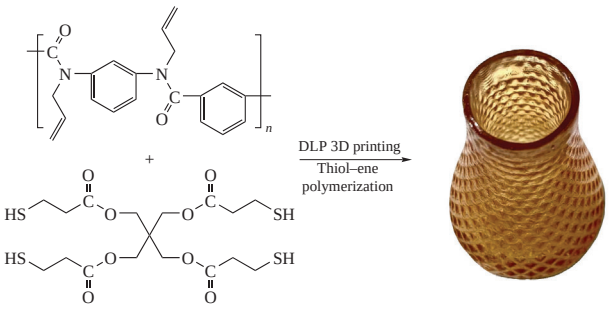
DOI: 10.1016/j.mencom.2022.03.026

N-allylated derivatives with a modification degree of 80% were obtained by reacting poly[*N*,*N*′-(1,3-phenylene)isophthalamide] with allyl bromide in the presence of a strong base. Using the obtained functionalized polyamide and pentaerythritol tetrakis(3-mercaptopropionate), we formulated new photosensitive compositions capable of forming crosslinked structures due to UV-initiated thiol–ene polymerization. High-resolution 3D objects that are heat resistant up to 380 °C were formed using digital light processing (DLP) 3D printing.



Keywords: aromatic polyamides, thiol–ene polymerization, DLP, 3D printing, photosensitive compositions, photopolymerization.

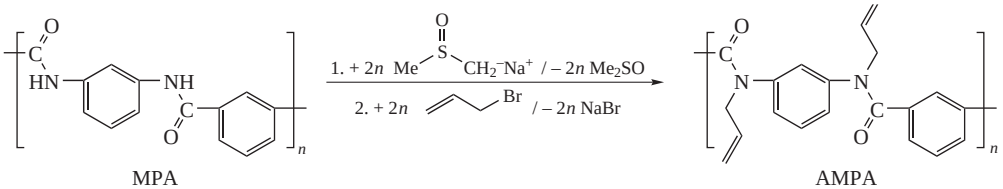
Aromatic polyamides (APA) are a particular class of structural heterochain polymers characterized by high thermal stability and mechanical strength.[1] The chains of APA macromolecules are rigid due to aromatic fragments and amide groups forming strong intermolecular hydrogen bonds, which result in a dense multilevel packing of macromolecules. Due to its increased rigidity and strong intermolecular interaction, APA is characterized by low deformability in the range of softening and fluidity temperatures, which causes difficulties when processing them into products by conventional methods.[1]

From these positions, 3D printing technologies, which can significantly speed up and simplify the formation of structures with complex geometry, are of great interest.[2,3] We have previously developed an approach involving the combination of photosensitive acrylamide components with an APA, poly[*N*,*N*′-(1,3-phenylene) isophthalamide] (MPA).[4–6] On the basis of such compositions by the method of laser stereolithography, we managed to obtain semi-interpenetrating polymer networks with high thermal stability. The disadvantages of such systems are the heterogeneity of the resulting polymer network and their sensitivity to air moisture and oxygen, which inhibit polymerization.[2] In recent years, photosensitive compositions based on mixtures of polyfunctional enes and thiols, capable of forming crosslinked three-dimensional structures by thiol–ene polymerization, have attracted much attention.[2,7] These compositions are free of the disadvantages mentioned above. Considering the above, the purpose of this work was to develop new photosensitive thiol–ene compositions based on APA.

N-allyl-functionalized MPA (AMPA) was used as an ene component of the photosensitive composition. Its synthesis was carried out in two stages using dimsyl sodium as a strong base and allyl bromide as an alkylating agent (Scheme 1), similar to the previously described procedure.[8,9] Successful grafting of allyl groups was confirmed by ^{1}H NMR spectroscopy. The spectrum of the initial MPA (Figure S1, Online Supplementary Materials) shows signals from the protons of the NH groups at ~10.5 ppm and aromatic protons at 7.3–8.6 ppm. In the ^{1}H NMR spectrum of the obtained AMPA (Figure S2), a significant decrease in the signal intensity of the NH groups is observed, as well as the appearance of new peaks at ~4.3 (NCH_2), 5.0 ($CH{=}CH_2$) and 5.7 ppm ($CH{=}CH_2$), which confirms the N-allylation of the amide groups. The modification degree calculated from the ratio of the integrated intensities of the allyl and NH group signals in the ^{1}H NMR spectra is 80%.

Replacing the amide proton with an allyl group leads to a looser packing and a serious weakening of intermolecular interactions, which significantly improves the polymer solubility in amide solvents *N*-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylacetamide and *N*,*N*-dimethylformamide. Moreover, unlike MPA, AMPA is soluble in chlorinated hydrocarbons CH_2Cl_2 and $CHCl_3$.

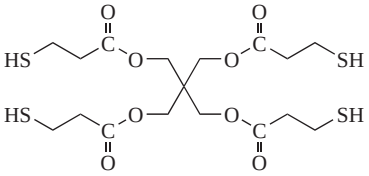
The good solubility of AMPA in NMP served as the basis for the preparation of liquid photosensitive thiol–ene resins since



MPA AMPA

Scheme 1 The synthesis of AMPA from MPA and allyl bromide.

their quantitative composition primarily depends on the solubility of the components. A commercially available tetrathiol, pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), was used as a thiol component, and Irgacure 819 was used as a photoinitiator. The AMPA content was 20 wt%, the photoinitiator content was 2 wt%, and the amount of PETMP was calculated so that the allyl and thiol groups were present at an equimolar ratio. It was found that at room temperature, the resulting composition is stable for no more than a month, and then irreversible gelation occurs. To increase the stability of the photosensitive composition, we added 0.1 wt% of hydroquinone as a polymerization inhibitor. In this case, gelation did not occur for at least three months.



PETMP

To assess the possibility of using the obtained photosensitive composition to produce volumetric products by digital light processing (DLP) 3D printing, we initially investigated its photocuring under LED irradiation. As a result of UV irradiation of the composition, an organogel containing a large amount of absorbed solvent (NMP) is formed. The solvent can be removed by heat treatment with a gradual increase in temperature from 20 to 200 °C. As a result, crosslinked films are formed, and the isotropic shrinkage of the samples is 32%.

The content of the gel fraction in the obtained samples was determined by NMP extraction. The highest yield of the gel fraction (95%) was observed for the sample prepared by UV irradiation of the photosensitive composition for 30 seconds. It should be noted that in the case of liquid thiol–ene compositions based on low molecular weight compounds, relatively low content of the gel fraction (~80%) is usually achieved[2,7] due to the rapid curing of the material with the formation of a rigid crosslinked structure, which makes it difficult to achieve complete conversion of monomers. In our case, the non-reactive solvent (NMP) plays the role of a plasticizer, which makes it possible to achieve a greater depth of thiol–ene polymerization. In addition, the use of high molecular weight AMPA as an ene component allows achieving the formation of crosslinked polymer networks even at relatively low degrees of conversion. Thus, the resulting AMPA-based thiol–ene composition was found to exhibit a high curing rate upon UV treatment. It should also be noted that, in the absence of a thiol component, the photocuring of the composition occurs extremely slowly: the content of the gel fraction does not exceed 40% after 5 minutes of UV treatment.

The thermal characteristics of the resulting photocured materials were investigated in comparison with the original MPA and AMPA [Table 1 and Figure 1(*a*)]. MPA has a thermal resistance characteristic of this class of polymers: a weight loss of 10% ($T_{10\%}$) is observed at 456 °C. Grafting of allyl groups to MPA macromolecules leads to a decrease in the temperature of the onset of destruction to 444 °C due to the lower resistance of aliphatic fragments to thermal impact. Photocured material based on AMPA–PETMP exhibits a lower heat resistance (380 °C) due to an even higher content of aliphatic fragments. Thus, AMPA–PETMP has 76 °C lower thermal stability than the original MPA. However, its thermal stability is significantly higher than that of other known compositions used in UV 3D printing technologies.[2]

Table 1 The thermal and mechanical properties of MPA, AMPA and AMPA–PETMP.

Sample	$T_{10\%}$/°C	σ/MPa	ε (%)
MPA	456	98.4 ± 3.2	12.7 ± 0.9
AMPA	444	62.7 ± 2.1	34.4 ± 3.9
AMPA–PETMP	380	87.9 ± 3.8	22.3 ± 1.6

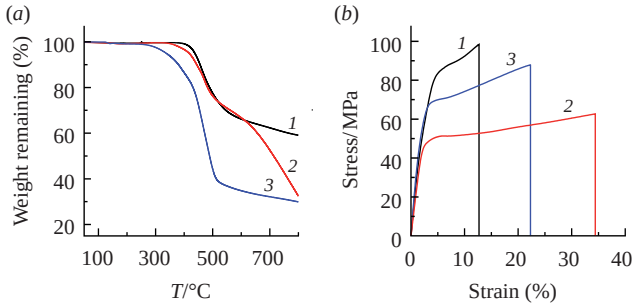


Figure 1 (*a*) TGA curves and (*b*) stress–strain curves for (*1*) MPA, (*2*) AMPA and (*3*) AMPA–PETMP.

The mechanical properties of the obtained materials also differ significantly [see Table 1 and Figure 1(*b*)]. As can be seen from the data presented, the photocured AMPA–PETMP material has excellent mechanical strength. Its tensile strength is slightly lower than that of the original MPA but significantly higher than that of AMPA. It is known that previously described materials for 3D printing have a tensile strength in the range of 30–50 MPa.[10] Thus, the APA-based photocurable material developed by us is significantly superior to most of the currently known compositions.

The results obtained served as the basis for investigating the possibility of forming mechanically strong heat-resistant objects by the DLP 3D printing method. It turned out that the photosensitive composition can be used in the commercial Anycubic Photon Mono 3D printer without any additional modifications. As shown in Figure 2, it is possible to form a three-dimensional object with high accuracy, which is probably achieved due to the action of the inhibitor, which excludes the polymerization of the active components of the composition outside the irradiation zone.[2,11] As with the production of photocured films, organogels containing absorbed NMP are formed during DLP 3D printing. Further drying in a vacuum with a gradual increase in temperature from 20 to 200 °C allows complete removing of the solvent and, at the same time, maintains the shape of the three-dimensional object. Isotropic shrinkage is about 30–35% and is practically independent of the geometry of the formed object, making it possible to predict the final product dimensions accurately.

Thus, it has been shown for the first time that an APA modified with unsaturated allyl groups can be used to prepare photosensitive thiol–ene compositions, based on which it is possible to form mechanically strong heat-resistant three-dimensional structures by DLP 3D printing.

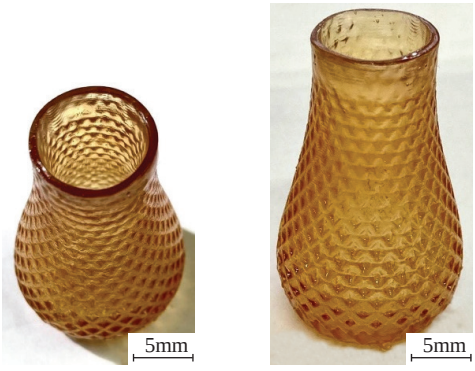


Figure 2 Images of an object formed by DLP 3D printing from AMPA–PETMP.

This work was supported by the Russian Science Foundation (grant no. 20-73-00004) in part of obtaining a photopolymer composition and by the Ministry of Science and Higher Education within the framework of the state assignment of the Baikal Institute of Nature Management, Siberian Branch of the Russian Academy of Sciences, in part of the development of additive technologies for the formation of three-dimensional polymer objects.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.03.026.

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Received: 18th August 2021; Com. 21/6648