



UV-curing kinetics and performance development of *in situ* curable 3D printing materials

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ABSTRACT

As three-dimensional (3D) printing technology is emerging as an alternative way of manufacturing, the high resolution 3D printing device often requires systems such as drop jetting printing of *in situ* UV-curable photopolymers. Accordingly, the key issue is process control and its optimization to ensure dimensional accuracy, surface roughness, building orientation, and mechanical properties of printed structures, which are based on the time- and temperature-dependent glass transition temperature (T_g) of the resin system under UV-curing. In this study, the UV-cure kinetics and T_g development of a commercially available UV-curable acrylic resin system were investigated as a model system, using a differential scanning photocalorimeter (DPC). The developed kinetic model included the limited conversion of cure that could be achieved as a maximum at a specific isothermal curing temperature. Using the developed model, the T_g was successfully described by a modified DiBenedetto equation as a function of UV curing. The developed kinetic model and T_g development can be used to determine the 3D printing operating conditions for the overlay printing and *in situ* UV curing, which could ensure high-resolution and high-speed manufacturing with various UV-curing materials.

1. Introduction

Three-dimensional (3D) printing has attracted great attention, due to the direct fabrication of desirable shapes without molds, and it offers the potential for almost unlimited and unconstrained structures, which can hardly be achieved by the traditional subtractive manufacturing processes [1,2]. 3D printing technology is considered for use in a variety of applications, such as do-it-yourself 3D printing, aerospace and automotive industries, and bioengineering. It offers a great deal of design flexibility, but still requires a variety of techniques and materials in accordance with the applications. In particular, the UV/laser light curable photopolymers are commonly used materials for the stereolithography apparatus (SLA), digital light processing (DLP), and multi-jet printing systems,

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taking advantages of their rapid curing reactions and high resolution optical sources [3,4].

Multi-jet printing selectively deposits droplets of building materials [5], which can produce highly complex geometries with a shiny surface in a roughness of $\pm 16 \mu\text{m}$ [3]. Since multiple print heads can be used, the liquid form of the UV-curable photopolymers and a supporting material are co-deposited [6]. These multiple print heads can produce a variety of products at a single time, which consequently increases the production volume [3]. Due to its high resolution and favorable processability, this technique has been extensively investigated focusing on the printing parameters, such as dimensional accuracy, roughness, and building orientation and mechanical properties of printed structures [7–12]. However, while the thermal and UV-induced reaction kinetics and their modeling simulation are not widely available in the open literature, they are critical to determining the optimal process conditions, such as the printing speed and UV-curing conditions.

The printing speed is dependent on the T_g -development speed of the UV-curable photopolymers, because the T_g of the UV-curable photopolymers should be higher than the ambient temperature, to maintain the shape of a layer, and to facilitate the layer-upon-layer process. Therefore, the prediction of T_g depending on the UV-cure conversion is significant for the printing speed. In addition, the UV-curing conversion, which is affected by the UV-curing conditions, such as curing time, intensity of light source, and ambient temperatures, is closely related to the ultimate properties of cured polymers [13]. It is reported that UV post-cure treatment of the UV-curable photopolymers promotes an increase in the flexural modulus, which indicates that the UV-curable photopolymers cannot reach the fully-cured state in the existing process conditions [10]. Kinetic characterization of the UV-curable photopolymers is required to attain the UV-curing conversion, which is the critical factor for process optimization.

In the polymerization of UV-curable photopolymers, the temperature at which the cure reaction occurs may affect the cure kinetics and the final conversion of the cure reaction, as well as the ultimate properties of cured polymers [14]. In the curing of thermosetting resins including photopolymers, two different rate-determining stages take place: the reaction controlled, and the diffusion-controlled stages [15,16]. In the reaction-controlled stage, the reaction rate dominantly depends on the concentration of unreacted monomers. As the polymer chain grows longer, the reaction rate is dominantly affected by the diffusion rate of unreacted monomers and/or growing polymer chains. Usually, the ultimate properties of thermosetting polymers are mainly attained in the final stage of cure, where the diffusion-controlled reaction is dominant. The isothermal cure temperature in photopolymerization may very well affect the transition from chemically controlled reaction to diffusion-controlled reaction, and subsequently the ultimate properties of cured polymers. In this sense, it is important to identify the dependence of temperatures on the reaction rate, i.e., the kinetics of UV-curable photopolymers.

In this study, a commercial multi-jet printing material was chosen as a model system for the study of the diffusion-controlled cure kinetics and the development of glass transition temperature in isothermal conditions. A phenomenological model for the diffusion-controlled cure kinetics was developed. The effect of cure temperature on the cure kinetics was investigated using differential scanning photocalorimetry (DPC). The practical applicability of the proposed model was verified by comparison with the isothermal experiments. The dependence of the kinetic model parameters on the cure temperature was also investigated.

2. Experimental

2.1. Material

The material investigated in this study was a widely used commercial UV-curable 3D printing resin (VeroWhitePlus RGD 835, Stratasys Ltd.), which is an opaque white liquid. As reported in the material safety data sheet, the UV-curable 3D printing resin is composed of a mixture of methyl acrylate and isobornyl acrylate monomers at 30 and 25 wt%, respectively, and phenol, 4,4'-(1-methylethylidene) bis-, polymer with (chloromethyl)oxirane, 2-propenoate oligomer at 15 wt%. The remaining weight fraction is a mixture of diphenyl-2,4,6-trimethylbenzoyl phosphine oxide, titanium dioxide, acrylic acid ester, propylene glycol monomethyl ether acetate, and phosphoric acid at 2, 0.8, 0.3, 0.1, and 0.002 wt%, respectively. The photoinitiator, diphenyl-2,4,6-trimethylbenzoyl phosphine oxide, has a maximum UV absorbance at 295, 368, 380, 393 nm. Titanium dioxide was used as a color additive, and phosphoric acid was used as an inhibitor.

2.2. Differential scanning photocalorimetry

The differential scanning photocalorimetry (DPC) measurement was performed by differential scanning calorimeter (DSC) equipped with a photo-calorimeter accessory (TA Instruments DSC Q1000/DPC system). The light source was a 200 W high-pressure mercury lamp with an average UV light intensity of 66 mW/cm^2 over a wavelength range of 320–550 nm. Samples weighing $3 \pm 1.0 \text{ mg}$ were placed in uncovered aluminum pans, which had thickness about 0.1 mm. For isothermal photo cure experiments, the DSC cell was maintained at the isothermal temperature at $-10, 0, 25, 50, 60,$ and $70 \text{ }^\circ\text{C}$ in a N_2 environment (50 mL/min), before each measurement run started. The UV light of prescribed intensity was then irradiated to the sample. A maximum temperature of $70 \text{ }^\circ\text{C}$ was chosen, corresponding to the convergence of the heat of reaction as a function of curing temperature, which is described in Figs. S2 and S3. At each temperature, the cure reaction was monitored, until no exothermal signal was detected. The glass transition temperature (T_g) of the partially cured samples at different isothermal temperature was determined under a constant heating rate of $5 \text{ }^\circ\text{C/min}$ from -40 to $100 \text{ }^\circ\text{C}$. The measurements of Fourier transform infrared (FTIR) spectroscopy with an attenuated total reflection (ATR) method were carried out using FTIR spectroscope (Bruker Tensor 27 IR). Thermogravimetric analysis (TGA, TA instruments Q50) was conducted in a nitrogen atmosphere from ambient temperature to $550 \text{ }^\circ\text{C}$ with heating rate of $10 \text{ }^\circ\text{C/min}$.

3. Results and discussion

3.1. Isothermal kinetic analysis

The reaction rate of thermoset polymers can be defined as a function of two variables, temperature (T) and the extent of conversion (α), in a separable form:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where $f(\alpha)$ is a conversion-dependent function, and $k(T)$ is a rate constant as defined by the Arrhenius equation [17–19]:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (2)$$

where A is the intrinsic pre-exponential constant, E is the activation energy, and R is the gas constant. The area under the DSC curve corresponds to the total heat of reaction at the isothermal temperatures. When the material is cured at a low isothermal temperature, the material will vitrify at an early stage of the reaction, releasing a small amount of heat. The heat of curing increases with the curing temperature, which should be accounted for in modeling the cure kinetics and glass transition. In this isothermal curing, the degree of cure may be defined as the heat of generation normalized by the total heat of reaction up to a specific time, expressed as:

$$\alpha = H(t)/H_T \quad (3)$$

where $H(t)$ is the heat of reaction as a function of time, and H_T is the total heat of cure. The reaction may be regarded as being finished when the exothermic curve levels off to the baseline. The total heat of cure (H_T) used for the normalization of the isothermal heat of cure was 336.1 J/g, which was obtained from the total area of the DPC curve at a maximum temperature of 70 °C, which corresponds to the convergence of the heat of reaction.

3.2. Phenomenological model

The photoinitiated free radical polymerization of the resin system is based on a typical polymerization mechanism of acrylates. After UV irradiation, Diphenyl-2,4,6-trimethylbenzoyl phosphine oxide photoinitiator is decomposed into two free radicals, which are free to react with monomers and oligomer by opening their carbon-carbon bond. The polymer chain propagates via reaction with available vinyl bonds that are on monomers, or on other polymer chains. The kinetics model of photoinitiated free radical polymerization is usually formulated based on four elementary reaction steps [20], which can be summarized as:



where I is the photoinitiator that produces primary radicals (R^*); M is the monomer; and RM^* is the chain radical. Eq. (4) indicates the initiation step which is temperature-independent since the energy for photoinitiator decomposition is supplied by the UV light. Eqs. (5) and (6) indicate that the reaction products are also involved in the propagation reaction, which often exhibits an auto-catalytic reaction mechanism, and is thus characterized by an accelerating isothermal conversion rate that typically reaches its

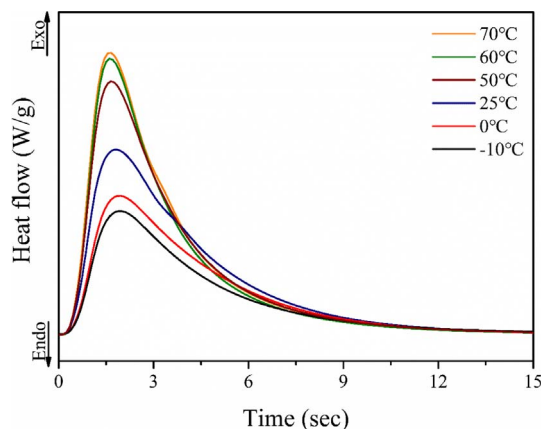


Fig. 1. Isothermal condition DPC thermogram of the RGD 835 system measured at five different isothermal temperatures, using an average light intensity of 66 mW/cm².

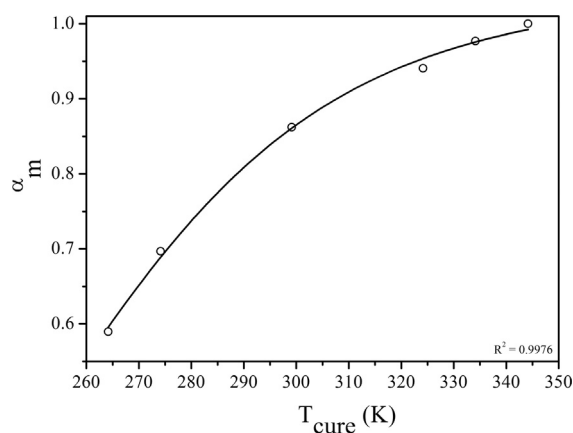


Fig. 2. Maximum degree of cure of the RGD 835 system plotted as a function of the isothermal cure temperature (open circles indicate experimental data, while the line represents the values calculated using Eq. (9)).

maximum after the initial stage of conversion.

Fig. 1 shows the isothermal DPC thermograms expressed as the rate of heat generation as a function of time at different temperatures. The figure shows that the rate of heat generation exhibits a maximum, giving a rapid increment at the beginning of the reaction, and then decreases with time, until it reaches a baseline. The cure reaction can be described by a simple phenomenological autocatalytic equation, which is expressed as:

$$\frac{d\alpha}{dt} = k\alpha^m(1-\alpha)^n \quad (8)$$

where m is the order of the initiation reaction, and n is the order of the propagation reaction. The curing reaction of the UV-curable resin seems to be completed within about 15 s, irrespective of the temperature. Fig. 1 also indicates that a higher cure temperature results in a faster curing reaction rate, and an increase in the peak heat flow.

The maximum degree of cure can be evaluated by integrating the exotherm peaks with respect to time (Fig. 1). Fig. 2 shows that as the isothermal cure temperature increases, the maximum degree of cure increases, and approaches 1.0. Table 1 shows the total heat of reaction and the maximum conversion of cure obtained at various isothermal temperatures. As previously mentioned, isothermal curing of thermoset systems may go through two curing stages that are affected by the chemical activity of reacting groups, and the physical mobility of polymer chains. In the early stage of the isothermal cure, the curing reaction proceeds in a liquid state, when the glass transition temperature (T_g) of the B-staged system is usually lower than the curing temperature (T_{cure}). In this stage, the apparent reaction rate is determined by the reactivity of unreacted monomers, until T_g approaches T_{cure} . When $T_g \approx T_{cure}$, the second stage of curing may be considered to begin, in which the material is in a vitrified state. In this temperature region, the reaction rates decrease considerably, due to the fact that the mobility of the reacting groups becomes very restricted [15,17,21]. The reaction time to reach $T_g \approx T_{cure}$ is often called the vitrification of the thermoset system [15,18]. In 3D printing, the time for the UV-curable polymer to reach the vitrification state is important, because it gives the allowable time for overlay printing. When the system reaches the glass-state by vitrification, the overall reaction rate is considered to be controlled by the diffusion rate of unreacted groups in polymer chains. The slow segmental motions caused by the structural relaxation of polymer chains are the only ones permitted in glass-state polymers, and the degree of cure often tends to exhibit a practically constant limiting value, thus preventing the full conversion of cure reaction [22–24].

Fig. 2 makes it evident that the curing reactions are restricted by the mobility of polymer chains in isothermal conditions. There have been several modifications of kinetic models in order to express the diffusion limitation of reacting polymer chains. For example, a phenomenological kinetic model has been derived that incorporates the diffusion-rate control into the reaction-kinetic expression, by using the maximum degree of conversion (α_m) achieved by isothermal curing [18]. However, it should be mentioned that a linear relationship was assumed in this approach between α_m and T_{cure} , which subsequently led to an infinite value of α_m with increasing

Table 1

Heat of reaction, peak maximum, and maximum conversion of cure obtained in isothermal cure conditions.

| Cure temperature (C) | $H(t)$ (J/g) | Peak maximum (s) | Conversion ^a (%) |
|----------------------|--------------|------------------|-----------------------------|
| –10 | 195.7 | 2.00 | 58.9 |
| 0 | 227.6 | 1.95 | 69.7 |
| 25 | 287.3 | 1.85 | 86.2 |
| 50 | 315.9 | 1.65 | 94.0 |
| 60 | 328.4 | 1.65 | 97.7 |
| 70 | 336.1 | 1.65 | 100 |

^a The base is taken to be H_T at 70 °C.

temperature.

Fig. 2 shows that with increasing curing temperature, the maximum conversion seems to approach 1.0, which corresponds to the fully cured state of the model system in dynamic heating conditions. Therefore, the maximum degree of cure can be expressed quantitatively as shown in Fig. 2, by using an empirical equation in the form of Hill functions:

$$\alpha_m(T) = a \frac{\alpha^c}{b^c + \alpha^c} \quad (9)$$

The values of fitting parameters a , b , and c obtained by a curve fitting method are 1, 256.8, and 12.69, respectively. Eq. (9) shows that the conversion approaches 1.0 with curing temperature, which desirably results in a limiting value of glass temperature ($T_{g\infty}$). Incorporating the maximum degree of cure represented by Eq. (9) into Eq. (8), the model equation may be expressed as:

$$\frac{d\alpha}{dt} = k \left(\frac{\alpha}{\alpha_m(T)} \right)^m \left(1 - \frac{\alpha}{\alpha_m(T)} \right)^n \quad (10)$$

It is likely that the term $\alpha/\alpha_m(T)$ expresses a normalized conversion that can be achieved in each isothermal cure temperature. Eq. (10) expresses the characteristic features of isothermal curing behavior, where as the reaction rate approaches zero, the degree of cure approaches α_m .

It is considered that UV light intensity is one of the key factors for the UV cure kinetics because the rate of photoinitiator decomposition depends strongly on the UV light intensity [25,26]. However, the rate of photoinitiator decomposition is almost independent of the reaction temperature since the energy for photoinitiator decomposition is supplied by the UV light [27,28]. In this investigation, we set a constant UV light intensity to focus on the dependence of the reaction temperatures on cure kinetics and T_g development. Due to this fact, the developed phenomenological model may be limited to be scaled to some level of UV energy that is different from 66 mW/cm², since the parameters are not related to the UV intensity but the temperature.

If the reaction order is correctly determined, according to Eq. (10), the reaction rate ($d\alpha/dt$) should give a linear relation, with the conversion dependent function providing the reaction rate constants from the slope of the relation [29,30]. Subsequently, the activation energy (E) and pre-exponential factor (A) were determined by plotting the reaction constant as a function of inverse temperature according to the Arrhenius expression. Fig. 3 shows E and A determined from the isothermal curing experiments as 8.14 ± 0.06 and 19.87 ± 0.14 , respectively. The considerably low value of E indicates that the activation energy of photoinitiator decomposition is not included in the overall activation energy for the cure reaction, which is usually found in photochemical polymerization [27]. The low E also indicates that the photoinitiator used in this investigation is not thermally decomposed in the range of temperature up to 70 °C. At higher temperature, the photoinitiator may undergo the thermal decomposition as well as the photochemical decomposition. In such case, both thermal and photochemical initiation must be considered. Taking the activation energy determined in Fig. 3 as a representative value of the model system, all the kinetic parameters of the model equation can be determined, and Table 2 shows the obtained values.

Fig. 4 shows the cure rate as a function of conversion for several isothermal cure temperatures. As the isothermal cure temperature decreases, the maximum cure rate appears at lower conversions, which may be caused from the transition of chemically-controlled reaction to diffusion-controlled reaction occurring at lower temperatures and/or the initiation efficiency, which drops more rapidly as the temperature is decreased. As the temperature increases, the degree of cure increases, due to a delay in vitrification of the resin.

As can be seen, the modified kinetic model is in good agreement with the experimental data in terms of the progress of curing reactions and the conversion equilibrium, which seemingly results from the diffusion-controlled rate of cure reaction. This demonstrates the validity of the modeling methodology, which is capable of describing such phenomenological results of cure reactions as thermally limited to a partial degree of cure in isothermal conditions.

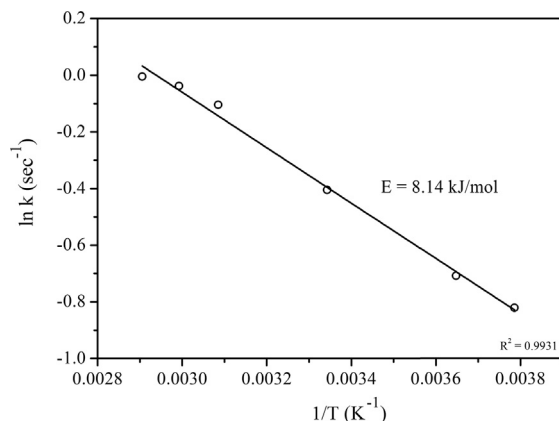


Fig. 3. Activation energy of the RGD 835 system obtained from isothermal cure experiments.

Table 2
Estimated parameters of the modified kinetic model using isothermal DPC data.

| Cure temperature (°C) | Kinetic parameters | | | | |
|-----------------------|---------------------------------------|-----------------------|---------------------|-----------------|-----------------|
| | $k (\times 10^{-2} \text{ min}^{-1})$ | $A (\text{min}^{-1})$ | $E (\text{kJ/mol})$ | m | n |
| -10 | 4.40 ± 0.06 | 19.87 ± 0.14 | 8.14 ± 0.06 | 0.52 ± 0.02 | 1.65 ± 0.05 |
| 0 | 4.92 ± 0.13 | | | | |
| 25 | 6.67 ± 0.08 | | | | |
| 50 | 0.90 ± 0.06 | | | | |
| 60 | 0.96 ± 0.12 | | | | |
| 70 | 10.0 ± 0.06 | | | | |

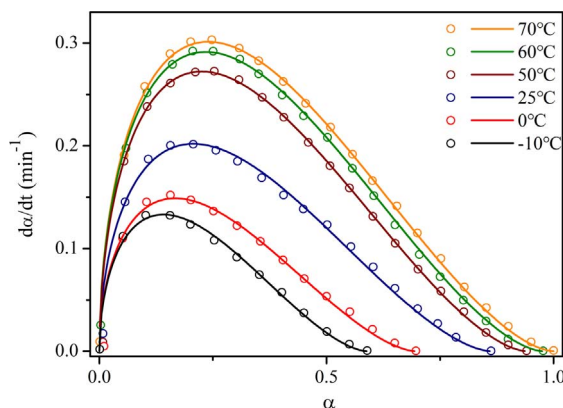


Fig. 4. The conversion rate of the RGD 835 systems plotted as a function of the degree of cure for each isothermal cure temperature, comparing experimental data with the modified autocatalytic model (open circles indicate experimental data, while the lines represent the values calculated using Eq. (10)).

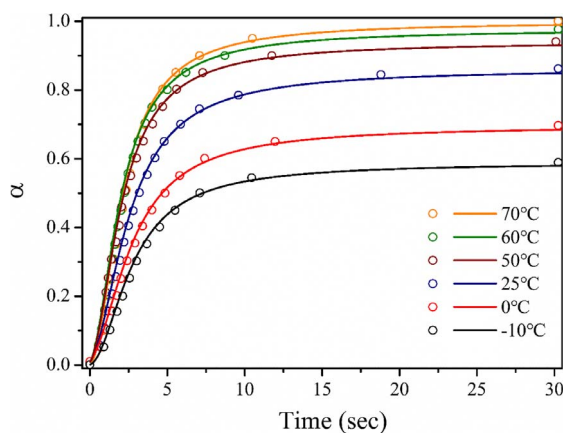


Fig. 5. The conversion of RGD 835 systems plotted as a function of time for each isothermal cure temperature, comparing experimental data with the modified autocatalytic model (open circles indicate experimental data, while the lines represent the values calculated using Eq. (10)).

3.3. Glass transition temperature development

The physical and chemical properties of thermosetting polymers usually depend on the degree of cure, which subsequently shows a strong dependence upon the glass transition temperature of the curing polymer. As the degree of cure increases, the glass transition temperature also increases, due to chain growth and molecular weight increment. DiBenedetto has derived a T_g conversion relation through an entropic consideration of idealized simple systems that consist of a mixture of fully cured network and monomer [18,31–33]. The simplified form of the DiBenedetto equation, including the adjustable parameter (λ), is:

$$T_g = T_{g0} + \frac{(T_{g\infty} - T_{g0})\lambda\alpha}{1 - (1 - \lambda)\alpha} \quad (11)$$

where T_{g0} is the T_g of the “uncured” monomer, $T_{g\infty}$ is the highest T_g of the “fully cured” material, and λ is a structure-dependent parameter. This relationship compares well with the glass transition temperature of our model as a function of conversion in Fig. 6.

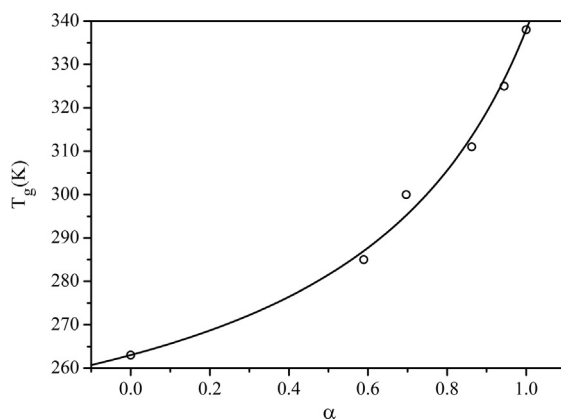


Fig. 6. Glass transition temperature as a function of the degree of cure compared with the DiBenedetto equation ($\lambda = 0.23$).

The maximum glass transition temperature ($T_{g\infty}$) of our model resin system is 64.9 °C, the T_g of the uncured resin (T_{g0}) is -10 °C, and λ is determined as 0.23.

In 3D printing, T_g is a significant property that should be considered in the stage of planning the printing, because the printing speed and UV-curing condition should be determined by the speed of T_g development. For example, when the printing is carried out at 298 K, the conversion (α) for $T_g = 298$ K is 0.75. The time for $\alpha = 0.75$ at 298 K is already described by Eq. (10), Table 2, and Fig. 5, which gives $t_{\alpha=0.81} = 6.7$ s at 298 K. This time indicates the allowable time for overlay printing, which should be considered for setting the printing time. When the ambient temperature is increased to 323 K, $\alpha = 0.92$ and $t_{\alpha=0.92} = 18.7$ s, which takes a longer time for overlay printing, but the higher conversion ($\alpha = 0.92$) may increase the mechanical properties of the cured polymers. The overlay printing time as a function of T_g was shown in Fig. S1. A trade-off between the printing speed and the UV-curing conversion, which is closely related to the ultimate properties, should be considered to determine the optimal process conditions.

4. Conclusions

Isothermal DPC experiments were conducted to investigate the cure kinetics and glass transition development of a commercially available 3D printing material, RGD 835. A kinetic model was developed to describe the limited conversion of cure as a function of isothermal curing temperatures, seemingly caused by the rate-determining diffusion of growing polymer chains. By incorporating the obtained maximum degree of cure into the developed kinetic model, the modified model accurately described the isothermal behavior of the model resin system. The T_g was described by a modified DiBenedetto equation as a function of conversion, which is used to determine the time for overlay printing. The developed kinetic model and T_g development can be used to determine the 3D printing operating conditions for the overlay printing and *in situ* UV curing, which could ensure high-resolution and high-speed manufacturing with various UV-curing materials.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.eurpolymj.2017.05.041>.

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