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B. Möginger, L. Kehret, B. Hausnerova, and J. Steinhaus

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B. Möginger[a], L. Kehret[a, b], B. Hausnerova[b] and J. Steinhaus[a]

[a]*Hochschule Bonn-Rhein-Sieg, von Liebig Str. 20, 53359 Rheinbach, Germany,*
bernhard.moeginger@h-brs.de

[b]*Tomas Bata University in Zlín, Faculty of Technology, Department of Production Engineering,*
Vavrečkova 275, 762 72 Zlín, Czech Republic
hausnerova@ft.utb.cz

Abstract. 3D-Printing is an efficient method in the field of additive manufacturing. In order to optimize the properties of manufactured parts it is essential to adapt the curing behavior of the resin systems with respect to the requirements. Thus, effects of resin composition, e.g. due to different additives such as thickener and curing agents, on the curing behavior have to be known. As the resin transfers from a liquid to a solid glass the time dependent ion viscosity was measured using DEA with flat IDEX sensors. This allows for a sensitive measurement of resin changes as the ion viscosity changes two to four decades. The investigated resin systems are based on the monomers styrene and HEMA. To account for the effects of copolymerization in the calculation of the reaction kinetics it was assumed that the reaction can be considered as a homo-polymerization having a reaction order n≠1. Then the measured ion viscosity curves are fitted with the solution of the reactions kinetics – the time dependent degree of conversion (DC-function) – for times exceeding the initiation phase representing the primary curing. The measured ion viscosity curves can nicely be fitted with the DC-function and the determined fit parameters distinguish distinctly between the investigated resin compositions.

Keywords: resin for 3D-printing, curing behavior, reaction kinetics, ion viscosity, dielectric analysis
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INTRODUCTION

In the Voxeljet 3D-Printing process a curable binder resin is printed on a flat powder bed consisting of spherical PMMA particles. After a certain initiation time the curing process starts as the binder has to mobilize and activate initiator molecules within the PMMA particles [1,2]. The curing behavior can be monitored by Dielectric Analysis (DEA) easily in terms of the ion viscosity which changes a factor 3 to 4 during the curing process [3], **FIGURE 1**. After an initiation phase lasting typically 20 to 30 minutes the polymerization starts and increases the ion viscosity within 15 to 20 minutes to its final value.
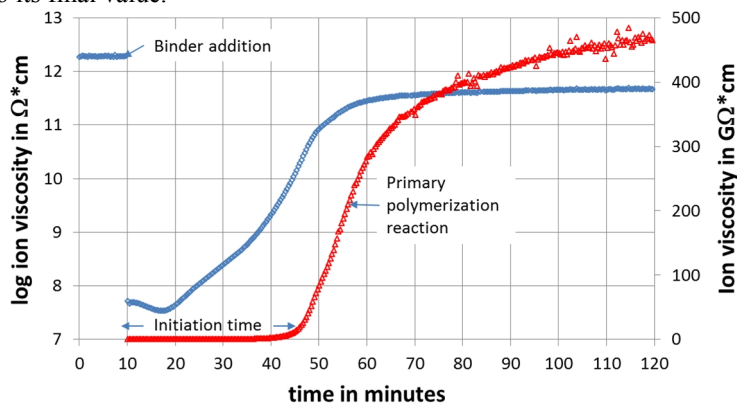

FIGURE 1. Change of ion viscosity curves of binder VXP-1 at 10 Hz

It is obvious that the time dependent ion viscosity contains information of the reaction kinetics of the curing process. The goal of this paper is to link the reactions kinetics in terms of time dependent degree of conversion to the measured ion viscosity curves of binder resins with modified compositions.

EXPERIMENTAL

In order to determine the curing behavior and reaction kinetics using DEA, the binder system VXP-1 was modified with respect to its composition, **TABLE 1**.

TABLE 1: Investigated modifications of binder VXP-1

Binder type	Styrene HEMA content	Comments
VXP-0	99,5%	Commercial binder without thickener
VXP-1	98%	Commercial binder with thickener
VXP-2	96%	Higher content of thickener
VXP-7	94,3%	Addition of 5% curing agent 1
VXP-9	90,5%	Addition of 9% curing agent 1
VXP-11	94,5%	Addition of 5% curing agent 2

The ion viscosity was measured using a NETZSCH DEA 230/1 Epsilon with IDEX sensors having a sensor area of (26 x 13) mm² and an electrode distance of 115 µm. The PMMA powder (0.66 g) was poured on the sensor which is framed by a PE mould, **FIGURE 2**. The binder (0.33 g) was dropped on the powder after 10 minutes. Total measuring time was 120 minutes at 26°C with a frequency of 10 Hz and a sampling rate of 3 points per minute [4].
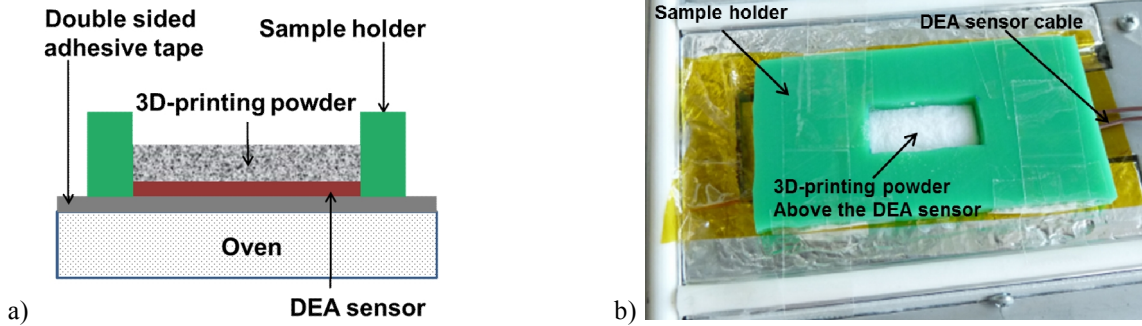

FIGURE 2. Experimental setup to measure ion viscosity – a) scheme, b) foto

CONSIDERATION OF THE REACTION KINETICS

As two monomers are polymerized the polymerization reaction represents two homo-polymerization and two copolymerization reactions with each having its own reaction constant. For modeling the reaction kinetics in terms of degree of conversion i) pseudo-homo-polymerization having a reaction order $n \neq 1$ and ii) radical concentration c_0^{rad} is in equilibrium are assumed leading to the time dependent change of monomer concentration c_M

$$\frac{dc_M(t)}{dt} = -k * c_0^{rad} * c_M^n(t) \tag{1}$$

with the mean reaction constant k. Solving of eq. (1) and transferring to the degree of conversion DC(t) yields

$$DC(t) = 1 - \frac{c_M(t)}{c_M(0)} = 1 - \left(1 - \frac{(1-n)}{c_M(0)^{1-n}} * \frac{t}{\tau_{reac}}\right)^{\frac{1}{1-n}} = 1 - \sqrt[(1-n)]{1 - \frac{(1-n)}{c_M(0)^{1-n}} * \frac{t}{\tau_{reac}}} \tag{2}$$

with the reaction time constant $\tau_{reac} = 1/(k*c_0^{rad})$. The short time approximation of eq. (2) yields

$$DC(t \to 0) = 1 - \left(1 - \frac{1}{(1-n)} * \frac{(1-n)}{c_M(0)^{1-n}} * \frac{t}{\tau_{reac}}\right) = \underbrace{\frac{1}{c_M(0)^{1-n} * \tau_{reac}}}_{inital\ slope\ of\ DC(t)} * t \tag{3}$$

In the fit procedure the start value of $1/(c_M(0)* \tau_{reac}) = S_0$ given by the slope of the DC(t)-curve in the initial linear range. The slope S_0 represents the minimum value as it is superimposed by time dependent initiation processes, **FIGURE 1**. Assuming that ion viscosity $\eta^{ion}(t)$ and degree of conversion DC(t) have the same time dependency and that the curing reaction starts after a certain initiation time t_{init} one ends up with

$$\eta^{ion}(t - t_{init}) = \eta_0^{ion} + \left(\eta_\infty^{ion} - \eta_0^{ion}\right) * \sqrt[(1-n)]{1 - (1-n) * S * (t - t_{init})} \tag{4}$$

leaving the parameters n, S and t_{init} to be determined in a fit procedure. As $\eta_0^{ion} << \eta_\infty^{ion}$, eq. (4) can be rearranged.

$$\eta_{rel}^{ion}(t - t_{init}) = \frac{\eta^{ion}(t - t_{init}) - \eta_0^{ion}}{\eta_\infty^{ion} - \eta_0^{ion}} \cong \frac{\eta^{ion}(t - t_{init})}{\eta_\infty^{ion}} = \sqrt[(1-n)]{1 - (1-n) * S * (t - t_{init})} \tag{5}$$

Eq. (5) fits only for times exceeding the initiation time. Therefore, the fit procedure consists of the steps:
1. Determination of $\eta_\infty^{ion} \cong \eta^{ion}(120 \text{ min})$ and normalization of the $\eta^{ion}(t)$-curve to η_∞^{ion}
2. Determination of the starting values for initial slope S_0 and initiation time t_{init}
   in the linear range of the $\eta_{rel}^{ion}(t)$ -curve
3. Determination of the parameters n, S and t_{init} t by fitting the $\eta_{rel}^{ion}(t)$ -curve to 0.9.

RESULTS AND DISCUSSION

The relative ion viscosities of the different binder resins depend significantly on their compositions by affecting initiation time and reaction rate which corresponds to the initial slope of ion viscosity curves, **FIGURE 3a**. Interestingly, the curing behavior of the modifications VXP-2 to VXP-11 lies between that of VXP-1 and VXP-0 which is identical to VXP-1 without thickener. Surprisingly, a higher thickener content as in VXP-2 does not increase initiation time and reduce reaction rate although the VXP-2 binder resin has the highest initial ion viscosity. If the content of curing agents is increased reaction rates are increased and initiation times are decreased – as expected – compared to the VXP-1 binder resin. However, doubling the content of curing agent in VXP-9 compared to VXP-7 does hardly affect the reaction rate but leads surprisingly to somewhat larger initiation times. The type of curing agent – VXP-7 versus VXP-11 – affects both initiation time and reaction rate in spite of the same mass amount. These results show that the curing behavior of such binder resins is very complex as the interaction of the different additives is not yet fully understood. Furthermore, while the initial ion viscosities η_0^{ion} differ by 20 to 30% due to composition, the final ion viscosities η_∞^{ion} differ a factor 10 to 15. This means that the curing process forms different network structures of the cured binder resins with respect to e.g. crosslink density and trapped monomers.
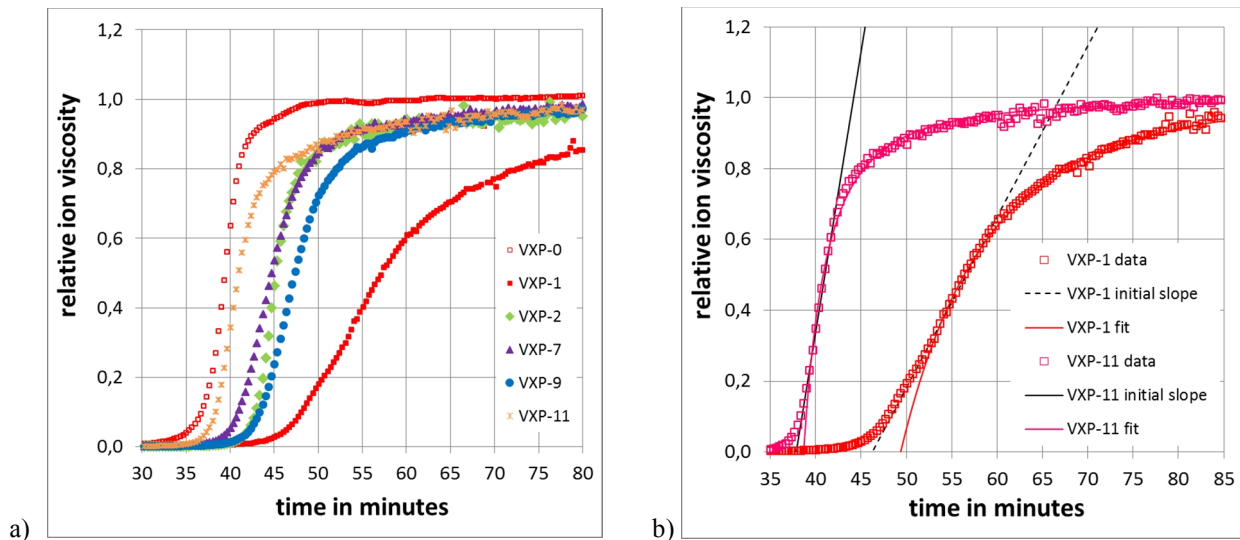

FIGURE 3. Relative ion viscosities of a) 6 binder resins during curing and
b) comparison of measured and fitted ion viscosities of VXP-1 and VXP-11 binder resins

The measured ion viscosities were fitted well by eq. (5) in the range of primary curing, **FIGURE 3b**. The kinetics parameters "reaction order n, initial slope S and initiation time t_{init}" are tabulated in **TABLE 2**. It can be seen that the initial slopes S change a factor 6 and the initiation times can be extended from 28 minutes to 40 minutes due to the composition of the binder resins. The determined reaction orders depend on the composition of the binder resins as the additives may affect the curing behavior in a complex way. The determined reaction orders n of VXP-7 and VXP-9 are very similar which may mean that the reaction order does hardly depend on variation of the amount of curing agent in the range of 5 to 10%. The initial slopes S determined by eq. (5) are typically a factor 2 to 3 larger than the initial slopes S_0 determined by fitting the linear range of the ion viscosity curves. This is attributed that in the determination of eq. (5) the time dependent initiation processes are neglected. If one fits the linear range the initiation processes for sure affect the determined slopes S_0.

TABLE 2. Effect of composition of binder resins on initial ion viscosity η_0^{ion}, final ion viscosities η_∞^{ion} and kinetics parameters "reaction order n, initial slope S and initiation time t_{init}"

Binder resin	η_0^{ion}	η_∞^{ion}	n	S	S_0	t_{init}
	$M\Omega$*cm	$G\Omega$*cm	-	1/min	1/min	min
VXP-0	31	38	1,143	0,476	0,212	27,8
VXP-1	34	433	1,234	0,107	0,048	39,4
VXP-2	38	514	1,577	0,631	0,200	33,7
VXP-7	34	383	1,194	0,287	0,118	32,0
VXP-9	34	515	1,204	0,249	0,108	34,2
VXP-11	33	462	1,573	0,398	0,158	28,7

CONCLUSION

DEA in terms of ion viscosity allows for an easy investigation of the curing behavior of binder resins for 3D-Printing. As all ion viscosity curves $\eta^{ion}(t)$ show an initiation phase and a linear increase basic kinetics information can be directly drawn out. A deeper insight in reaction kinetics of such binder systems is provided if the ion viscosity curves are linked to the time dependent degree of conversion DC(t) allowing for the determination of the kinetics parameters "reaction order n, initial slope S and initiation time t_{init}". The proposed reaction kinetics equation [eq. (5)] works well for the primary curing but ignores completely the initiation processes. As all investigated binder resins are based on a at least 90% styrene-HEMA-mixture the different final ion viscosities indicate that the cured final binder network differ in structure.

ACKNOWLEDGMENTS

REFERENCES

1. Voxeljet Technologies GmbH, patent DE 10 2006 038 858 (21 February 2008)
2. F. Chen, R. Lorenz, J Shen, patent DE 10 2007 026 006 (17 April 2008
3. J. Steinhaus et al, "Characterization of the Auto-Curing Behavior of Rapid Prototyping Materials for Three- Dimensional Printing Using Dielectric Analysis, Polymer Eng. Sci 2015. DOI 10.1002/pen
4. M. Harrach, Online-Messung der Reaktionskinetik von Reaktivsystemen im 3D-Druckverfahren, bachelor thesis, Hochschule Bonn-Rhein-Sieg, 2009