Self-standing and shape-memorable UV-curing epoxy for three-dimensional (3D) continuous-filament printing
Self-standing and shape-memorable UV-curing epoxy for three-dimensional (3D) continuous-filament printing

H. Sun, a Y. Kim, b Y. C. Kim, a I. K. Park, b J. Suhr, a,b,c D. Byun, c K. Keon, d O. H. Baek, d Y. K. Jung, d H. J. Choi, e K. J. Kim f and J. D. Nam a,b,*

In the development of three-dimensional printable materials for high-speed and high-resolution printing, UV-curing polymers can guarantee a fast and precise printing of high performance load-bearing structures, but the injected drops of the monomers tend to spread over the substrates due to their low viscosity. In this study, we imposed self-standing and shape-memorable capability to an epoxy acrylate (EA) monomer to ensure a continuous filamentary 3D printing while maintaining its low viscosity nature. Using octadecanamide (ODA) with EA, the strong hydrogen-bond networks (-N-H∙∙∙O=C-, -N-C=O∙∙∙H-O-, -N-H∙∙∙N-) was additionally achieved in the material system and the developed material distinctively exhibited rheological duality in different processing stages: Low-viscosity liquid-like behavior (~50 Pa∙s of viscosity) while passing through the nozzle, and self-standing solid-like behavior (~364 Pa of static yield stress) right after being printed. This reversible liquid-to-solid transitional capability was quantified by viscoelastic complex moduli providing a dynamic yield stress (τ_y,d) as 210 Pa corresponding to the upright stacking up to ca. 3.2 cm (3 wt% of ODA). The time (t_y,d) required for the conformational rearrangement was evaluated as fast as ca. 10^-2 sec. After UV curing, the 3D printed layers exhibited no air pockets or weld lines at the stacked interfaces, which could guarantee excellent mechanical performance and structural integrity.

Introduction

Three-dimensional (3D) printing is a promising fabrication technology that attracts a great deal of attention in the manufacturing fields ranging from aerospace and automotive to bioengineering. 1-4 This additive manufacturing method offers almost unlimited and un constrained structures in a customized way without using molds, which can hardly be achieved by the traditional subtractive manufacturing technology. 5-9 As 3D printing becomes more and more central in the small-scale manufacturing fields, versatile 3D-printable inks are urgently needed to achieve not only feasible processing characteristics for fast printing but also robust structural properties for being used in load-bearing structures. 10-12 Currently, the 3D printing methods may be classified into two main categories in light of feedstock materials: continuous-filament and drop-jetting 3D printing.

The continuous-filament printing commonly uses thermoplastic polymers as a feedstock. It allows a rapid fabrication of 3D structures (ca. 5-15 cm/hr in the Z-axis), where the extruded filaments quickly solidify to construct the shapes. 13 However, the viscosity of its feedstock thermoplastics is usually high in the printing region of shear rate (e.g., ~10^3 Pa∙s for PLA), which inevitably requires large nozzle diameter (>250 μm) resulting in poor resolution of final products. 14, 15 On the other hand, the drop-jetting 3D printing usually adopts low-viscosity thermosetting monomers (most commonly UV-curable acrylates), which desirably allows a small nozzle size and high-resolution printing. However, the jetted droplets of thermoset monomers (1-5 μm diameter droplets) usually tend to spread over the substrate resulting in poor stacking capability (i.e., low aspect ratio of the injected drops) and low printing speeds (ca. ~3 cm/hr in the Z-axis in commercial machines). 16-19 Accordingly, if an upright standing capability is imposed to those thermoset monomers, a continuous-filamentary printing could be ensured in the 3D printing of thermoset monomers, which may not only overcome the poor stacking capability of drop-jetting 3D printing but also achieve higher resolution than continuous-filament printing. Our work, therefore, focuses on ensuring a continuous-filament printing using a thermoset-monomer feedstock, which allows small nozzle size and high printing speed.

Recent work has focused on controlling the rheological behaviours of 3D printing materials to apply the desired methods including the continuous-filament and drop-jetting
3D printing. Especially, for the direct-write printing, shear-thinning inks was utilized due to the different rheological response by the extent of physical stimulus such as shear stress. These fluids possessing self-standing and shape-memorable features have been classified as yield-stress fluids (or Bingham plastic fluids), which is often observed in mayonnaise, ketchup, whipping cream, toothpaste, etc. They behave like a solid in the quiescent condition but flow like an ordinary liquid when a certain level of stress (i.e., yield stress) is applied. For thermoset monomers, the yield-stress characteristics may be imposed by adopting hydrogen-bonding network in the fluids. The hydrogen-bonding network can lead to forming skeletal structures in thermoset monomers to maintain its shape against gravity, which is represented by the yield stress. This reversible self-assembly features of hydrogen-bonding can be used in the strategy of implementing yield-stress characteristics resulting in the phase transition between the liquid-like and solid-like states within several seconds.

Hydrogen bonding can be induced using functional groups between hydrogen attached to electrical negative atoms (e.g., N, O, F) and electron donator such as carbonyl oxygen (C=O). The self-assembled hydrogen-bonding skeletal structure allows the printed structure to maintain its shape against gravity, and simultaneously be crumbled with ease by an external shear force or agitation. Accordingly, if this yield-stress capability is imposed to a high-performance thermosetting monomer, most likely epoxy resins, a novel 3D-printing feedstock can be developed, which can flow through the printing nozzle or connection tubes with ease at a very low viscosity, but behave like a solid immediately after being printed.

As used in this study, epoxy resins are widely considered as one of low-viscosity (ca. 5-50 Pa s) and high-performance thermosetting polymers used for a variety of engineering applications due to superior mechanical properties, thermal and dimensional stability, chemical resistance and ease of processing. Particularly, it should be noted that the UV-curable acrylated (−CH2=CHCOO−) epoxy has both electron acceptors and donors for hydrogen bonding, corresponding to hydrogen (C=O) and carbonyl oxygen (C=O), respectively, as schematically depicted in Fig. 1A. In order to induce a strong hydrogen-bond network, as used in this study (Fig. 1B), amides can be additionally used as an appropriate self-assembly agent because they contain both electron acceptors (NH) and donors (C=O) to form networks by itself as well as with epoxy acrylates, e.g., N−H−O−C. In the self-assembly agent, it is important to choose appropriate chain lengths and the equivalent molecular weight of NH, each influencing the speed and the strength of hydrogen-bond network. Comparing with other chemicals, we carefully selected octadecyamide (ODA) as a self-assembly agent composed of 17 aliphatic C−C−chains (ca. 2.4 nm) containing amide groups corresponding to an equivalent molecular weight of 141.7 g/eq, which is compatible with epoxy acrylate and exhibits the appropriate rheological behaviours under the printing condition exerting a strong yield-stress behaviour. This epoxy/self-assembly agent system can guarantee low-viscosity, UV-curable, and self-assembly characteristics as a yield-stress fluid, which subsequently makes it as an ideal 3D printing feedstock ensuring a versatile additive manufacturing.

In this paper, we propose a novel epoxy acrylate system including amide as a self-assembly agent exhibiting solid-liquid reversible responses ensuring the 3D continuous-filament printing. The rheological characteristics of the developed material was thoroughly investigated under static and dynamic conditions identifying the yield stress, viscosity, phase-transition speed, and allowable height of stacking. The self-standing and shape-memorable capability of the materials was clearly demonstrated by printing a stacked structure in the z-direction.

Experimental

Materials

A bisphenol A type epoxy diacrylate resin (EA) with 500 g/mol of the molecular weight and 2,4,6-trimethylbenzoyl diphenyl phosphinoxide (TPO) were purchased from ENTIS (South Korea). 1,6-hexanediol diacrylate (HDDA) and octadecanamide (ODA) were purchased from Sigma-Aldrich and Arkema, respectively. TPO was used as a photoinitiator, which has a maximum UV absorbance of 395 nm. HDDA and ODA were used as a diluent material and a self-assembly agent, respectively. Specially, comparing with our materials system, polydimethylsiloxane (PDMS) was used as a reference material that has a high viscosity (~10^5 Pa s) without yield stress (purchased from TA Instruments, silicone standard #700.01011). As seen in Fig. 1, EA had potential hydrogen bond sites (O−H and C=O) and ODA three potential hydrogen bond sites (two N−H and one C=O). 30 g of EA was mixed with 10g of HDDA and vigorously stirred using a mechanical stirrer and 1 wt% of TPO was added. 1 wt% and 3 wt% of ODA were added to the neat EA, each corresponding to droplet and continuous-filament shape, respectively. Although not included here, the extrudate at 2 wt% of ODA exhibited a state in the middle of these two representative states at 1 and 3 wt%, and there was no significant change in the shape of extrudates when the ODA composition was over 3 wt%. Three different concentrations, 0, 1 and 3 wt% of ODA in the neat EA, were referred to as neat EA, EA/ODA1 and EA/ODA3, respectively, for the study of continuous-filament 3D printing.

Characterization

2 J. Mater. Chem. C, 2017, 00, 1-7
The rheological characteristics were measured using a rotational rheometer (MCR 300, Physica, Germany) equipped with a parallel plate geometry (disk diameter: 20 mm, gap size: 1 mm). Flow sweep tests were carried out at shear rate from $10^{-2}$ to $10^2$ sec$^{-1}$. The dynamic oscillatory tests were performed as increasing the oscillation amplitude up to 100% at a frequency of 1 Hz. A frequency sweep experiments (0.01-100 Hz) were performed at 1% strain. 3-step interval thixotropy experiments were conducted in three oscillation steps: the samples were subjected to a strain of 0.01%, subsequently a strain of 10% was applied and finally a step of 0.01% strain was implemented. The duration of each step was 60, 30 and 60 sec, respectively. All measurements were performed at 25°C. The optical images of extruded features were taken using a CCD camera.

**Printing**

The 3D printing machine (NP-expert, Enjet Inc.) employed in this study was designed to control the movement of the substrate stage in the X-Y axis and the nozzle in the Z-axis by a computer software. A micro-syringe pump (Harvard, new PHD UltraTMnanomite) was used to supply the prepared inks from a syringe (1 ml) into a stainless nozzle (21G: I.D. of 0.51 mm and O.D. of 0.80 mm). The flow rate was kept 15 μl/min. The detailed equipment and printing conditions were reported elsewhere. To build up the 3-D structures, the nozzle is located on a desired position and the ink deposition is commenced by working the pump. After stacking one layer of a desired feature, the nozzle is raised up a constant height. When the final height is reached, the ink deposition is stopped and the nozzle is vertically lifted up in order to disconnect the 3-D printed structure.

**Results and discussion**

Fig. 2A shows liquid state of neat EA and solid-like state of EA/ODA, where ODA imparts yield stress to the neat EA to become a solid-like state due to the molecular skeletal structure through the hydrogen bonds. Low-viscosity neat EA flows toward tiling direction, while EA/ODA exhibits no flow against gravity force. Fig. 2B shows a state in the middle of printing, where EA/ODA is stacked in three layers. In this printing, the EA/ODA shows two different stages each corresponding to liquid-like state inside the nozzle and solid-like state right after being printed in the stacked feature. When the ink is inside the nozzle, the shear rate or shear stress is applied to EA/ODA, which breaks the hydrogen-bonding network between ODA and EA molecules, resulting in a low-viscosity liquid at around ~50 Pa·s. After the ink being printed out of the nozzle, however, the molecular assembly quickly occurs to such an extent as to maintain filamentary feature, and the printed parts become a solid-like state at an infinity viscosity to maintain the shape of extruded filaments against gravity force. It constitutes that EA/ODA exhibits typical behaviour of yield stress fluids caused by the molecular self-
assembly via hydrogen bonding. This liquid-solid transition of
the ink could be quite advantageous as a 3D printing material
offering a low viscosity ink inside the nozzle and an infinity
viscosity extrude constructing a self-standing 3D-printed
structures. It facilitates that EA/ODA passes through the
syringe nozzle and rapidly solidifies, which is referred to as a
self-standing and shape-memorable capability.

Figs. 3A and 3B depict the apparent viscosity ($\eta$) and the
shear stress ($\tau$) as a function of shear rate ($\dot{\gamma}$) over $10^{0}$ to $10^{7}$
sec$^{-1}$ comparing neat EA, EA/ODA1, EA/ODA3 and PDMS. In Fig.
3A, the viscosity of EA/ODA specimens (EA/ODA1 and
EA/ODA3) is lower than that of PDMS, which is a reference
material exhibiting a typical pseudoplastic behaviour, in the
entire shear-rate range. Their viscosity continues to drop fast
with increment of $\dot{\gamma}$, which is considered that our ink system is
the thixotropic fluid exhibiting variable viscosity with respect
to shear rate. For example, the viscosity of EA/ODA3 is
decreased to $\sim 10^{3}$ Pa$s$, which is substantially lower than $\sim 10^{7}$
Pa$s$ of PDMS both measured at 10 sec$^{-1}$. It is clear that
EA/ODA specimens are more advantageous than PDMS for
printing through the fine nozzles due to their lower viscosity
than PDMS. In the logarithmic plots $\tau$ vs. $\dot{\gamma}$ (Fig. 3B), the neat
EA ink shows a typical Newtonian fluid behaviour exhibiting a
linear increment of $\tau$ with $\dot{\gamma}$, and $\tau$ of PDMS is increased
without a plateau region. On the other hand, $\tau$ of EA/ODA
specimens clearly shows a typical yield-stress fluid behaviour
exhibiting a constant $\tau$ with an increment of $\dot{\gamma}$, which
demonstrates the presence of “static yield stress ($\tau_y$),” i.e., a
shear-stress plateau as $\dot{\gamma} \to 0$.

Herein, the yield stress can be obtained by the extrapolation
of shear stress to the zero shear rate region. Yield-stress fluids
or Bingham fluids have been described by the Herschel-Bulkley
model (H-B model) as follows:\textsuperscript{41}

$$\tau = \tau_y + K\dot{\gamma}^n$$

(1)

Fig. 3 The rheological characteristics of the neat EA, EA/ODA1, EA/ODA3 and PDMS:
apparent viscosity (A) as functions of shear rate and shear stress (B) as function of
shear rate compared with the Herschel-Bulkley model description (solid lines). Digital
images extrudates of PDMS (C) and, EA/ODA3 (D), whose heights plotted as a function of
time in (E).

where $K$ is the consistency factor, and $n$ is the flow behavior
index. Analyzing the results in Fig. 3B based on Eq. (1), it can be
seen that the H-B model compares well with the experimental results of neat EA and EA/ODA specimens with
the model parameters summarized in Table 1. PDMS is not
applicable for the H-B model. EA/ODA1 and EA/ODA3 give $\tau_y$
of 71.6 Pa and 364 Pa, respectively, which should be compared
with that of 0 Pa for neat EA. When we assume that gravity is
only applied to the printed structure of yield stress fluids, the
structure can stand their own weight against gravity by the
quantification of yield stress and their theoretical heights can
be estimated, viz:\textsuperscript{26}

$$h = \frac{\tau_y}{\rho g \delta}$$

(2)

where $h$ is the theoretical height, $\rho$ is the density of the yield
stress fluids and $g$ is the acceleration of gravity. Using Eq. (2),
$h$ Table 1 The parameters ($\tau_y$, $K$, and $n$) of Herschel-Bulkley model,
theoretical height ($h$) and dynamic yield stress ($\tau_{y,d}$) for neat EA, EA/ODA1
and EA/ODA3.

<table>
<thead>
<tr>
<th></th>
<th>$\tau_y$ (Pa)</th>
<th>$K$</th>
<th>$n$</th>
<th>$h$ (cm)</th>
<th>$\tau_{y,d}$ (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat EA</td>
<td>0</td>
<td>3.13</td>
<td>0.999</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>EA/ODA1</td>
<td>71.6</td>
<td>138</td>
<td>0.714</td>
<td>0.6</td>
<td>40</td>
</tr>
<tr>
<td>EA/ODA3</td>
<td>364</td>
<td>150</td>
<td>0.746</td>
<td>3.2</td>
<td>210</td>
</tr>
</tbody>
</table>

of the extruded filaments of EA/ODA3 could be estimated as
3.2 cm, which is the visualized upright capacity corresponding
to the yield stress ($\tau_y$) of 364 Pa. It should be compared with
the yield stresses of such materials as mayonnaise, ketchup
and tooth paste corresponding to the yield stresses of 100, 30,
and 215 Pa, respectively. In the other words, the extruded
filaments can be overlaid repeatedly up to that height without
spreading or collapsing by the gravity without any solidification
steps. In practical printing processing, the overlaid structure is
usually solidified in-situ by UV curing subsequently extending
the theoretical heights of inks.

The yield-stress characteristics may be confirmed by
observing the the extrudate shapes changing with time after
being printed. In Figs. 3C and 3D, the height of PDMS, whose
viscosity is much higher than EA/ODA, decreases by nearly 20%
after 5 min. After 30 min, PDMS collapses by nearly 70%,
spreading over the substrate. On the other hand, EA/ODA3
keeps its initial shape and height, where the spreading
phenomena is not observed even after 30 min. Imposing yield-
stress characteristics to EA, it demonstrates that the low-
viscosity epoxy can be used as a feedstock of 3D continuous-
filament printing device in a way of stacking the filaments just
like high-viscosity thermoplastic polymers.

The gravitational spreading phenomena of a high-viscosity
drop may be evaluated as a function of time assuming that a
drop flows by the gravity force in the quasi-steady state:\textsuperscript{42}

$$\frac{h_t}{h_0} = \left(\frac{3}{2 \pi \nu t}\right)^{1/4}$$

(3)

where $h_t$ is the transient height, $h_0$ is the initial height, $\nu$ is the
kinematic viscosity, $V$ is the volume of a drop, $t$ is the time. Eq.
Fig. 4 Viscoelastic properties of EA/ODA1, EA/ODA3 and PDMS plotted by storage modulus, \( G' \), loss modulus, \( G'' \), (A) and \( \tan \delta \) (B) as function of shear stress. \( G' \) and \( G'' \) as a function of frequency (C) from 0.01 to 100 Hz under constant strain of 0.1% for EA/ODA specimens. The crossover point means the time scale of phase change between solid-like behavior and liquid-like behavior. \( G' \) and \( G'' \) as a function of three time-steps at the applied strain in a low-high-low (0.01%-10%-0.01%) fashion using a frequency 1 Hz (D). The solid line represents the corresponding strain applied to the specimens.

(3) describes well the experimental results of PDMS as seen in Fig. 3E, where \( h_t \) decreases in proportion to \( t^{-1/4} \). Compared with the collapsing PDMS, it is clearly seen that EA/ODA3, which is a yield-stress fluid, maintains the initial height against the gravity force regardless of time. It proves that EA/ODA3 exhibit the self-standing and shape-memorable capability that could substantially increase the printing speed and resolution by such a rapid stabilization of printed structures.

In this study, the phase transition of our ink systems between solid-like and liquid-like states are clearly demonstrated by analysing the viscoelastic properties each corresponding to storage modulus \( (G') \) and loss modulus \( (G'') \) of materials. When \( G' \) is higher than \( G'' \), the material is in a predominant solid-like state, and vice versa. In this sense, the crossover point of \( G' \) and \( G'' \) can be attributed to the transition from the solid-like to the liquid-like states, which may very well correspond to the yield point of the material. In the oscillatory experiments, \( G' \) and \( G'' \) of EA/ODA specimens and PDMS are plotted as a function of \( t \) in Fig. 4A. EA/ODA1 and EA/ODA3 exhibit that \( G' \) is maintained higher than \( G'' \) up to the crossover points of 40 Pa and 210 Pa, respectively, followed by the region, where \( G'' \) is higher than \( G' \). The obtained crossover points in Fig. 4A provide the dynamic yield stress \( (\tau_{Y,G}) \) of EA/ODA1 and EA/ODA3, which agrees well with \( \tau_{y,G} \) at 71.6 and 364 Pa in Table 1, respectively. When the ink flows through a nozzle, the wall shear stress in our experimental conditions can be estimated as 1825 Pa for EA/ODA3, which is higher than the yield stress \( (\tau_{Y,G}) \) of our material. It supports that EA/ODA3 should flow in the liquid-like state inside nozzle at 50 Pa-s (Fig. 3A). However, when the ink is extruded out of the nozzle as filament, the applied shear stress becomes nearly zero, which it turns into a solid-like state. It can be further analysed using \( \tan \delta \) (\( G''/G' \)), which quantifies the elastic or viscous contributions by the borderline conditions of the phase transition at \( \tan \delta = 1 \). Fig. 4B shows \( \tan \delta \) of EA/ODA specimens and PDMS as a function of \( \tau \). The \( \tan \delta \) of EA/ODA specimens increases with \( \tau \) passing through the borderline at \( \tan \delta = 1 \) representing a liquid-like behavior in the low shear-stress region and a solid-like one in the high shear-stress region. It is clear that the shear stress at \( \tan \delta = 1 \) consists with \( \tau_{Y,G} \) as measured in Fig. 4A. On the other hand, the \( \tan \delta \) of PDMS is 1.0 in the entire region. The time \( (t_{Y,G}) \) required for the reversible liquid-to-solid transition may be evaluated by the frequency-sweep tests. Fig. 4C shows \( G' \) and \( G'' \) of EA/ODA specimens measured as a function of frequency (f). The crossover points of EA/ODA1 and EA/ODA3 specimens are observed at \( f = 20 \text{ Hz} \) and 100 Hz each corresponding to \( t_{Y,G} = 1/f = 0.01 \text{ sec} \) and 0.05 sec, respectively. The crossover point of \( G' \) and \( G'' \) is related with the phase transition, which may very well correspond to time required for the liquid-to-solid or solid-to-liquid transitions. This time may be ascribed to the time for EA and ODA molecules to form the skeletal network of hydrogen bonding. It should be associated with the time for the hydrogen bonding kinetics, viscosity and diffusion mobility of EA monomers and ODA, on the other hand, the hydrogen bond has a weak effect on the mechanical properties of our ink as seen in Fig. S1. Fig. 4D depicts the 3-step interval thixotropy test of EA/ODA specimens, which shows the typical characteristics of thixotropic fluids: the recovery of viscosity and/or moduli after the structure was broken down under the changing shear rates. They exhibit \( G' \) higher than \( G'' \) at a low strain at 0.01% but it turn vice versa at a high strain at 10%. When the low strain is applied again, the initial value of \( G' \) is rapidly increased and recovered. The first and last region (at low strain) shows the build-up of network structure and the middle region indicates the breakdown of the structure. This rapid and reversible response stems from the molecular self-assembly via hydrogen bonding allowing the breakdown or
reassembly of our ink system depending on the extent of deformation. In this regard, our inks have the reversible thixotropic nature, which is desired for 3D printing materials because they can easily flow through the nozzle and maintain the continuous-filament shape after extrusion.

Fig. 5 compares the sequential images of the low yield-stress ink (EA/ODA1) and high yield-stress ink (EA/ODA3) extruding out of the tip of the syringe needle. In general, as a spherical drop grows until the drop volume exceeds a critical weight for the drop to fall down. The maximum size of the drop held by the surface tension at the tip of the needle can be expressed by the following equation:

$$V_{max} = \frac{\sigma D}{g}$$

where $V_{max}$ is the maximum volume of the drop, $\sigma$ is the surface tension of liquid and $D$ is the diameter of the nozzle. In yield-stress fluid, however, the yield stress ($\tau_y$) is additionally exerted to hold the drop at the nozzle tip resulting in a drop in a long-neck pendent shape (Fig 5A), whose volume is bigger than $V_{max}$, or a continuous-filament shape (Fig. 5B) when the yield stress is further increased. Accordingly, it is clear that the yield stress is likely to be added to the intrinsic surface tension subsequently increasing the drop volume to surpass the gravity force resulting in the shape-memorable capability (retention of filamentary shape).

Using our high yield-stress ink (EA/ODA3), Fig. 6A demonstrates a stacked rim structure in a way of continuous-filament 3D printing. Due to high yield stress, the filaments are stacked with ease without buckling or spreading even before UV curing. When UV-cured (Fig. 6B), the printed rim structure turns yellow and becomes strong and robust maintaining its structural integrity even such a bending deformation. Figs. 6C and 6D show the cross-sectional images of the 5-layer printed rim after UV curing. It indicates that no filamentary boundaries between individual printed filaments demonstrating that the interfaces of the printed layers are well cohered each other, which is the quite different from the printing cases of most thermoplastic materials. In thermoplastics, the overlaid boundaries often exhibit weld-lines leaving air pockets or weak interface lines due to the intrinsically-long relaxation time (or healing time) of high-molecular polymer chains. Fig. 6E shows the height and width of printed structures as a function of the stacking number of layers. The width is nearly constant, while their height is linearly increased. The thickness of each layer is 520 μm, which resultantly gives a structural height of 2.6 mm by stacking up only five filaments. To demonstrate the upright capacity of our high yield-stress ink (EA/ODA3), we printed a stacked wall structure (7.5 mm) composed of 40 stacked layers in a way of continuous-filament 3D printing as shown in Fig. 6F. Fig. 6G shows a printed symbol demonstrating the capability of our ink system printing complex patterns or shapes, e.g., a ginkgo-leaf feature, which is composed of multiple radii and sharp angles.

Conclusions

In this study, we developed a novel epoxy-based resin system, which has a shape-memorable and self-standing capability. The hydrogen-bond network was imposed by using an appropriate amide compound. Depending on the level of yield stress, the theoretical height of 3D printed structures could be predicted by theory and confirmed by experiments. The extrudate shape and spreading phenomena were identified...
with time. Additionally, the tanδ accurately demonstrated the liquid-solid phase transition in the printing operating conditions. The yield stress and tanδ indicates that our high yield-stress fluid can be utilized by continuous-filament 3D printing, which would enable low-viscosity thermosetting polymers systems to exert the self-standing and shape-memorable capability.

Conflicts of interest
There are no conflicts to declare.

Acknowledgements
This work was supported by the National Research Foundation of Korea (NRF), the Ministry of Science, ICT & Future Planning (NRF-2014M3C1B2048175, 2016R1A2B1007134, and NRF-2017R1A2B4006091), and the Ministry of Trade, Industry and Energy (MOTIE) (10067690). We also appreciate the project and equipment support from Gyeonggi Province through the GRRC program of Sungkyunkwan University. KJK would like to acknowledge the partial financial support from the US National Science Foundation (#1545875).

Notes
J. D. Nam designed the experiments. H. Sun carried out the experiments and wrote the manuscripts. Y. Kim, Y. C. Kim and I. K. Park contributed to the data analysis. K. Keon, K. Park contributed to the data analysis. J. Suhr and D. Byun conceived the idea. All the authors reviewed the manuscript.

References
The wall stress in the Hagen-Poiseuille equation is 
\[ \tau_w = \frac{\Delta P R}{2L} \]. The experimental conditions of our printing are 
\( R = 250 \mu m, \Delta P = 146,000 \) Pa and \( L = 1 \) cm, which gives \( \tau_w = 1833 \) Pa.

47 J. Mewis and N. J. Wagner, Advances in Colloid and Interface 

48 G. K. Batchelor, An introduction to fluid dynamics, 