DETECTION AND MODELLING OF THERMAL AND RHEOLOGICAL TRANSITIONS OF A 2-STEP-CURING THERMOSET USING DIELECTRIC AND STANDARD MEASURING TECHNIQUES

Alexander Chaloupka[1], Renato Bezerra[1], Vinay Madaksira[1], Iman Taha[1,2] and Natalie M. Rudolph[1,3]

[1] Fraunhofer ICT branch Functional Lightweight Design
Am Technologiezentrum 2, 86159 Augsburg, Germany
Email: alexander.chaloupka@ict.fraunhofer.de
web page: http://www.ict.fraunhofer.de/de/komp/fil.html

[2] Ain Shams University
Khalifa El-Maamon St, 11566 Cairo, Egypt
Email: iman_taha@eng.asu.edu.eg, web page: http://www.asu.edu.eg

[3] Mechanical Engineering, University of Wisconsin Madison
1513 University Avenue, Madison WI 53706, USA
Email: natalie.rudolph@wisc.edu, web page: http://www.engr.wisc.edu

Keywords: Composites, Kinetic modelling, Dielectric, Pultrusion, 2-step curing

ABSTRACT

Process monitoring is gaining increased attention in the field of fiber reinforced plastic manufacturing. One of the vital aspects hereby is the control of the curing degree of the components, in order to ensure the quality of the composite. In this work dielectric analysis (DEA) as an online-capable monitoring system is investigated in comparison to standard thermo-physical and rheological measurement techniques. Therefore, a pultrusion-grade two-step curing hybrid thermoset matrix was analyzed using DEA as well as rheometry and differential scanning calorimetry (DSC). The measurements were performed under dynamic temperature profiles (constant heating rates of 0.5, 1 and 5 K/min) in the range of -20 to 185 °C. A good qualitative correlation was found for both reaction steps between the shear viscosity measured by oscillated parallel plate and electric-based ion viscosity detected by DEA. The observed reaction steps were confirmed with DSC measurements. By fitting measured data of different heating rates, kinetic models for DEA, DSC and rheology were developed, allowing the prediction of the curing degree under varying process conditions. The models were finally validated through various temperature profiles, proving good agreement between measured and predicted data.

1 INTRODUCTION

Carbon fiber reinforced plastics (CFRPs) can be manufactured by a number of different processes, depending on permissible cycle times, component design and application. In this respect, the pultrusion process (as illustrated in Figure 1) is one of the most well established technologies for the production of continuous fiber reinforced profiles, due to its high potential for automation and cost saving.

In a common pultrusion process unidirectional fiber, braided or woven strands are impregnated with resin and pulled through a heated stationary die, where the resin undergoes polymerization. The die cavity can have different geometries, varying from simple flat to cylindrical T- or H-profiles. [1] A modification of the pultrusion process, however, targets the use of this principle as a pre-forming stage only. In this case the impregnated but still uncured material is further transferred to a subsequent forming station (for example blow molding), as illustrated in Figure 1. For this purpose a two-step curing system is of great benefit, where a rubber-like B-stage is reached at the end of the pultrusion die. At this condition, the resin is able to stabilize the geometry, but still allows further post-forming to a more complex shape. During this second forming step the resin system is again triggered by heat leading to complete cross-linking and thus curing.

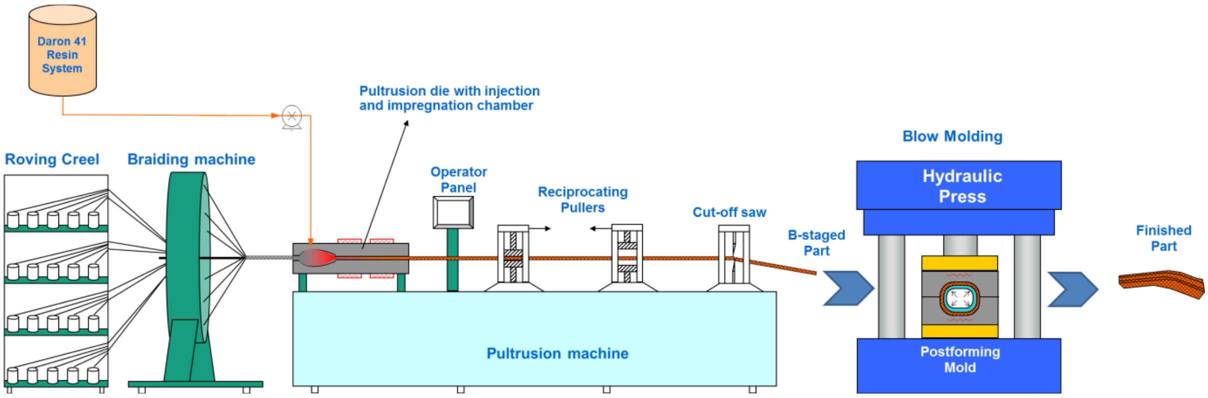

Figure 1: Pultrusion process chain.

The reaction steps take place in the pultrusion die (B-staging urethane) and in the blow molding tool (radical polymerization). In order to find the optimal processing parameters for the production of high quality components, shear viscosity (a crucial parameter influencing fiber wetting), as well as temperature and time dependent curing behavior have to be known. Such information is commonly obtained using the thermo-physical differential scanning calorimetry (DSC) technique and rheology.

Recently, the dielectric measurement principle has been explored for cure characterization. This technique offers a great potential not only for laboratory research but also as an online monitoring system [2-4]. Maazouz et al. [5] have reported the appropriateness of the dielectric measurement technique for the detection of the chemorheological behaviour of polyurethane and unsaturated polyester. Good agreement with rheological and DSC measurements was observed. [5]

The dielectric measurement principle is based on the penetration of a material using a specific voltage U and the detection of the response signals in terms of the current I and the corresponding phase shift ϕ. Assuming an electrical equivalent circuit with a resistor R_p and a capacitor C_p in parallel (describing the investigated sample) the ion viscosity ρ is given according to ASTM D150 by

$$\rho = \frac{R_p\,A}{d}\,, \tag{1}$$

where

$$R_p = \frac{U}{I\,cos\varphi}\,. \tag{2}$$

A/d is a geometrical ratio for the one-sided sensor determined using ASTM D150 analogue to a parallel plate capacitor.

For rheological measurements the dynamic shear modulus (storage modulus G' and loss modulus G'') is obtained to calculate the complex viscosity η^* [6]:

$$\eta' = G'' / \omega\,, \tag{3}$$

$$\eta'' = G' / \omega\,, \tag{4}$$

$$\eta^* = \eta' + i\,\eta''\,, \tag{5}$$

$$|\eta^*| = \sqrt{\eta'^2 + \eta''^2}\,. \qquad (5)$$

ω is the applied angular frequency in rad/s. According to the Cox-Merz rule, the complex viscosity agrees relatively well with the apparent viscosity of viscoelastic materials for low shear rates [7].

2 EXPERIMENTAL

Material. For the purpose of this study the Daron ZW 015864 (DSM Composite Resins, Zwolle, NL) two-step-curing resin is used. The resin consists of six different components including the resin itself (which is in turn diluted in styrene) premixed with an inhibitor for the second reaction step, a catalyst, internal mould release, a di-isocyanate (MDI) and organic peroxide as initiator of the second reaction step. The first reaction between isocyanate and hydroxyl functional groups, which are still present in the resin backbone, results in the formation of polymer chains by urethane linkage at elevated temperatures. This is the step from a liquid resin system to a reacted-stage matrix. The second step, the irrevocable cross-linking, is initiated by subjecting the material to even higher temperatures. Here, cross-linking of these polymer chains and styrene takes place based on a radical polymerization initiated by the organic peroxide.

Dielectric Analysis. Dielectric measurements were conducted using a DEA288 from Netzsch-Gerätebau GmbH (Figure 2 - a). For electric field application and response detection a tool-mountable re-usable sensor with a radial arrangement and a line spacing of 500 µm was used (Figure 2 - b).

(a) (b)

Figure 2: (a) Netzsch DEA288 and (b) tool-mountable sensor.

This sensor type is advantageous due to its one-sided measurement allowing easy integration into manufacturing tools (here: into the blow mold tool following the pultrusion process). For the material analysis purpose of this study the sensor (embedded in a metallic holder) was placed into a small laboratory furnace from Netzsch-Gerätebau GmbH. The uncured resin system was applied onto the surface of the tool-mountable sensor with a layer thickness of about 1 mm.

To investigate the curing behaviour a heating run was carried out at rates of 0.5, 1 and 5 K/min in the range of -20 °C – 185 °C under nitrogen atmosphere. Dynamic cooling was then performed at a rate of 5 K/min, and the obtained data was further analysed to make sure that no subsequent reactions take place. The applied frequencies were varied between 1 Hz and 1 MHz with four frequencies in each decade. For analysis and kinetic modelling the 20 Hz signal of the ion viscosity ρ is used.

Differential Scanning Calorimetry. Calorimetric measurements were performed with a Netzsch DSC204 F1 Phoenix following the same heating and cooling procedures used for the dielectric studies under inert nitrogen atmosphere. The samples (mass between 16 – 18 mg of formulated resin) were placed into aluminium pans with pierced lids (75 µm hole).

Rheology. Oscillating rheology measurements were conducted using an MCR301 rheometer from Anton Paar GmbH, equipped with a parallel plate setup. The temperature was varied between 20 °C – 180 °C at rates of 0.5, 1 and 5 K/min while the system was under a controlled normal force of zero N and the gap was constantly adjusted during the measurement. The oscillation frequency was set to 1 Hz and the strain to 0.2 % (corresponding to a deflection angle of 0.16 mrad).

Kinetic modelling. Kinetic models were developed using Netzsch Kinetics. Based on the different constituents of the resin system, a three-step reaction path was chosen as indicated in Equation 3.

$$A \overset{1}{\rightarrow} B \overset{2}{\rightarrow} C \overset{3}{\rightarrow} D\ , \tag{3}$$

Path 1 describes an autocatalytic reaction of initial chain formation followed by paths 2 and 3, involving subsequent autocatalytic and n-th step reactions of irrevocable network formation, respectively. The kinetic model describes the temperature dependent reaction rate as per Equation 4.

$$\frac{d\alpha}{dt} = W(T) \cdot f(\alpha)\ . \tag{4}$$

W(T) is conversion rate and $f(\alpha)$ is the mathematical description of the reaction mechanism. For this model the conversion rate is supposed to underlie an Arrhenius behavior. Thus, it can be described as

$$W(T) = A \exp\left(\frac{-E_A}{R \cdot T}\right)\ . \tag{5}$$

E_A is the activation energy of the reaction, R is the universal gas constant, T the temperature and A describes the collisions per minute between molecules and thus functions as a fitting parameter in terms of the probability of reaction initiation. Although it is known that this collision factor is temperature dependent, the influence on the kinetic model is much lower in contrast to the exponential temperature effect in the Arrhenius equation. The used mathematical models for the reaction mechanisms are given by Equations 6 and 7.

n-th order: $$(1-\alpha)^n\ , \tag{6}$$

n-th order with autocatalysis: $$(1-\alpha)^n(1+\mathrm{K}\alpha)\ , \tag{7}$$

where K is the catalytic factor.

3 RESULTS AND DISCUSSION

The discussion is divided into two complementary sections. First, the outcomes of the DEA, rheological and DSC measurements in comparison to each other are discussed. Later on the fractional reaction as defined by DEA and DSC kinetic models is presented. Correlations between the kinetic models of DSC and DEA are discussed.

3.1 Study of the curing behavior using DEA, Rheology and DSC

The effect of increasing temperature at various heating rates on the curing behavior of the Daron41 resin system is presented in Figure 3. The reaction behavior is accompanied by variations in ion viscosity ρ, shear viscosity η and heat flow as observed using DEA, rheometry and DSC, respectively. It is to be noted that both ion and shear viscosities are presented in logarithmic values, whereas the heat flow is given in a linear scale. Both chain formation as well as final cross-linking can be clearly associated with either a peak (exothermic reaction in DSC) or a step (viscosity in DEA or rheometer).

As expected all three techniques show the common trend that increasing heating rates shift the chain formation as well as cross-linking to higher temperatures . This is often associated with a thermal retardation of the sample at higher heating rates, which delays the material’s reaction. Therefore, the material responds later, which is seen in terms of higher reaction temperatures.

Chain formation. The first chain formation reaction can be observed at low temperatures around -10°C to 100 °C for the various heating rates. However, this representation does not allow a precise identification of the reaction stage, especially in case of DEA and rheology. This is attributed to the reaction steps associated with these techniques, where an overlap of contrary effects takes place. On the one hand, shear viscosity η and ion viscosity ρ increase because of the chain formation, whereas on the other hand, signals decrease based on higher mobility at elevated temperatures. Therefore, the first derivative of both of the viscosity data sets is presented in Figure 4. Here the reaction region can be determined between -10 and 100 °C at the low heating rate of 0.5 K/min, in contrast to -10 and 110 °C at 1 K/min and finally -10 to 120 °C at 5 K/min. This is comparable to the temperature intervals detected in the heat flow. In general however, the results show that shear rheology detects such phase changes at higher temperatures in contrast to observations made via DEA and DSC. This can be attributed to the different physical measurement principles.

Cross-linking. In contrast to the first chain formation reaction, the second curing reaction can be well depicted in Figure 3. In the DSC-signal, cross-linking is visible as an exothermic process, which can be correlated to an increase in both ion and shear viscosities. All three measurement techniques show network formation within the same temperature range between 100 and 120 °C for 0.5 K/min, 100 and 130 °C for 1 K/min and 120 to 150 °C for 5 K/min. The use of the derivative representation in Figure 4 confirms these observations. It becomes obvious that the reaction peaks overlap. Similar to the first reaction step, the increase in heating rate causes a delayed reaction, which is shifted towards higher temperatures.

Furthermore, Figure 4 shows that the DSC signal ends in the expected linear baseline, denoting the end of reaction. The ion viscosity is continuously decreasing after the end of the reaction. This is related to the increasing mobility of the chains, free ions and charges. In contrast to ion viscosity, the shear viscosity shows the expected constant value after curing and a small decrease to another plateau in the range of the glass transition. The subsequent noisy signal is caused by crack formation between the rotating rheometer plates and the sample surface and can be neglected. The hardening of the resin takes place in the same temperature range as can be seen in the signals of DEA and DSC. For 0.5 K/min between 100 and 120 °C, for 1 K/min between 110 to 130 °C and 5 K/min between 130 and

145 °C.

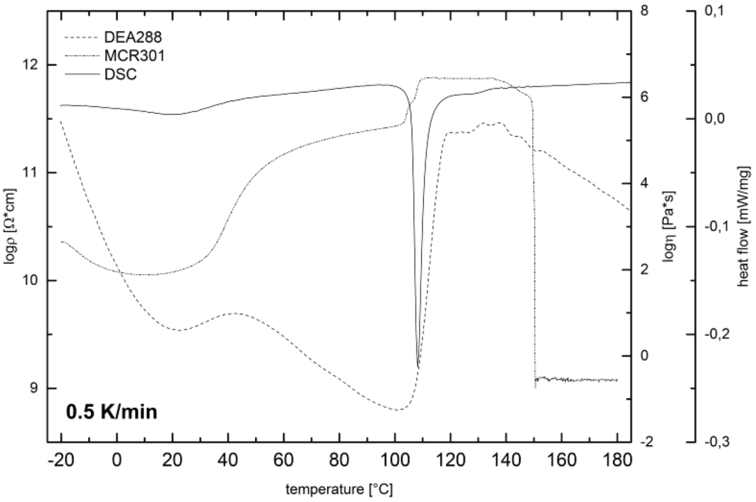

Figure 3a: 0.5 K/min.

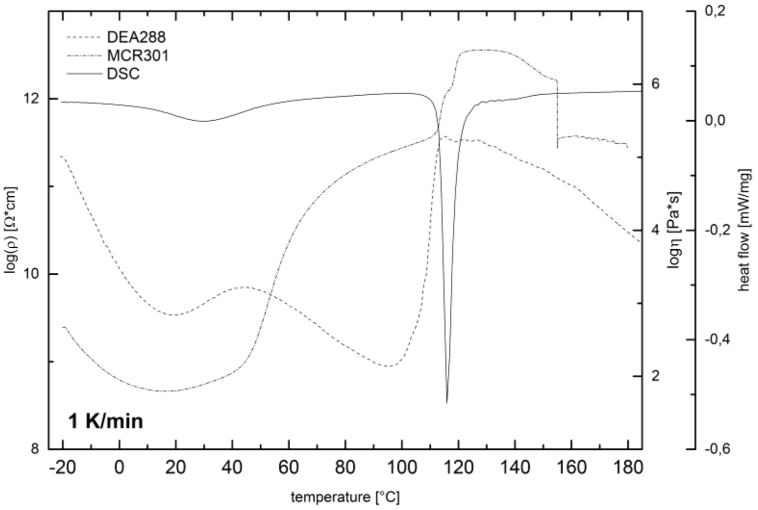

Figure 3a: 0.5 K/min.

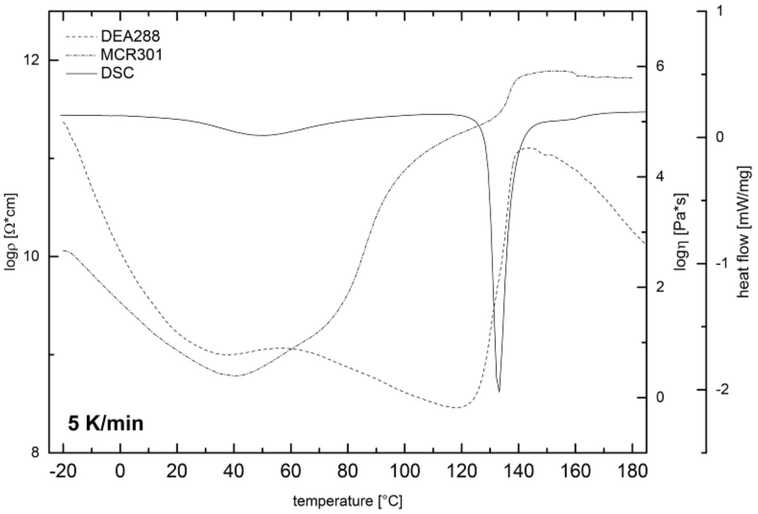

Figure 3a: 0.5 K/min.

Figure 3: Comparison of ion viscosity ρ, shear viscosity η and heat flow.

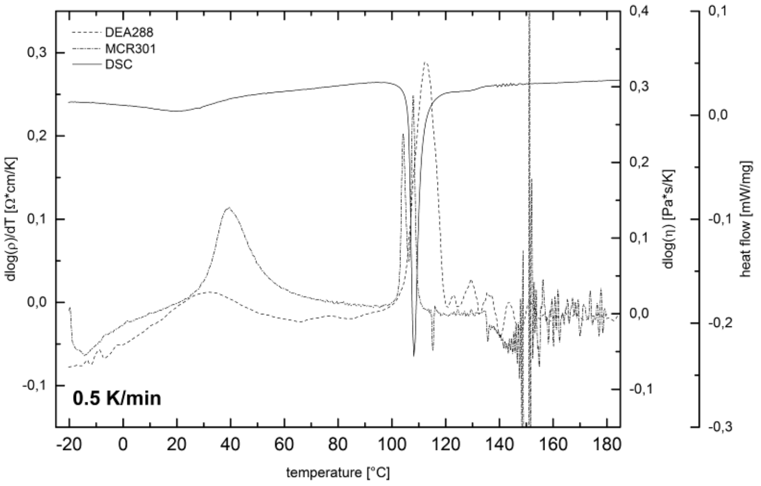

Figure 4a: 0.5 K/min.

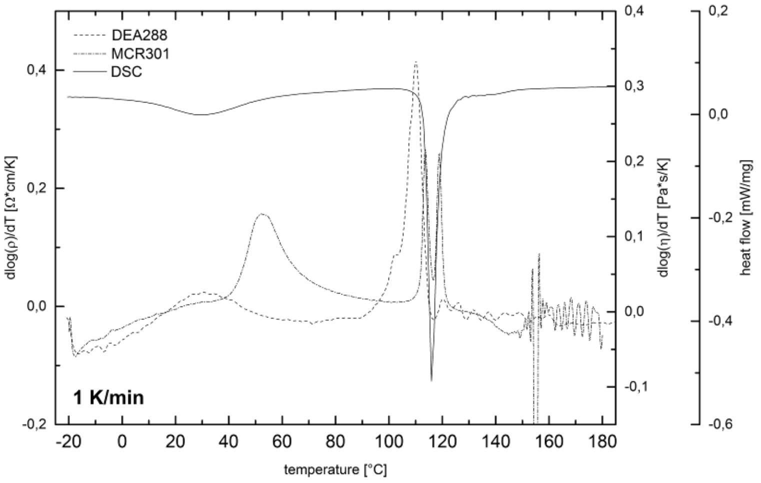

Figure 4b: 1 K/min.

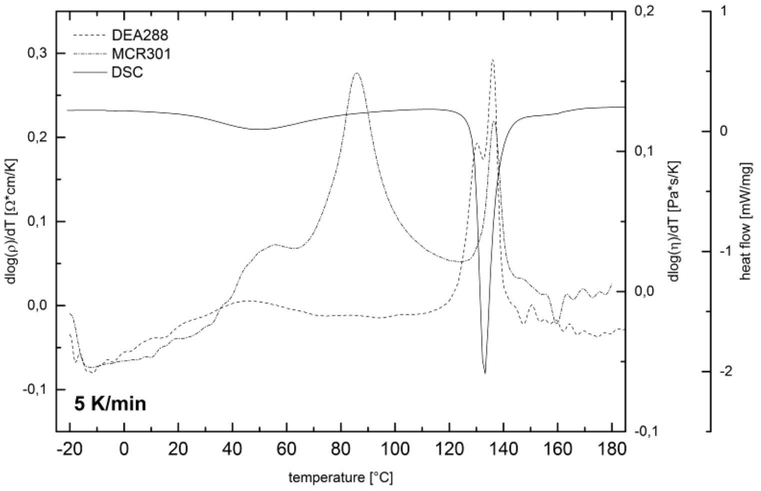

Figure 4c: 5 K/min.

Figure 4: Comparison of heat flow and derivatives of ion viscosity ρ and shear viscosity η.

Table 1 represents characteristic values for onset-, end- and peak-temperatures for all three measurement techniques, DSC, DEA and rheology, regarding both chain formation as well as cross-linking reactions. These data are based on the analysis of Figure 4. The onset is typically defined as the point of intersection of two tangents, one at the inflection point during the reaction and the other at the linear baseline, denoting start and end of reaction, respectively. The peak is determined at the highest value within the reaction stage. A manual four-point determination of onset- and end-temperatures had to be performed because the derivatives of shear viscosity and ion viscosity are sometimes too noisy for automated analysis.

0.5 K/min								
	chain formation [°C]				cross-linking [°C]			
	onset	peak		end	onset	peak		end
DSC	-2.94	18.75		46.93	103.94	108.17		111.00
DEA	-2.63	32.26		57.25	104.87	112.73		119.13
Rheology	30.41	39.17		55.23	102.84	104.16	107.91	109.29
1 K/min								
	chain formation [°C]				cross-linking [°C]			
	onset	peak		end	onset	peak		end
DSC	6.00	29.91		56.48	113.03	115.94		119.78
DEA	-1.88	30.67		56.28	103.30	102.31	110.14	114.53
Rheology	42.43	52.92		69.60	111.76	113.58	118.83	120.75
5 K/min								
	chain formation [°C]				cross-linking [°C]			
	onset	peak		end	onset	peak		end
DSC	1.91	50.23		88.15	128.97	133.28		138.20
DEA	-1.12	45.45		72.05	123.03	129.99	135.97	140.99
Rheology	31.61	55.42	85.83	99.94	131.62	136.67		141.17

Table 1: Characteristic temperatures for chain formation and cross-linking.

Especially the values for onset and end of the two reaction step correlate very well between DSC and dielectric data.

Closer observation of the rheology data shows that the onset and peak of both reactions is shifted to higher temperatures. This can be related to the disturbance of both chain formation and cross-linking due to the oscillatory motion of the rheometer. Only the end value lies in a reasonable interval compared to values determined by DSC and DEA.

3.2 Kinetic Modelling

Based on the above presented DSC and DEA data, kinetic models for the prediction of resin behavior under different process conditions, were derived. Figure 5 shows a theoretical temperature profile and the corresponding DEA and DSC kinetic fractional reactions. The term fractional implies the extent of reaction advancement and directly correlates with the degree of cure. It can be seen that there is a direct relationship between the fractional reactions observed with both DSC and DEA, whereas the exothermic heat generated during polymer chain growth has a larger impact on the total enthalpy of DSC in contrast to the motional limitation of the ion viscosity. The begin of the curing reaction after about 17 minutes is almost the same in both cases. A difference can be seen at the end of the curing where both DSC and DEA run into a horizontal plateau. The fractional reaction of the DEA shows a polymerization of nearly 100 % whereas DSC measurements indicate a degree of 95 %. After the initial cross-linking the slope in the DSC model is higher compared to that of the dielectric simulation. This can be caused by the comparison of absolute measurement data of the DSC in contrast to relative data of the dielectric analysis.

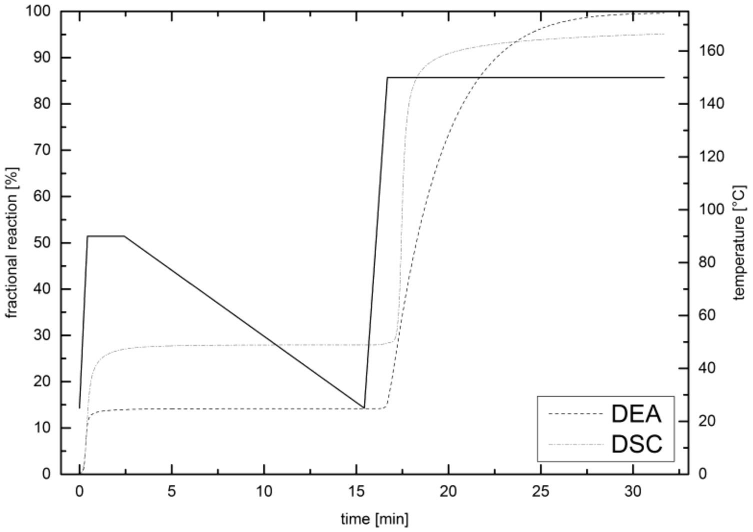

Figure 4: Kinetic determination of the fractional reaction for DEA and DSC for a specific temperature profile (continuous line).

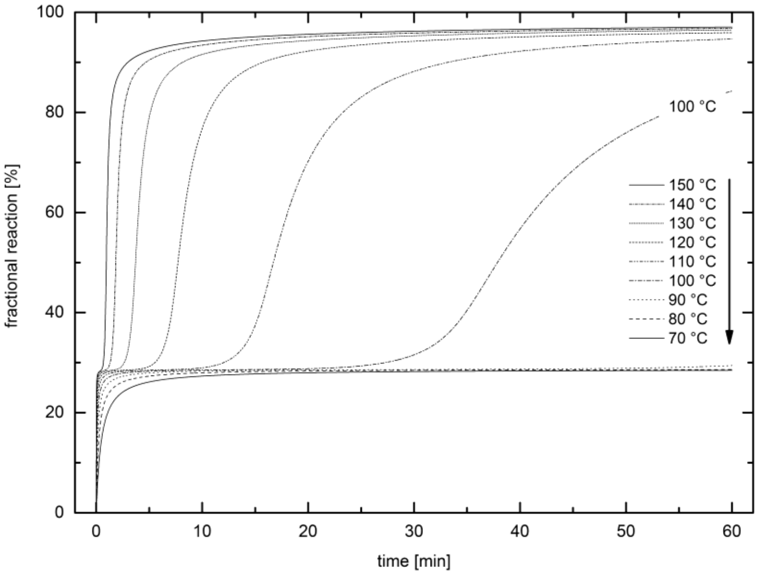

Figure 6: Fractional reaction for isothermal temperatures between 70 °C and 150 °C calculated by DSC-kinetics.

Fehler! Verweisquelle konnte nicht gefunden werden. demonstrates the effect of time on the fractional reaction at different isothermal temperatures within the range of 70 °and 150 °C. As anticipated it can be seen that the second reaction cannot be initialized at temperatures below 100 °C even at prolonged heating times of up to 60 minutes. The reason for this is the presence of the inhibitor that prevents network formation. Above 100 °C the inhibitor is decomposed and the curing reaction takes place.

4 CONCLUSIONS

The pultrusion process but especially the post-forming of pultruded profiles needs a perfectly adapted resin system to ensure the high performance of the composite system. Therefore, a two-step curing polyurethane based resin was used. For a deeper understanding of the behavior of this multi-component mixture, a comprehensive thermo-physical examination was conducted. Additionally, measured data were modelled to be able to predict processing behavior with different parameters and to adjust these for a faster and more reliable manufacturing process.

The above results show that the dielectric analysis provides similar outputs to those measured by standard thermo-physical DSC equipment. However, it is the only measurement technique that can be used online Laboratory results and the correlation of DSC, DEA and rheology measurements demonstrate that the curing stage of the resin system under investigation can be successfully determined by any of the three techniques. Derived ion viscosity of online-capable DEA measurements show almost the same behavior and curve shape compared to the heat flow measured with DSC. The shear viscosity reveals an increase during network formation within the same temperature range as detected by DSC and DEA, whereas the increase of the polymer chain growth is shifted towards higher temperatures compared to ion viscosity and heat flow.

ACKNOWLEDGEMENTS

This research and development project is partly funded by the German Federal Ministry of Education and Research (BMBF) within the Framework Concept ”Research for Tomorrow’s Production” (funding number 02PJ2035) and managed by the Project Management Agency Karlsruhe (PTKA). General start-up of the project group, facilities and key technology equipment in Augsburg is funded by the Region of Bavaria, City of Augsburg, BMBF and the European Union (in the context of the program “Investing In Your Future” – European Regional Development Fund). The authors would like to give special thanks to Netzsch-Gerätebau GmbH for their collaboration and support of their DEA288.

REFERENCES

[1] Starr, T., Pultrusion for engineers, CRC Press, Boca Raton FL, 2000.

[2] J.O. Simpson and S.A. Bidstrup, Rheological and dielectric changes during isothermal epoxy-amine cure, *Journal of Polymer Science Part B: Polymer Physics*, Volume 33, Issue 1, 1995, pp. 55-62.

[3] G. Levita, A. Livi, P.A. Rolla and C. Culicchi, Dielectric monitoring of epoxy cure, *Journal of Polymer Science Part B: Polymer Physics*, Volume 34, Issue 16, 1996, pp. 2731-2737.

[4] A. McIlhagger, D. Brown, B. Hill, The development of a dielectric system for the on-line cure monitoringof the resin transfer moulding process, *Composites Part A*, 31, 2000, pp. 1373-1381.

[5] A. Maazouz, J. Dupuy and G.Seytre, Polyurethane and unsaturated polyester hybrid networks: chemorheological and dielectric study for the resin transfer molding process (RTM), *Polymer Engineering and Science*, Vol. 40, No. 3, 2000.

[6] Ferry, J.D., Viscoelastic Properties of Polymers, John Wiley & Sons Inc, 3. Auflage, 1980.

[7] Cox; W.P., Merz, E.H., Correlation of Dynamic and Steady Flow Viscosities, *Journal of Polymer Science*, Vol. 28, issue 118, pp. 619-622.