Cure kinetics of bismaleimides as basis for polyimide-like inks for PolyJet™-3D-printing

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ABSTRACT: Since polyimides are well known for their excellent chemical and thermal stability and outstanding mechanical properties there is increasing interest in developing polyimide-based inks to produce additively manufactured parts with properties superior to those of currently available materials. Usage of bismaleimides (BMI) as precursors allows polyimides to be fabricated via PolyJet™ printing (Stratasys Ltd., Rehovot, Israel). Characterization of the curing kinetics is a central part of process development, as fast curing initiated by UV light is desired. Here, a comprehensive study of thermal and UV curing of BMI oligomers with various molecular weights and chemical structures is presented. Fourier transform infrared spectroscopy serves as a tool for determining the curing degree. Furthermore, an estimation of the activation energy for thermal curing is performed. UV curing of the selected BMIs leads to highly cross-linked, thermoset polymers with excellent chemical resistance and thermal stability which are of great interest for PolyJet™ 3D printing.

INTRODUCTION

PolyJet™ 3D printing is a promising method that enables multiple materials to be used to create complex components which are impossible to create in any other way. The working principle of PolyJet™ 3D printing includes (i) jetting layers of low viscosity liquid photosensitive monomers and oligomers onto a build tray and (ii) subsequent curing by UV light.1

Polyimides (PIs) are desirable materials for 3D printing since they have a variety of outstanding characteristics, including high thermal stability, excellent mechanical properties, wear resistance, vacuum compatibility, radiation resistance, inertness to solvents, a low dielectric constant, and good adhesion strength.2,3 PI synthesis routes include polycondensation and polyaddition mechanisms. Aromatic PIs are generally prepared from aromatic diamines and aromatic tetracarboxylic dihydrides in a two-step procedure. However, this polymerization by condensation is less compatible with 3D printing procedures than polyaddition, mainly because of slow thermal curing.4 Bismaleimide (BMI) resins are a family of high-performance thermosetting PIs that have a range of attractive properties for industrial applications, particularly in the aerospace materials sector.5 Since BMIs are polymerized by an addition mechanism, they are promising candidates for PI ink printing using the PolyJet™ technology.6 BMIs are low molecular weight oligomers consisting of imide moieties with reactive terminal or pendant groups that undergo thermal or catalytic homo- and/or co-polymerization.7,8 The rheological properties of BMI-based materials can be tuned by tailoring the molecular weights of the oligomers.9 Typical properties associated with cured BMI-based systems include high glass-transition temperatures (230–380 °C), good hot-wet performance, excellent electrical properties, and low flammability.10–15 The BMI-materials used in this study have very flexible backbones, resulting in low shrinkage during curing and yielding...
polymers that show high thermal stability (decomposition temperature typically >400 °C). At the same time, these flexible BMI polymers have a low modulus (<500 MPa) and lower glass-transition temperatures than classical BMI resins.5

Due to the reactive maleimide groups, BMIs can act both as polymerizable monomers for thermal and photo-polymerization and as photoinitiators. The maleimides form initiating radicals upon UV exposure, which makes them uniquely valuable for copolymerization with various co-monomers, such as vinyl ethers and acrylates.16,17 Further, UV homo-polymerization of BMIs is possible without an additional photoinitiator. Upon UV exposure, the maleimide double bonds of BMI undergo cyclo-dimerization to form a cyclobutane ring.18 BMI oligomers can be linked together via this mechanism to yield thermoset polyimides with excellent thermal stability and chemical resistance. Depending on whether a photoinitiator is used for polymerization, the polymers are formed either by photo-polymerization or by photo-cyclo-dimerization (see Figure 1).

Customization of BMI-based materials for inkjet printing allows additively manufactured polyimide structures to be produced by PolyJet™ 3D printing. High photoreactivity and suitable viscosity for jetting are the key parameters to be considered in designing the ink formulation.

In this work, commercial BMI oligomers with molecular weights (MWs) ranging from 689 to 5000 g mol⁻¹ were characterized in terms of their thermal curing and UV curing behaviors. Oligomers with MWs of up to 1700 g mol⁻¹ are liquid, while oligomers with MWs of 3000 g mol⁻¹ and above are powders. The number in the BMI name denotes the MW of the oligomer. As an example, BMI-1500 has a MW of 1500 g mol⁻¹. The types of oligomer used were linear chain-extended aliphatic BMI [Figure 2(a)] and imide-extended BMI [Figure 2(b–d)]. Using BMI precursors with higher MWs has the advantage of increasing polymer chain flexibility due to lower crosslinking density, which results in an impact strength that is higher than that of highly crosslinked BMI-based polymers. The polyimides formed of imide-extended

![Figure 1. Cyclo-dimerization of N-functionalized maleimide (a, b) and photo-polymerization (c) of N-substituted maleimides.18](image-url)
BMIs have higher thermal stability than those of aliphatic extended BMIs. Due to their low viscosity, low-molecular-weight products, such as BMI-689, are promising PolyJet™ ink candidates. Low-viscosity BMI oligomers can be used in ink formulations with high solid content, allowing jettablility and printability under typical PolyJet™ conditions at printing temperatures of 50–70 °C.

Designing new materials for PolyJet™ printing involves characterizing the UV curing kinetics, since fast polymerization of oligomers upon UV irradiation is desired to keep printing times short. At the same time, optimal rheological properties of the ink are to be maintained.

Various ways of studying curing reactions have been reported in the literature: Fourier transform infrared (FTIR) spectroscopy for monitoring polymerization reactions has become increasingly popular since the late 1990s. Other examples include Raman spectroscopy and differential scanning calorimetry (DSC). FTIR spectroscopy is a very convenient method for monitoring the curing reaction, as it is fast, easy, and broadly applicable. The intensities of the bands corresponding to the reactive double bonds are considered in order to follow the curing reaction, while the decrease in absorption band area is used to assess the degree of curing α according to:
For thermal curing of BMI resins, a Nabertherm muffle DSC 204 calorimeter and a Mettler AT200 balance with a 200 W mercury arc lamp in connection with a Netzsch apparatus were carried out using the OmniCure S2000 XL UV-Setup of a Perkin Elmer Lambda 35 spectrometer. Photo-DSC measurements were performed at 200, 225, and 250 °C.

Here, we present a comprehensive study of the curing kinetics of selected BMI oligomers, including activation energy measurements and the rate of thermal- and photo-polymerization. Further, we describe the influence on polymerization speed of temperature in the case of thermal curing and of wavelength of the UV source, UV intensity, and type of photoinitiator in the case of photo-curing.

**EXPERIMENTAL**

**Materials**

BMI-oligomers with various molecular weights (BMI-689, BMI-1500, BMI-1700, BMI-3000 powder, and BMI-5000 powder) were purchased from Designer Molecules Inc, San Diego, California, USA. Dichloromethane, 1, 4, 6-trichlorobenzene (TCB) and N-methylpyrrolidone (NMP) were purchased from Sigma Aldrich, Vienna, Austria. All solvents were in analytical grade and used as received. The photoinitiators, Omnirad 819 (O-819), Omnirad 907 (O-907), Omnirad TPO-L, (O-TPO-L), and Omnirad 2959 (O-2959) were provided by IGM Resins.

**Methods**

FTIR spectra were recorded using a Bruker Tensor 37 spectrometer with MIRacle ATR-bridge. A Perkin Elmer DSC8000 DSC was used to obtain kinetic information about the BMI curing reaction. A Pyris Series TGA4000 thermogravimetric analyzer (TGA) was employed to determine the temperature stability of crosslinked BMI-based materials. UV-vis absorption was measured by means of a Perkin Elmer Lambda 35 spectrometer. Photo-DSC measurements were carried out using the OmniCure S2000 XL UV-Setup with a 200 W mercury arc lamp in connection with a Netzsch DSC 204 calorimeter and a Mettler AT200 balance.

For thermal curing of BMI resins, a Nabertherm muffle furnace model L3/11/P330 was employed. Thermal curing of BMI resins was performed at 200, 225, and 250 °C under ambient atmosphere.

UV sources used in this study include UV-LED arrays (with various wavelengths and powers) and mercury lamps (see Table S1 in the supporting information). The intensities of the UV sources were measured by a UV-Micro Puck Multi Integrator (UV-Technik Meyer, Ortenberg, Germany).

A Sartorius CPA225D balance with 0.01 mg accuracy was employed in order to measure the weight loss after solvent resistance tests.

Dynamic mechanical analysis (DMA) was performed by means of an Anton Paar Physica MCR 501 at 0.1% deflection to obtain information about the thermomechanical properties of the cured BMIs.

For thin-film preparation (1–2 μm), 100 mg mL⁻¹ solutions of BMI-oligomers in dichloromethane were spin-coated on glass and KBr substrates. Films of pure liquid oligomers with 12 μm thickness were produced by applying the doctor-blading technique.

**RESULTS AND DISCUSSION**

Kinetic studies were carried out to gain comprehensive information about the curing reaction for both thermal- and UV-induced BMI polymerization. In the PolyJet™ printing process, the UV-curing kinetics are of central importance and here, we compared them to the kinetics of the classical thermal curing process. In the case of thermal curing, we carried out DSC measurements at various scan rates to obtain the apparent activation energy from the peak shifts according to the Kissinger33 and Ozawa34 methods. The results were compared with the activation energies calculated from the classical Arrhenius plots. FTIR spectra were used to obtain the curing degree as a function of the curing conditions.

**Activation Energy of BMI Polymerization**

Together with other kinetic parameters (including the polymerization rate $R_p$ and the kinetic rate constant $k$), the activation energy $E_a$ for thermal curing of BMI resins is essential to understanding the curing reaction of this system. Methods for determining the apparent activation energy by DSC include the Kissinger33 and the Ozawa34 models. Applying these methods, we calculated the activation energy from the peak shift of the exothermic polymerization peak from DSC scans at various heating rates [eqs. (2) and (3)]. Figure 3 shows DSC scans of BMI-689, where the shift of the polymerization peak maximum depends on the heating rate $\beta$. According to the Kissinger method, the activation energy $E_a$ can be determined by plotting the logarithm of the heating rate $\beta$ over the squared peak temperature $T_p$ against the inverse peak temperature:

$$\frac{d}{d\left[\frac{T_p^2}{T_p}\right]} \ln \beta = -\frac{E_a}{R}$$  \hspace{1cm} (2)

![Figure 3. DSC scans of BMI-689 showing a shift in the polymerization peak maximum for various heating rates.](s varios heating rates. [Color figure can be viewed at wileyonlinelibrary.com])
where $R$ denotes the universal gas constant.

The Ozawa method uses a plot of the logarithm of the heating rate $\beta$ versus the inverse peak temperature $T_p$ to calculate the activation energy:

$$
\frac{d[\ln\beta]}{d\left[\frac{1}{T_p}\right]} = -1.052 \frac{E_a}{R} \tag{3}
$$

The Kissinger and Ozawa plots of BMI-689 are shown in the supporting information (Figures S1 and S2).

The values for the activation energy determined by the Kissinger and Ozawa methods were compared to those obtained from the classical Arrhenius equation:

$$
k = Ae^{\frac{E_a}{RT}} \tag{4}
$$

where $A$ denotes the pre-exponential factor.

The logarithm of the rate constants for curing at three different temperatures (200, 225, and 250 °C) were plotted against the inverse curing temperatures according to:

$$
\ln k = \ln A - \frac{E_a}{RT} \tag{5}
$$

The rate constants used for the activation energy calculation are shown in Figure 5(c). We determined the activation energies from the slopes of the Arrhenius plots (see supporting information Figure S3 for the BMI-689 and BMI-1500 plots).

Table I lists the activation energies of BMI-689 and BMI-1500 determined by applying the Kissinger, Ozawa, and Arrhenius methods. For thermal curing of BMI-689, activation energies of 90 and 93 kJ mol$^{-1}$ were calculated by means of the Kissinger and the Ozawa methods, respectively. The activation energy determined by the Arrhenius equation from the kinetic rate constants at three different temperatures was 118 kJ mol$^{-1}$. For BMI-1500, the Kissinger, Ozawa, and Arrhenius methods gave activation energies of 112, 122, and 99 kJ mol$^{-1}$, respectively. Taking measurement accuracy into account, the activation energies calculated by the Kissinger and Ozawa models are in good agreement with the experimental values obtained from the Arrhenius plot.

Similar activation energies of 90–160 kJ mol$^{-1}$ have previously been reported for thermal polymerization of BMI-based materials in bulk.\cite{28,35–38} Compared to radical polymerization of BMIs in solution, the activation energies for bulk polymerization are higher because viscosity is higher and diffusion limitation plays a more significant role. For polymerization of maleimides in solution, the activation energy is around 20 kJ mol$^{-1}$\cite{39}.

**Evaluation of the BMI-Curing Kinetics**

Based on experimental FTIR data, an assessment of the curing kinetics of BMI thermal- and photo-polymerization was carried out. In order to determine the curing degree $\alpha$, we followed the polymerization progress via the decrease in maleimide double bond concentration [eq. (1)]. FTIR spectra were recorded after various exposures to thermal treatment or UV doses. Figure S4 shows the FTIR spectrum of BMI-689 as an example (see supporting information).

During polymerization, the reactive maleimide double-bond bands at 696 and 825 cm$^{-1}$ decreased in intensity, as shown in Figure 4.

Figure S5 in the supporting information shows the decrease in maleimide double-bond band area and the corresponding curing degree during thermal polymerization of BMI-689 at 225 °C. Assuming that, in systems consisting of pure BMIs, the polymerization rate depends only on the concentration of BMI precursors, the kinetic rate constant is obtained via the first-order kinetic equation\cite{40} (see equations S1–S3 and Figure S6, supporting information). Comparison of the experimental data with the theoretical conversion curves (calculated using kinetic rate constants) shows that a first-order kinetic equation is a good approximation of the BMI curing reaction.

**Thermal Curing of BMIs**

Thermal curing of BMIs was performed at temperatures of 200, 225, and 250 °C under ambient atmosphere. Figure 5 shows the corresponding curing degrees of selected BMI-oligomers (a), the rates of polymerization (b), and the kinetic rate constants depending on temperature (c). As an example, the curing degree and polymerization rate obtained during polymerization at 225 °C are shown. It can be seen that the crosslinking speed is influenced both by molecular weight and chemical structure. For imide-extended BMIs, smaller molecules with more reactive double bonds relative to molecular weight show lower crosslinking speeds, whereas higher molecular-weight oligomers crosslink faster. In contrast, the aliphatic BMI-689 shows a different curing behavior and a crosslinking speed between those of BMI-1700 and BMI-3000 [Figure 5(a,b)]. Unlike other oligomers, BMI-1500 is not fully crosslinked, but exhibits a plateau at $\alpha = 85\%$, reflecting the rigidity of the polymer chains. More thermal energy...
would be needed to reach a higher conversion of the double bonds in BMI-1500. The polymerization rate is highest for BMI-3000 and BMI-5000, whereas for BMI-689, BMI-1500, and BMI-1700, polymerization proceeds more slowly. The kinetic rate constants for thermal polymerization of BMI oligomers show an exponential increase with increasing temperature, as illustrated in Figure 5(c). The aliphatic oligomer BMI-689 shows the highest increase in kinetic rate constant with increasing temperature.

**UV-Curing of BMI**

BMIs can be activated by UV light to form initiating radicals for homo-polymerization or co-polymerization with various monomers. The UV absorbance of BMIs studied in this work was highest at 230–250 nm (see Figure S7 in the supporting information). The parameters influencing the photopolymerization rate of the BMI resins include UV intensity and wavelength and the addition of photoinitiators. Addition of a photoinitiator increased the response to UV irradiation and consequently the curing speed.

**Influence of UV Intensity on BMI Curing**

In contrast to the standard precursors used for PolyJet™ printing, which contain highly reactive acrylic double bonds, BMI oligomers have maleimide double bonds, which—as is commonly known—require more energy for polymerization to be initiated. For this reason, high power is necessary for, and beneficial to, fast curing of BMI resins. Figure 6 shows the curing degree of selected BMI oligomers after exposure to various doses of UV light with 395 nm wavelength (FJ200, 11.4 W cm⁻²) (a), the

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**Table 1. Activation Energies of Aliphatic BMI-689 and Imide-Extended BMI-1500 Determined by the Kissinger, Ozawa, and Arrhenius Methods**

| Material       | $E_a$ Kissinger (kJ mol⁻¹) | $E_a$ Ozawa (kJ mol⁻¹) | $E_a$ Arrhenius (kJ mol⁻¹) |
|----------------|---------------------------|------------------------|---------------------------|
| BMI-689        | 90                        | 93                     | 118                       |
| BMI-1500       | 112                       | 122                    | 99                        |

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**Figure 5.** Curing degree (a) and rate of polymerization (b) of various BMI oligomers during thermal curing at 225 °C, and kinetic rate constants (c) for thermal polymerization of BMI-oligomers at 200, 225, and 250 °C. The films were prepared by spin-coating of 100 mg mL⁻¹ solutions of BMI in dichloromethane. The symbols represent the experimental values, while the solid lines show the corresponding calculated fits. [Color figure can be viewed at wileyonlinelibrary.com]
corresponding polymerization rates (b), and the kinetic rate constants obtained by using the corresponding first-order kinetic equations, versus UV intensity (c). Analogously to the case of thermal curing, the polymerization rate increases with increasing power for all BMI oligomers.

The photo-polymerization rate at 395 nm wavelength is highest for BMI-689, BMI-3000, and BMI-5000, while for BMI-1500 and BMI-1700, the polymerization speed is slower, as illustrated in Figure 6.

**Influence of UV Wavelength on the Curing Reaction**

The wavelength of the UV source used for crosslinking the BMI resin has a considerable influence on the crosslinking speed. Figure 7 shows the curing degree of BMI-689 during exposure to LEDs with 340, 365, and 395 nm peak wavelength (a). At the same dose, using a UV-LED with a wavelength of 365 rather than 395 nm significantly increases the reaction rate constant and exposure to a UV-LED with a wavelength of 340 nm results in a further boost. This increase in polymerization speed is due to the UV absorption maximum of BMI-689 being at 230 nm, as shown in the supporting information (Figure S7). At lower wavelengths, a significantly higher amount of energy is taken up by the BMI-oligomer, which leads to greater polymerization speed. Figure 7 (b) plots the curing degree of BMI-689 during irradiation with a mercury lamp with 0.45 W cm$^{-2}$ intensity at an irradiation distance of 15 mm. The broad spectrum of the lamp allows very fast curing of BMI, exploiting the highest reactivity of the system, as BMI absorbs mostly in the UV-C region of 230–250 nm.

As fast photopolymerization of BMI is desired in PolyJet™ printing, the usage of a mercury lamp is most effective.

**Influence of Photoinitiator on BMI Curing**

The influence of type and amount of photoinitiator (PI) on the curing speed of BMI-689 was determined by Photo-DSC measurements. Figure 8 plots the exothermic polymerization peaks for BMI-689 with and without addition of various types and

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**Figure 6.** Curing degree (a) and polymerization rate (b) of various BMI oligomers during UV polymerization at 395 nm and an intensity of 11.4 W cm$^{-2}$ and kinetic rate constants of polymerization versus UV power (c). The films were prepared by spin-coating of 100 mg mL$^{-1}$ solutions of BMI in dichloro-methane. The symbols represent the experimental data, while the solid lines show the corresponding calculated fits. [Color figure can be viewed at wileyonlinelibrary.com]
amounts of PI after 2 s irradiation with a mercury halide lamp. Only those curves are shown that exhibit an increase in UV-response compared to that of the pure BMI-689 oligomer. A specific amount of PI is beneficial, while higher concentrations can inhibit the curing reaction. Pure BMI-689 shows a broad exothermic peak after the UV pulse. BMI-689 with 2 wt % O-819 also exhibits a broad peak after UV irradiation, but the polymerization peak area is significantly larger. In contrast, mixtures with other PIs (i.e., O-TPO-L, O-369, and O-907) show a very sharp response to the UV pulse.

Figure 9 compares the photopolymerization peak areas of pure BMI-689 with those of mixtures of BMI-689 with various types and amounts of PI. Addition of 2 wt % O-819 to BMI-689 results in the largest increase in the polymerization peak, while higher amounts of the PI are not beneficial. In the case of O-TPO-L and O-369, the optimal amount is 5 wt %. The photo-initiator O-907 decreases the reactivity of BMI-689 when increasing amounts are added. In general, O-819, and O-TPO-L show the best reactivity in combination with BMI-689, as it is illustrated by Figure 9. Amounts of 2 wt % O-819 and 5 wt % O-TPO-L are most successful in creating a fast and high UV curing response.

Properties of Cured BMI-Films
We observed that crosslinked BMI-based films exhibit excellent chemical resistance and have good thermomechanical properties. Films of BMI-based materials cured with the high-power UV-LED FJ200 (395 nm) without additional thermal post-treatment were used for testing chemical resistance. Fully crosslinked BMI-689 is even resistant to harsh solvents at elevated temperatures. The tests were carried out with 2 wt % polymerized BMI-689 in various solvents at room temperature (RT) and 40 °C and in an ultrasonic bath. The solvent resistance test was followed by solvent evaporation and determination of weight loss. The solvents used were THF, 2,4,6-trichlorobenzene (TCB) and N-methyl-pyrrolidone (NMP). In all tests, no measurable loss or gain in

Figure 7. Curing degree of 12 μm thick pure BMI-689 irradiated with UV light of various peak wavelengths (340, 365, and 395 nm) with the fastest curing reaction at 340 nm (a); curing degree during irradiation with a mercury halide lamp with 0.45 W cm⁻² at the substrate (b). The symbols represent the experimental values obtained for the curing degree, and the solid lines show the corresponding calculated fits. [Color figure can be viewed at wileyonlinelibrary.com]

Figure 8. Photo-DSC measurements of BMI-689 with and without addition of various photoinitiators. The photo-response to a 2 s pulse with a mercury lamp is shown. [Color figure can be viewed at wileyonlinelibrary.com]

Figure 9. Comparison of exothermic reactions of BMI-689 with and without addition of various types and amounts of photoinitiator after a 2 s UV pulse based on Photo-DSC measurements. [Color figure can be viewed at wileyonlinelibrary.com]
weight was observed. The parameters for the solvent resistance tests are listed in Table II.

The thermal stability of the BMI-based materials was assessed by TGA measurements. UV-cured BMI-based films exhibit very good thermal stability, as can be seen in the TGA curves of the BMI polymers shown in Figure 10. The film prepared by UV curing of the aliphatic extended BMI-689 shows a weight loss of <2% at 271 °C, while the film prepared from the imide-extended BMI-3000 exhibits the highest temperature stability with a weight loss of <2% at 431 °C; the other BMI materials characterized in this study have values between those of the former two. According to the TGA measurements, the BMI polymers have decomposition temperatures between 422 and 464 °C.

Table III lists the temperatures for 2% weight loss ($T_{2\text{wt \%}}$) and the decomposition temperatures ($T_d$) for the different BMI materials.

### Table II. Parameters of the Solvent Resistance Tests of the Fully Cross-linked BMI-689 Polymer

| Solvent   | Parameters                  |
|-----------|-----------------------------|
| THF, TCB, NMP | RT, 1.5 h                   |
| THF, TCB, NMP | 40 °C, 1 h                  |
| THF, TCB, NMP | RT, ultrasonic bath, 30 min |
| THF, TCB, NMP | 40 °C, ultrasonic bath, 30 min |

### Table III. Temperatures for 2% Weight Loss and Decomposition Temperatures as Determined by TGA for the BMI-Polymers Analyzed

| Polymer   | $T_{2\text{wt \%}}$ (°C) | $T_d$ (°C) |
|-----------|--------------------------|-----------|
| BMI-689   | 271                      | 422       |
| BMI-1500  | 346                      | 453       |
| BMI-1700  | 358                      | 450       |
| BMI-3000  | 431                      | 464       |
| BMI-5000  | 411                      | 450       |

Figure 10. TGA curves of BMI-polymers, cured by UV light (365 nm). [Color figure can be viewed at wileyonlinelibrary.com]

Figure 11 shows the DMA curve of UV-cured BMI-689 resin compared to the curves of UV cured BMI resin with additional thermal post-treatment and a mixture of UV cured BMI-689 and BMI-1500 resins with additional thermal post-treatment. Films with dimensions of 40 × 10 × 1 mm were cured in silicone molds by 30 passes per side through a DYMAX UVC conveyor. To ensure homogeneous crosslinking of the thick film, thermal post-curing was performed in an N₂ atmosphere at 200 °C for 1 h. The storage modulus of UV-cured BMI-689 of 340 MPa decreases continuously until a temperature of 100 °C, when the rubbery plateau is reached and the storage modulus stays at 60 MPa. Due to decomposition, the storage modulus starts to decrease again at 325 °C. The UV cured BMI-689 polymer, which was subjected to an additional thermal treatment, shows a slight increase in storage modulus compared to the polymer without additional treatment. This suggests that thermal post-curing improves the mechanical properties of the BMI material due to a reorganization of the polymer backbones above the glass-transition temperature. Heating above the glass-transition temperature can release stresses that were built up in the fast UV-curing process. The BMI-689/BMI-1500 co-polymer has a storage modulus of only 180 MPa at room temperature, which decreases until 40 MPa at the rubbery plateau. However, addition of the imide-extended BMI-1500 leads to higher thermal stability. The specimen containing BMI-1500 begins to deteriorate mechanically at higher temperature (350 °C) than the pure aliphatic BMI-689 polymer.

### CONCLUSIONS

The curing kinetics of commercial aliphatic (BMI-689) and imide-extended BMIs (BMI-1500, BMI-1700, BMI-3000, and BMI-5000) with various molecular weights and structures were evaluated using the FTIR, DSC, and Photo-DSC techniques. The properties of the cured BMI-based materials were assessed by TGA and DMA measurements. We have shown that cured BMI-based materials exhibit high temperature stability, chemical resistance, and good thermomechanical properties.

The BMI resins studied form highly crosslinked thermoset polymers upon either irradiation with UV or thermal curing at
temperatures of 200–250 °C. The average activation energies for thermal curing, obtained by the Kissinger, Ozawa and classical Arrhenius methods were 100 ± 15 kJ mol⁻¹ for BMI-689 and 111 ± 12 kJ mol⁻¹ for BMI-1500.

For thermal curing, kinetic rate constants in the range of minutes were obtained, while curing initiated by high-power mercury halide lamps or UV-LEDs showed a faster reaction with rate constants in the range of seconds. The curing speed depends on both molecular weight and chemical structure of the BMI precursor. Imide-extended BMIs with higher molecular weight cure faster than lower molecular-weight BMIs with a similar structure. Aliphatic BMIs exhibit polymerization rates between those of high molecular-weight and low molecular-weight imide-extended BMIs.

Due to its relatively low precursor viscosity and suitable photoreactivity, the aliphatic BMI-689 resin is the most promising candidate for a PolyJet™ ink formulation.

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