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Polymers for Additive Manufacturing Research Letter

New "*all-in-one*" silicone pastes for additive manufacturing of elastomer parts

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Abstract

A new type of silicone ink materials for additive manufacturing is described. We call them *"all-in-one"* pastes since they contain all necessary components for efficient and practical printing, including filler(s), crosslinking systems, and necessary or desired additives. The pastes can be easily tuned for the most appropriate rheology for selected printing operation, have long shelf life stabilities for practical manipulation and storage, and enable quick and complete crosslinking by hydrosilylation at room temperature in air to facilitate permanent fixing of shapes of printed objects.

Introduction

In search of elastomers for additive manufacturing (AM), silicones have attracted well-deserved attention because their 3D crosslinked rubbers represent some of the best high-tech elastomers known to polymer science.[1] This is based on unique combinations of properties that these organo-inorganic materials exhibit, including:

- exceptional low temperature flexibility (to as low as − 100°C and below, if completely amorphous),
- high temperature thermal and thermo-oxidative stability (to and above 400–450°C in different atmospheres),
- some of the widest ranges of application temperatures known for elastomers (from respective glass or melting temperatures to the onset of degradation: close to or even more than 500 °C),
- unique surface properties (such as some of the lowest surface energies, high hydrophobicity (non-wetting), and pronounced non-stick characteristics),
- excellent electrical insulation,
- biocompatibility and non-toxicity,
- low viscosity-temperature coefficients and almost flat viscosity-temperature curves over extended intervals of operating temperatures,
- pronounced resistance to atmospheric conditions (including acid rain and marine environments), and
- good mechanical properties when properly filled.

As a consequence, several reports have been recently published on developing silicone materials for AM applications using different curing chemistries from moisture cure of oxime-functionalized polysiloxanes reported by Plott and Shih,[2, 3] to UV-activated thiol-ene addition cure developed by Sirrine, Williams, Long et al.,[4] and Zheng and Brook,[5] to thermally induced hydrosilylation cure described by the group from Lawrence Livermore National Laboratory,[6] and to UV-activated cure by researches from Wacker Chemie AG,[7–9] and Dow Corning.[10]

It is not an easy task to develop elastomers for AM applications. The difficulty consists of three main challenges each of which presents several problems that must be successfully resolved in a coherent system of interrelated solutions. These challenges include: (a) design and development of base polymers with structures and compositions that are appropriate for the desired AM technology and targeted application(s), (b) design and development of AM-usable (i.e., printable) material(s) (i.e., pastes) based on such base polymers, and (c) manufacturing (i.e., printing) and subsequent permanent fixing of shapes of printed objects.

The polymer design and development challenge includes: (i) tailoring of functional polymers with precisely predefined optimal composition, molecular chain linearity, built-in crosslinking functionality, absence of crystallinity (i.e., amorphicity), as well as molecular weight and molecular weight distribution, (ii) development of their syntheses such that these can be closely controlled (i.e., monitored) in real-time, verification of reproducibility and scale-up, and (iii) development and specification of precise and complete analytical protocols for characterization of the obtained products.

The AM material (“printing ink”, or “*paste”*) must satisfy: (i) specific process requirements such as preferred viscosity and, most importantly for elastomers, thixotropy and yield stress, and (ii) easy and practical handling, transportation and storage. The former requires development of specific composition(s) (which usually include base polymer, filler, crosslinker(s), catalyst(s), and other possibly desired additive(s)), while the latter greatly depends on crosslinking chemistry selected for permanent shape fixing of manufactured objects.

Finally, the manufacturing (i.e., printing) process should be selected such that it takes advantage of all good properties of the printing paste, and is able to easily, effectively, and with high output print shapes that can be quickly and permanently fixed to ensure not only all desired materials’ properties (mentioned above), but also their undisturbed retention for extended periods of application times (potentially tens of years of continuous service) even under changing operating conditions.

To meet all these stringent requirements, we recently developed three types of α,ω-telechelic dimethylvinylsilyl-terminated terpolysiloxanes, containing predominantly (93–96 mol%) dimethylsiloxy, -[$SiMe_2O$]-, DiMeS, repeat units, with small amounts (3–7 mol%) of (A) diphenylsiloxy-, -[$SiPh_2O$]-, DiPhS, or (B) diethylsiloxy-, -[$SiEt_2O$]-, DiEtS, or (C) methylphenylsiloxy-, -[SiMePhO]-, MePhS, crystallization disrupting repeat units, and traces (less than 0.5 mol%) of methylvinylsiloxy-, -[$SiMe(CH{=}CH_2)O$]-, MeViS, crosslinkable repeat units (shown in Fig. 1).[11–13] Here, we describe some preliminary results obtained from an investigations of the use of these terpolymers for preparation of what we call *“all-in-one”* silicone pastes for AM applications, their properties, direct ink write (DIW) printing, and permanent shape fixing of printed objects.

Materials and methods

Paste preparation

Approximately, 50 g paste batches were prepared from all three types of base polymers using a *FlackTek DAC 150.1 FV SpeedMixer*™, a dual asymmetric centrifugal mixer, from FlackTek Inc., Landrum, SC. In a typical preparation, terpolymer base, crosslinker, thixotropic additive and catalyst-inhibitor mutual solution were added to a mixing cup, followed by successive additions of trimethylsilylated AEROSIL® R 812 S fumed silica filler in small portions. After addition of each filler increment the pastes were mixed for 20 s at 3000 rpm until the total desired amount of filler was added. Once the final portion of filler was added, the pastes were mixed one final time for 1 min at 3000 rpm.

DIW printing of test samples

Direct Ink Write (DIW), a computer-controlled, multi-axis motion stage in combination with a deposition head or nozzle to build parts layer-by-layer was used in this work. Machine code controlled the toolpath to generate the pattern for each layer while a rheologically controlled paste or ink was extruded from the deposition head. It was critical that these inks were able to flow from the deposition head while under stress, but have appropriate thixotropy to recover quickly and hold their shape following extrusion. This allowed for three-dimensional parts to be built with highly controlled structures and geometries.

Results and discussion

Polymers

The polymers of this work were prepared by a dimethylsilanolate-initiated anionic ring opening polymerization (A-ROP) of various cyclic siloxanes with equilibration in the presence of difunctional dimethylvinylsiloxy end-blocker and molecular weight regulator (DiViEB), as shown in Fig. 1, and as described in more details in our earlier publications.[11–13]

These polymerizations were initiated in bulk with a difunctional oligomeric dimethylsiloxydimethylsilanolate initiator (TMAS), and they were closely controlled by monitoring their occurrence in real-time by size exclusion chromatography (SEC), nuclear magnetic resonance spectroscopy (NMR), and/or thermal gravimetric analysis (TGA) (preferably by combination of all three of these techniques),[12] to yield reproducible, linear, completely amorphous and multifunctional polymer products of targeted molecular weights.[11–13] Recently, we successfully scaled these reactions to a half-kilo level, sufficient for further paste development and printing trials.

Pastes

The terpolymers described above were found excellently suited for bases of printing pastes that contain *all* necessary components for successful AM, including fillers (for adjusting paste rheology and enhancing mechanical properties of printed rubber parts), crosslinking systems (for permanent fixing of printed shapes after the printing), and other (possibly) desired additives (such as rheology modifiers, dyes, thermo-oxidative stabilizers, porogens, magnetic or conducting particles, etc.). We refer to such pastes as “*all-in-one pastes”* (A-1/P) since once compounded by the manufacturer they are ready for printing the moment they arrive to the printer and require no further manipulation (except for proper storage) before the onset of AM operation. These pastes exhibit three fundamentally important groups of properties:

- their rheology is adjustable to the requirements of selected printing technique,
- they are able to quickly crosslink into 3D covalent networks after the printing to permanently fix the printed shapes for extended periods of application time, and
- they are stable enough for long-term handling and storage between the manufacturing and printing operations.

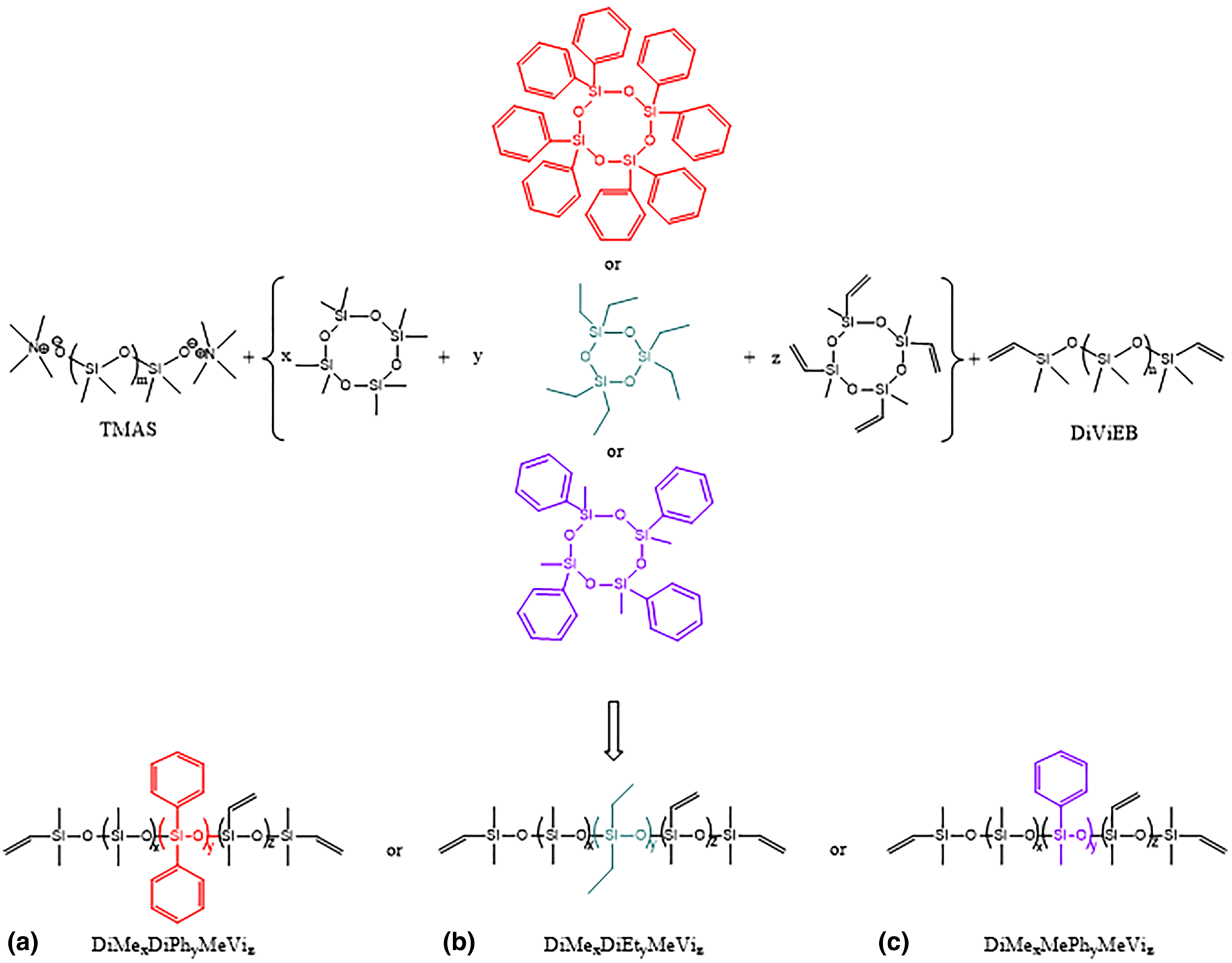

Figure 1. A generalized reaction scheme for preparation of vinylsiloxy-functionalized terpolymers A-C used in this work. The diphenylsiloxy-, diethylsiloxy- and methylphenylsiloxy- repeat units shown in colors were introduced to suppress well-known low temperature crystallization characteristic for pure polydimethylsiloxane and thus extend the terpolymers' flexibilities as close as possible to their respective glass temperatures.

The requirement of rheological properties suitable for elastomer AM generally includes paste viscosity, thixotropy and yield stress. All of these are dictated by the selected method of printing, and the last two are of specific and critical importance for elastomers. Namely, the main reason why most polymers that have reached application in AM to date are thermoplastics is that they melt quite conveniently above the room temperature. Because of this, they can be easily heated in the printing machine to make them flow through it in their molten state, and then quickly solidify into a printed shape on cooling to room temperature after exiting the printing nozzle. In contrast to this, elastomers either melt significantly below room temperature (e.g., natural or synthetic rubbers, pure polydimethylsiloxane, etc.) or do not crystallize at all (i.e., completely amorphous polymers, such as the terpolymers of this work), and the required liquid-to-solid transition for shape fixing at the end of the AM process and its subsequent retention must be accomplished in some other way. One convenient way is the well-known thixotropy: the property of some materials to flow like liquids when exposed to a certain shearing stress (yield stress), but quickly "solidify" (i.e., change into a solid-like state in which, at least transiently, they retain their established shapes) upon stress release (i.e., upon exiting the printing nozzle). Figure 2 illustrates this feature for one of our as-prepared A-1/P pastes (B) from a viscous liquid base polymer (A) to a solid-like form capable of retaining its shape even in a form of a "funny" artistic object (such as C). Importantly, the "solid"-like objects can retain their stable shapes for many months if unstressed at room temperature.

This thixotropic behavior can be well-characterized by its distinguishing hysteresis loop in steady shear rheometry, and the yield stresses can be determined by oscillatory shear experiments. We found that paste rheology and yield stresses can be very conveniently and precisely dialed-in by adding small

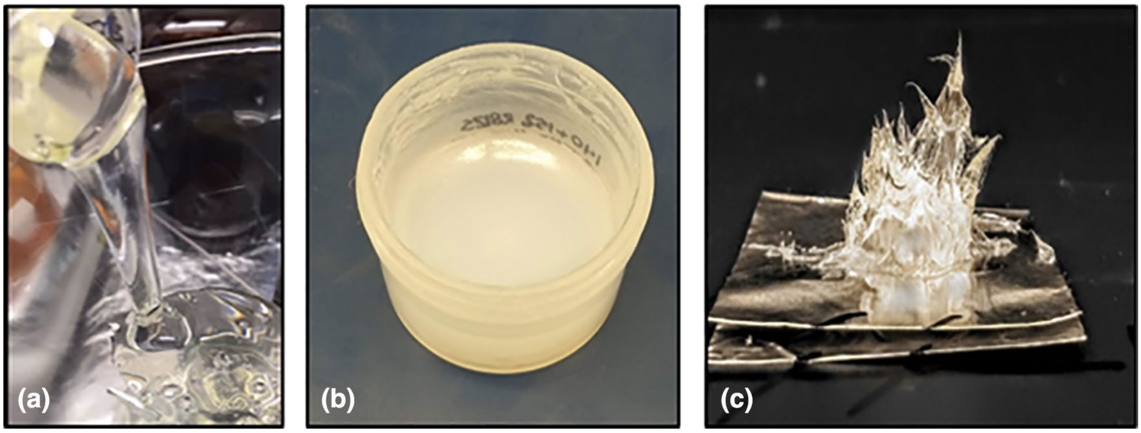

Figure 2. Physical appearances of: (a) a base polymer of Fig. 1; (b) an A-1/P paste prepared from such base polymer; (c) a "funny" artistic object molded from such a paste.

quantities (ca 1 wt.%) of a thixotropic additive BLUESIL™ THIXO ADD 22646, and proper selection of filler and its loading. For example, with a trimethylsilylated (i.e., "hydrophobic") fumed silica filler AEROSIL® R 812 S at 15–20 wt% concentrations in base polymers A–C of Fig. 1 (of ca. 50,000 weight average molecular weights), these can be adjusted to mimic the behavior of the well-known, thixotropic Dow Corning SE 1700 material.

The second fundamental requirement of A-1/Ps for successful AM application is quick permanent fixing of printed shapes that will last for extended periods of time (i.e., tens of years if needed) under targeted application conditions, including changes in ambient temperature and exposure to external stresses (which may or may not surmount the value of material's yield stress). In order to satisfy this requirement, the base polymers for these A-1/Ps were functionalized with vinylsiloxy-groups, –O–Si–CH=CH_2 (at chain ends and pendant to the main chain backbone), that easily undergo crosslinking into well-defined 3D covalent siloxane networks that provide the required fixing of printed shapes.

There are several different ways of crosslinking vinylsiloxy-functionalized silicones, and some of them have been explored in the previous works in this field, as mentioned above.[2, 4–7, 10] In this work, however, for reasons of operational simplicity and convenience, we focused on room temperature hydrosilylation crosslinking reaction that can be accomplished within seconds in air at room temperature in the presence of appropriate catalyst systems by irradiation with appropriate light source (see Fig. 3). The reaction results in almost quantitative polymer crosslinking and provides elastomeric products that possess and retain all highly desired and unique physical and chemical properties of silicone rubbers, as listed above.

We found that this approach was highly effective and versatile, and that with pastes containing methylhydrido-co-dimethylsiloxane crosslinker (Gelest: HMS-151; MW = 1800–2000; 15–18% MeHS; average Si–H functionality of 4) in the amounts corresponding to [Si–H]/[Si–Vi] = 1:1 molar and platinum(II) bis(acetylacetonate), Pt(AcAc), or trimethyl(methylcyclopentadienyl)platinum (IV), $MeCpPt(Me)_3$, catalysts with diethyl azodicarboxylate, DEAD, as catalyst inhibitor, in the amounts corresponding to [DEAD]/[catalyst] = 1:1 molar, the UV-activated crosslinking could be accomplished within less than 30 s depending on the catalyst used and its concentration.

The third main requirement of A-1/Ps for AM applications is that in addition to satisfying the aforementioned, they also need to remain stable for what could be extended periods of time between manufacturing and printing operations. This requires that the crosslinking catalyst system be at the same time (a) extremely effective when irradiated (i.e., when final shape fixing is performed), *and* (b) as inactive as possible in the absence of irradiation (so that no crosslinking can onset during the pastes' transportation and/or storage). Although, these two requirements may seem somewhat contradictory, at least at the first glance, success can be accomplished by careful selection of the crosslinking catalyst system. In our preliminary studies described in this report, we looked at several different candidate systems before selecting Pt(AcAc) and $MeCpPt(Me)_3$ as the most promising candidates. We found that while these catalyst systems were able to activate and complete on UV irradiation the hydrosilylation crosslinking in air and at room temperature in seconds (see above), they also allowed undisturbed manipulation, handling and storage of pastes in typical laboratory light for generally 6 to 9 days, and in dark for several months to a year, depending on exact paste formulation. More details about these *"all-in-one"* pastes and their respective properties will be described soon.

Printing

Several independent investigations of various printing processes using these A-1/Ps are currently in progress and their results will be published in the near future. However, it is already evident that not only these A-1/P pastes satisfy all of the above discussed property requirements exceptionally well,

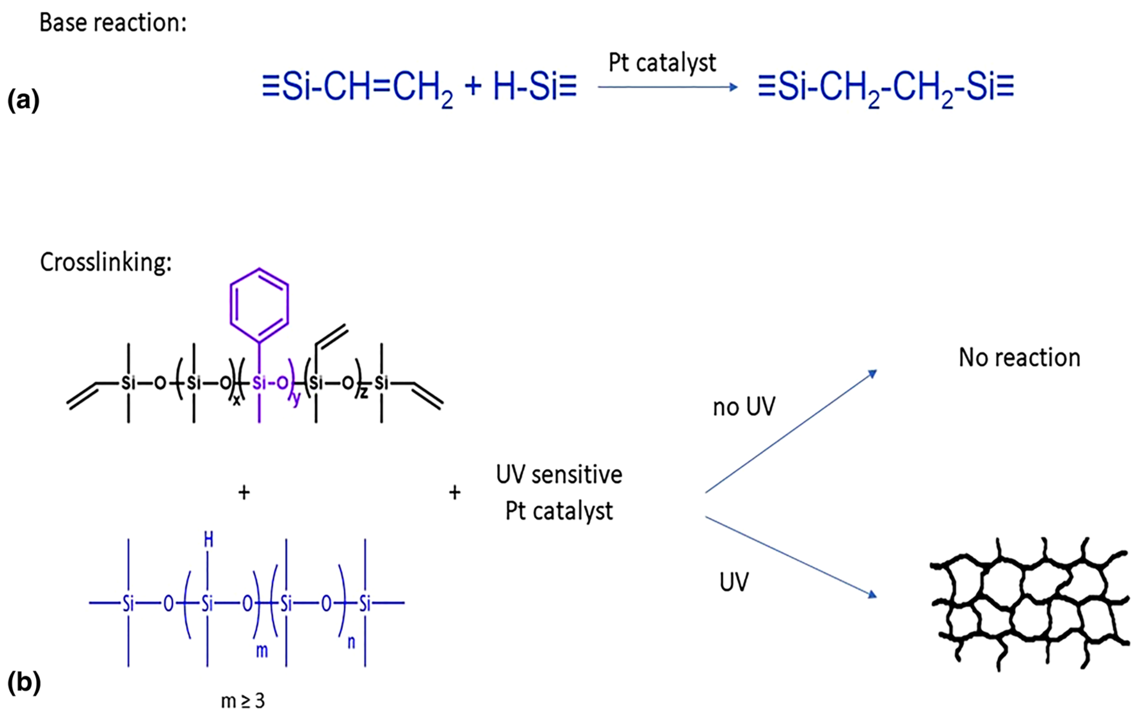

Figure 3. Pt-catalyzed hydrosilylation: (a) base reaction is an addition of hydrosilane (Si–H) across unsaturated group such as vinylsiloxy- (–O–Si–CH=CH_2); (b) crosslinking in the presence of a UV-sensitive Pt catalyst occurs only when the system is irradiated with UV light and both reagents, the terpolysiloxane (C of Fig. 1) and the hydrosilyl crosslinker (Gelest HMS 151), have functionalities higher than two.

but that they also enable reproducible printing of fine resolution objects under a variety of different, but quite convenient conditions. For early DIW trials, A-1/P's were loaded into opaque 30 cc syringes and centrifuged for 10 min at 4000 rpm for degassing prior to printing. The shear thinning behavior of these materials allowed for pneumatic or volumetric dispensing at a feature size (internal nozzle diameter) of 250 microns without issue. The thixotropy of the A-1/P's was exemplified by excellent shape retention following extrusion with consistent bead diameters observed. An example of a printed A/1-P sample and a cross-section of the part can be seen in Fig. 4. As-printed samples held their shape throughout each build prior to crosslinking via UV chamber (Fusion UV Systems Series 300).

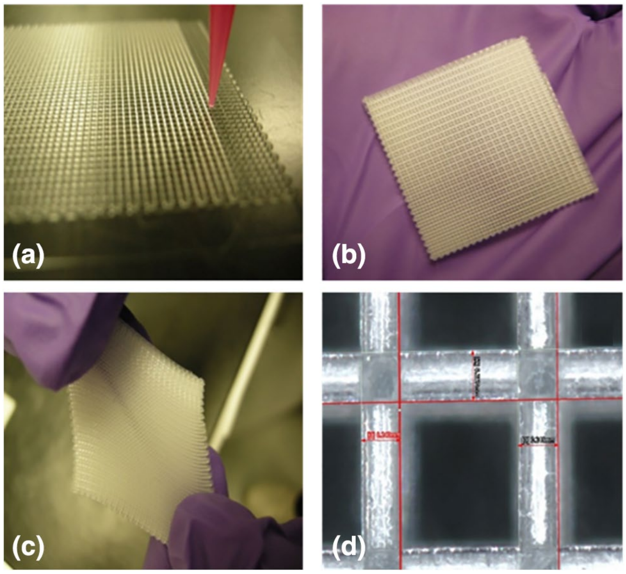

Figure 4. (a) a snapshot of a frozen-in-time moment in the course of a DIW printing process using A-1/P of this work; (b) the silicone rubber pad printed in process (a); (c) a demonstration of pronounced flexibility of the printed rubber pad (b); and (d) a cross-section of printed part at ×120 magnification, verifying consistent bead diameter.

Conclusions

Completely amorphous α,ω-telechelic vinylsiloxy-functionalized terpolysiloxanes of Fig. 1 have been found extremely useful for preparation of *"all-in-one"* pastes (A-1/P) for additive manufacturing of silicone rubber objects under typical printing conditions in direct ink write (DIW) process. These novel pastes show tunable, highly desirable rheological properties, enable quick (in a matter of seconds) permanent fixing of printed shapes when exposed to a UV light source at room temperature in air, and exhibit very long lifetimes when properly handled and stored. They provide a great level of convenience for paste manipulation, transportation and storage, not available before with silicone materials for additive manufacturing (AM). More details about these new, extremely practical silicone systems will be described soon.

Acknowledgments

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