

Modelling of Measurement Data on the Curing Reaction of HTPB with Isocyanate Obtained by Heat Flow Microcalorimetry and Pressure Decrease in Closed Vessel Cells

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Abstract

Composite rocket propellants have often three-dimensional polyurethane elastomers as binders. One of the high performance binders is HTPB (hydroxyl-terminated polybutadiene) cross-linked to an elastomer with an isocyanate in polyaddition reaction. It is essential for the mechanical properties of the final rocket propellant that cross-linking or curing has reached a high degree of conversion during the heat treatment of the initially liquid propellant mix. To assess the degree of curing is especially important, when evaluating and assessing the ageing. Therefore, one should understand the kinetics of the curing reaction in order to know, when residual curing during in-service time does not interfere with loss in strain capacity by ageing. Some binder and propellant mixes were investigated (1) via the reaction heat followed by heat flow calorimetry and (2) by volume shrinkage caused by cross-linking, at several temperatures in the range of 50°C to 80°C. The shrinkage of the volume V_g of the reaction mixture was followed in a closed pressure curing cell (PCC) by measurements of the system pressure p_s . A kinetic model based on the bimolecular reaction between OH-terminated pre-polymer and poly-isocyanate was developed, which describes the heat generation rates dQ/dt and the volume change rates dV_g/dt or pressure change rates dp_s/dt . The equivalent ratio between OH-groups and NCO-groups is considered in the model. However, the application of the model is not straightforward in spite of the basic simplicity of the model. The reason is that the reaction of second order between two components demands the knowledge of the real start point in time of the reaction, as well as the start concentrations of the reactants. Further on, there are many handling procedures as kneading with the isocyanate, taking out the samples from the batch, transportation of samples to the laboratory, filling of measurement cells and finally the preparation of the measurement itself. During all these steps, the reaction is already in progress and a certain conversion is achieved already up to the time from where the measurement of heat generation rate or volume shrinkage is usable for evaluation. Therefore, a special modelling procedure was developed to take into consideration of all these time-temperature sections with their pre-reactions with regard to the main part of the curing reaction in the microcalorimeter or in the PCC. By this procedure, the heat flow curves dQ/dt and the pressure rate curves dp_s/dt or the system pressure course $p_s = f(t)$ can be at first reconstructed and secondly described. With measurements at several temperatures, the Arrhenius parameters are obtained and conversion curves can be established. By this, the curing reactions can be assessed and suitable curing times can be defined. Further, the molar heat of reaction and the molar volume of reaction for one molar conversion of NCO were determined. The effect of curing catalysts are easily recognizable.

Keywords: HTPB curing; modelling of curing; microcalorimeter measurement; volume shrinkage by curing; molar heat of reaction; molar volume of reaction

1. Introduction

Curing reactions, means cross-linking reactions, are of great importance in polymer bonded explosives, means here elastomer bonded explosives; typical PBX systems are based on the cast-cure procedure, often with HTPB binder. Composite rocket propellants (CRP) are mostly based on polyurethane (PUR) binders using pre-polymers as GAP, DesmophenTM, HTPB. To investigate the ageing of CRPs the post-curing part has to be known. The determination of the curing behaviour of typical binder systems for CRPs was undertaken with curing of HTPB and isocyanate. For this the reaction kinetic curing model is established. The model is applied to curing data obtained at one hand from microcalorimetric measurements and on the other hand from volume shrinkage in a closed volume by pressure measurements. One complication should be mentioned: with the microcalorimetric signal alone and with system pressure alone, one cannot distinguish between parallel reactions proceeding with similar rates. But this aspect seems not a matter of concern with the here selected materials. A further discussion of the description of isocyanate reactions based on NCO-groups of different reactivity is given in the Appendix.

2. Used substances and instruments

In Table 1 the composition of the here used binder formulation TS-07 [1] is given. From the equivalent masses of the binder pre-polymer HTPB R45 HTLO and the curing agent DesmodurTM E305 the equivalent ratio Req is calculated. The curing agent has equal NCO groups with regard to their reactivity and sterical environment. It is HDI (hexane diisocyanate) based and chain elongated by some short polyether chain [2]. In good approximation, all the OH groups of the HTPB have also equal reactivity. The kneading was done in planetary-rotary or planetary-centrifugal vacuum mixer [3]. The device is called Thinky MixerTM, type ARV-310 (distributing company in Germany: C3 Prozess- und Analysentechnik GmbH, D-85540 Haar, Germany; the manufacturer is Thinky Corporation, 7F, Chiyoda-ku, Tokyo, Japan). The rotation speed was 1600 cycle per minutes and the pressure range 10 to 50 mbar.

Table 1: Composition of binder formulation TS-07 and characteristic numbers of this formulation. No curing catalyst was added.

Substance type	Substance	Amount in kneader [g]	Equivalent mass [g/mol-eq]	Equivalent number (EN)	Molar mass [g/mol]	Molar number
Binder (Polyol)	HTPB R45 HTLO	63.85	1205	0.0529876		
Curing agent (Polyisocyanate, PI)	Desmodur TM E305	15	328.1	0.0457178		
Plasticizer	DOA	20	-	-	370.576	0.053970
Antioxidant	Vulkanox TM BKF	1.15	-	-	340.6	0.003376
	Sum [g]	100				
Curing catalyst (in mass-% phr)	-	-				
	$Req = (EN - NCO)/(EN - OH)$	0.863				

The curing reaction of TS-07 was followed by heat flow microcalorimetry (HFMC), which is an established method to measure the heat flow of chemical reactions, see for example [4]. So-named TAMTM II and TAMTM III instruments manufactured by Thermometric AB and Waters Inc., BU TA Instruments, respectively, were used to measure the heat production of the curing reaction. The applied property for assessment

is heat generation rate (HGR) dQ/dt , measured in stainless steel ampoules with inserted glass vials to prevent direct contact between steel and the sample. From heat generation rate dQ/dt the heat generation Q is obtained by integration over time. Isothermal measurement temperatures were 60°C, 70°C, 80°C. All measurements have had enclosed air in the ampoules. The formulation was protected against oxidation by an antioxidant. Two further samples were investigated with DSC at different heating rates and the evaluation was done with the generalized Kissinger equation, see later. These two formulations were TS-38 and TS-44, HTPB-IPDI (Req = 0.869), 25 mass-% DOA and 1.53 mass-% Vulkanox™ BKF. Both contained the curing catalyst TPB in an amount of 0.02 mass-% phr [1]. A fourth binder formulation was re-manufactured, named AV00, also based on HTPB-IPDI (Req = 0.870), with 25 mass-% DOA, with 1.0 mass-% antioxidant Irganox™ 565 and with 0.04 mass-% TPB. It was already investigated [9]. The last investigated formulation in this paper is TS-78 [1, 5]. The composition is given in Table 2. It contains ammonium perchlorate (AP) and aluminium.

Table 2: Composition of formulation TS-78 and characteristic numbers of this formulation [5]. The curing catalyst TPB was added. The formulation TS-78 was used to follow its volume shrinkage during curing in a PCC (Pressure Curing Cell).

Substance type	Substance	Amount in kneader [g or %]	Equivalent mass [g/mol-eq]	Equivalent-number (EN)	Molar mass [g/mol]	Molar number
Binder (Polyol)	HTPB R45 HTLO	10.684	1205.0	0.008866		
Curing agent (Polyisocyanate, PI)	IPDI	0.926	111.0	0.008342		
Plasticizer	DOA	6.00	-	-	370.576	0.053970
Antioxidant	Vulkanox™ BKF	0.24	-	-	340.6	0.003376
Bonding agent	HX 878	0.15	200.0	0.00075		
Oxidizer	AP 200 µm, AP 45 µm	56.0 12.0	-			
Fuel	Al, 18 µm	14.0	-			
	Sum [g]	100				
Curing catalyst (in mass-% phr)	TPB	0.02				
	Req = (EN -NCO)/(EN-OH)	0.868				

To follow volume shrinkage, one needs to place the reacting mixture in a closed volume under a slight overpressure. Then the pressure decrease during the cross-linking and the curing reaction can be followed. For this, one of us (GM) designed so-called Pressure Curing Cells (PCC) and ten of them were manufactured from stainless steel at Fraunhofer ICT [6]. The Fig. 1 shows a schematic drawing of the pressure cell. The diameter of the PCC has been chosen in such a way to fit into existing aluminum heating block ovens, which can be precisely controlled to $\pm 0.05^\circ\text{C}$ to $< \pm 0.1^\circ\text{C}$ in the time range of measurement. The resulting mechanical stress by compression of the sample, measurable as pressure, is related to the state of deformation by its material law, which has the bulk (compression) modulus κ of the material as characteristic property. Sutton gives an empirical value for κ of 1.4 GPa [7]. According to this quite high value, the value of the pressure derivative with respect to time is much higher than the one of the triggering volume change. Consequently, the accuracy of the measurement principle is satisfying. But necessary is a very constant temperature reservoir for the PCCs.

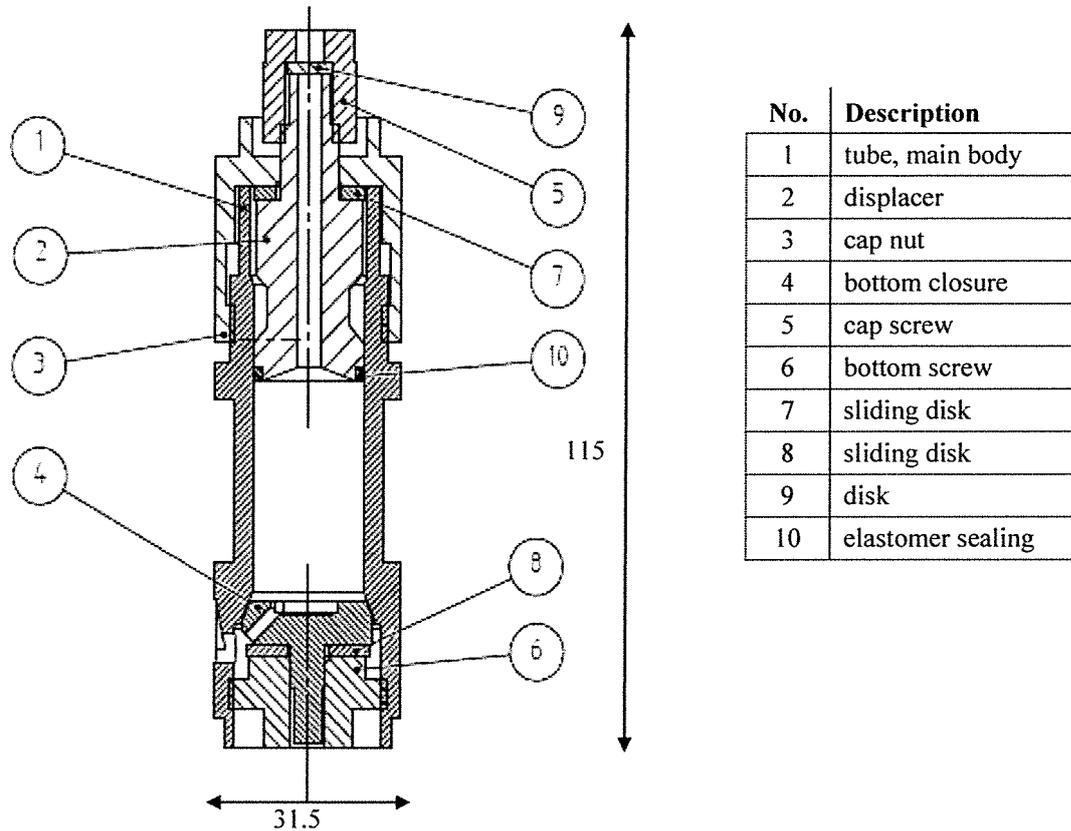


Fig. 1: Schematic drawing of the Pressure Curing Cell (PCC) with volume of about 10.71 ml. Measures are in millimetres [6].

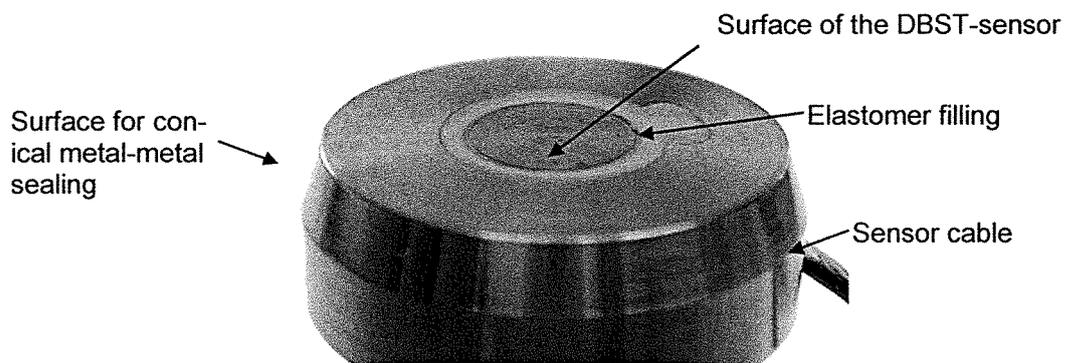


Fig. 2: Bottom closure (part no. 4 in Fig. 1) of the PCC with build-in DBST sensor (containing a pressure transducer and a temperature sensor) [6].

The pressures are recorded by DBST (dual bond stress and temperature) sensors from Micron Instruments, Simi Valley, CA, USA [8], using the appropriate data loggers, see Fig. 2. They operate principally as very sensitive and over time very stable pressure transducers. Details on functioning and operation of a PCC can be found in [6] and [9].

3. Model formulation

3.1 Reaction kinetic expression for consumption of the isocyanate

The start point for the model formulation is the bimolecular reaction between the OH groups of the pre-polymer, named B and the isocyanate groups NCO of the polyisocyanate, named A. By the addition reaction between A and B the urethane group AB is formed, Eq.(1), connected with molar reaction heat $\Delta H_{R,A}$ and molar reaction volume $\Delta V_{R,A}$, both with respect to the conversion of reactant A.



In principle, the isocyanate can further react with the urethane group forming an allophanate and even this product is able to react again with isocyanate to form a biuret. In section Appendix, this is shown in more detail and extended kinetic formulations are given. But it is reasonable to concentrate on the primary reaction between A and B forming urethane, because it is by far in advantage when using polymeric alcohol groups as hydroxyl-terminated polymers. In the following the reactivity of all OH groups and all NCO groups are each considered equal and the formulation of the model is established from the view of the consumption of the NCO groups. If one can apply measurement methods, which can distinguish between the different NCO groups, for example those of IPDI (isophorone diisocyanate), then at least two of the following equations can be applied. However, the situation with IPDI is much more complex, see Appendix.

To facilitate the model formulation, so called normalized concentrations are used, means the actual concentrations $A(t)$ and $B(t)$ are divided by the start concentration by the species governing the reaction, here $A(0)$. In Eq.(2) the resulting reaction rate equation is shown, formulated in molar concentrations of A and B. The concentrations in the following equations are in mol per unit (volume or mass of mix), if not otherwise indicated.

$$\left(\frac{d \left(\frac{A(t)}{A(0)} \right)}{dt} \right)_{IT} = -k_2 \cdot A(0) \cdot \frac{A(t)}{A(0)} \cdot \frac{B(t)}{A(0)} \quad (2)$$

The concentration $B(t)$ can be easily expressed by Eq.(3) because of molar relationship between A and B. Considered is also a start concentration of B, which must not be equal to $A(0)$. If $B(0) = A(0)$ the formalism changes to an ordinary reaction of second order. Introducing Eq.(3) in Eq.(2) the Eq.(4) is obtained.

$$B(t) = B(0) - (A(0) - A(t)) \quad (3)$$

$$\left(\frac{d \left(\frac{A(t)}{A(0)} \right)}{dt} \right)_{IT} = -k_2 \cdot A(0) \cdot \frac{A(t)}{A(0)} \cdot \frac{B(0) - (A(0) - A(t))}{A(0)} \quad (4)$$

Useful abbreviations are introduced now: $Ar(t) = A(t)/A(0)$ and the equivalent ratio Req between NCO and OH groups is defined by $Req = A(0)/B(0)$. Finally the reaction rate constant k_2 is changed to $k_{2A} = k_2 \cdot A(0)$. This leads to Eq.(6), the model formulation with regard to isocyanate consumption.

$$\left(\frac{dAr(t)}{dt} \right) \Big|_{\tau} = -k_2 \cdot A(0) \cdot Ar(t) \cdot \left(\frac{B(0)}{A(0)} - 1 + Ar(t) \right) \quad (5)$$

$$\left(\frac{dAr(t)}{dt} \right) \Big|_{\tau} = -k_{2A} \cdot Ar(t) \cdot \left(\frac{1}{Req} - 1 + Ar(t) \right) \quad (6)$$

The integration of Eq.(6) with the start condition $Aro = Ar(0) = 1$ gives the Eq.(7) or in somewhat rearranged form the Eq.(8).

$$\frac{A(t)}{A(0)} = Ar(t) = \frac{(Req - 1)}{Req - \exp\left(+\left(\frac{1}{Req} - 1\right) \cdot k_{2A} \cdot t\right)} \quad (7)$$

$$\frac{A(t)}{A(0)} = Ar(t) = 1 - \frac{1 - \exp\left(+\left(\frac{1}{Req} - 1\right) \cdot k_{2A} \cdot t\right)}{Req - \exp\left(+\left(\frac{1}{Req} - 1\right) \cdot k_{2A} \cdot t\right)} \quad (8)$$

But often the situation is encountered that the bimolecular reaction has already started before the measurement can be started. This means the conversion has already reached a value corresponding to a formal start concentration $Aro < 1$. The integration of Eq.(6) has the initial condition $Ar(0) = Aro$. The resulting expression for $Ar(t)$ is shown in Eq.(9). With $Aro = 1$ the Eq.(7) follows.

$$Ar(t) = \frac{(Req - 1)}{Req - \left(\frac{1 - Req}{Aro} + Req\right) \cdot \exp\left(+\left(\frac{1}{Req} - 1\right) \cdot k_{2A} \cdot t\right)} \quad (9)$$

3.2 Reaction kinetic expression for heat generation rate dQ/dt

To connect heat generation rate with the concentration of the looked for species $A(t)$ the Eq.(10) is the start point, which states that heat generation rate dQ_A/dt caused by reaction of A is equal to the substance change rate $dA(t)/dt$ times the molar heat of reaction ($-\Delta H_{R,A}$) in energy/mol. The convention to have negative data with exothermal reactions is here converted, because in heat flow microcalorimetry the standard convention is to have exothermal heat output data as positive.

$$\left(\frac{dQ_A(t, T)}{dt} \right) \Big|_{\tau} = - \left(\frac{dA(t, T)}{dt} \right) \Big|_{\tau} \cdot (-\Delta H_{R,A}) \quad (10)$$

The formal integration of Eq.(10) between time $t = 0$ and t gives Eq.(11).

$$Q_A(t) - Q_A(0) = (A(0) - A(t)) \cdot (-\Delta H_{R,A}) \quad (11)$$

At the end of the measurement at time t_e , which corresponds to non-measurable changes in the signal, Eq.(12) is valid. From this the Eq.(13) is immediately derived, whereby $A(t_e) = 0$ and $Q_A(0) = 0$. All quantities Q_A have the unit of energy. Remark: because the polyurethane reaction is an addition reaction without changing the reaction gas volume, the reaction heat $\Delta Q_{R,A}$ and the reaction enthalpy $\Delta H_{R,A}$ are formally identical.

$$Q_A(t_e) - Q_A(0) = (A(0) - A(t_e)) \cdot (-\Delta H_{R,A}) \quad (12)$$

$$Q_A(t_e) = (-\Delta H_{R,A}) \cdot A(0) \quad (13)$$

Using the normalized quantities Q_{Ar} and A_r , the Eq.(15) is obtained. It states that the normalized quantities are directly proportional. The conversion α_A is defined as shown with Eq.(16). From these equations, the Eq.(17) and Eq.(18) can be derived. Further, together with Eq.(15) and Eq.(7) the Eq.(19) is found, which is the looked for model to describe the heat generation rate of a bimolecular reaction.

$$Q_{Ar}(t, T) = Q_A(t, T) / Q_A(t_e) \quad (14)$$

$$\left(\frac{dQ_{Ar}(t, T)}{dt} \right) \Big|_T = - \left(\frac{dA_r(t, T)}{dt} \right) \Big|_T \quad (15)$$

$$\alpha_A(t) = \frac{Q_A(t) - Q_A(0)}{Q_A(t_e) - Q_A(0)} = 1 - A_r(t) \quad \frac{d\alpha_A(t, T)}{dt} = \frac{dQ_A(t, T)}{dt} \frac{1}{Q_A(t_e)} \quad (16)$$

$$Q_A(t) - Q_A(0) = (1 - A_r(t)) \cdot (Q_A(t_e) - Q_A(0)) \quad (17)$$

$$(Q_A(t_e) - Q_A(t)) = (Q_A(t_e) - Q_A(0)) \cdot \frac{(Re q - 1)}{Re q - \exp\left(+\left(\frac{1}{Re q} - 1\right) \cdot k_{2A} \cdot t\right)} \quad (18)$$

$$\frac{dQ_A(t)}{dt} = k_{2A} \cdot \frac{(Re q - 1)}{Re q - \exp\left(+\left(\frac{1}{Re q} - 1\right) \cdot k_{2A} \cdot t\right)} \cdot \left(\frac{1}{Re q} - 1 + \frac{(Re q - 1)}{Re q - \exp\left(+\left(\frac{1}{Re q} - 1\right) \cdot k_{2A} \cdot t\right)} \right) \cdot Q_A(t_e) \quad (19)$$

3.3 Reaction kinetic expression for pressure decrease caused by volume shrinkage

The formation of the urethane group causes a shrinkage in volume, because the molar reaction volume $\Delta V_{R,A}$ is negative. This originates from the fact that formation of chemical bonds between reaction partners

normally reduces the volume. This effect can be used to follow the cross-linking of the binder in rocket propellants, by looking on the total volume of the reaction mix. The total volume V_g at time t is given by Eq.(20) or Eq.(21), using molar concentrations and the individual molar volumes v_j . The individual volume components can be expressed via Eq.(22). Index F stands for filler.

$$V_g(t) = V_A(t) + V_B(t) + V_{AB}(t) + V_F \quad (20)$$

$$V_g(t) = A(t) \cdot v_A + B(t) \cdot v_B + AB(t) \cdot v_{AB} + F \cdot v_F \quad (21)$$

The volume part of the filler(s) does not change during curing, so V_F is not a function of time.

$$\left. \begin{aligned} V_A(t) &= A(t) \cdot v_A \\ V_B(t) &= B(t) \cdot v_B = B(0) \cdot v_B - (A(0) \cdot v_A - A(t) \cdot v_A) \cdot \frac{v_B}{v_A} \\ V_{AB}(t) &= AB(t) \cdot v_{AB} = (A(0) \cdot v_A - A(t) \cdot v_A) \cdot \frac{v_{AB}}{v_A} \end{aligned} \right\} \quad (22)$$

The molar reaction volume $\Delta V_{R,A}$, which corresponds to the molar reaction conversion from A+B to AB, is given by Eq.(23). By this the Eq.(22, third) is reformed to Eq.(24). The total volume V_g is now expressed by the individual volume parts and by rearrangement the Eq.(25) results and finally, by introducing the quantity $V_g(0)$, the Eq.(26) is reached. The relation between substance decrease rate and volume decrease rate gives Eq.(27).

$$\Delta V_{R,A} = v_{AB} - v_A - v_B \quad (23)$$

$$V_{AB}(t) = AB(t) \cdot v_{AB} = (A(0) \cdot v_A - A(t) \cdot v_A) \cdot \frac{\Delta V_{R,A} + v_A + v_B}{v_A} \quad (24)$$

$$V_g(t) = F \cdot v_F + B(0) \cdot v_B + A(0) \cdot v_A + (A(0) - A(t)) \cdot \Delta V_{R,A} \quad (25)$$

$$V_g(t) - V_g(0) = (A(0) - A(t)) \cdot \Delta V_{R,A} \quad (26)$$

$$\left(\frac{dV_g(t, T)}{dt} \right) \Big|_T = - \left(\frac{dA(t, T)}{dt} \right) \Big|_T \cdot \Delta V_{R,A} \quad (27)$$

Finally, the volume parts V_F of solid or liquid fillers, which do not change during curing, play no role in following the curing reaction by pressure decrease. The course of the measurement is made in such a way that the reaction mixture always fills up the total volume V_{PCC} of the measurement device, here the pressure curing cell (PCC). This is achieved by putting a slight overpressure on the material, maximum up to 40 bar. This low pressure does not change intramolecular distances between atoms and does not change in very good approximation the molar volumes, especially with the small 'hard' substances like the isocyanates. With bigger polymer coils some slight pressure influence could appear. Also temperature could change the volume of the polymer coil. Then the molar reaction volume becomes slightly pressure and temperature dependent. However, because the HTPB is a liquid with relatively high density, its compressibility is low.

The case considered here is that with volume decrease a pressure decrease results, means it is not a normal compression. It is handled according to Eq.(28).

$$\left(\frac{dp_s}{dV_g} \right) \Big|_T = + \frac{K}{V_{PCC}} \quad (28)$$

p_s ,system' pressure, the pressure measured in the PCC
 V_g the total volume of the reaction mixture
 V_{PCC} volume of the PCC, it is always filled up by the reaction mixture
 K 'decompression' constant, independent of reaction conversion and of pressure in the considered experimental pressure range of maximum 30 bar. Assumption: All reaction participants have the same molecular stiffness against pressure, so K does not change with pressure.

The integration of Eq.(28) gives Eq.(29) and at the end of reaction at time t_e the Eq.(30) is valid. With these both equations together the Eq.(31) is formed, and with Eq.(26) the Eq.(32) is obtained. Because at end of reaction the concentration $A(t_e)$ of the isocyanate is zero, the Eq.(33) results. Inserting Eq.(7) gives finally the looked for equation Eq.(34). Please note the quantity used to followed by the curing extent is the volume $V_g(t)$, in spite of the fact that when the actual measurement quantity is pressure. In a first step the reaction rate constant is considered pressure independent.

$$p_s(t) - p_s(0) = + \frac{K}{V_{PCC}} \cdot (V_g(t) - V_g(0)) \quad (29)$$

$$\left. \begin{aligned}
 p_s(t_e) - p_s(0) &= + \frac{K}{V_{PCC}} \cdot (V_g(t_e) - V_g(0)) \\
 \Delta p_s = (p_s(t_e) - p_s(0)) &= + \frac{K}{V_{PCC}} \cdot \Delta V_g
 \end{aligned} \right\} \quad (30)$$

$$p_s(t) = (p_s(t_e) - p_s(0)) \cdot \frac{V_g(t) - V_g(0)}{V_g(t_e) - V_g(0)} + p_s(0) \quad (31)$$

$$p_s(t) = (p_s(t_e) - p_s(0)) \cdot \frac{(A(0) - A(t)) \cdot \Delta V_{R,A}}{(A(0) - A(t_e)) \cdot \Delta V_{R,A}} + p_s(0) \quad (32)$$

$$p_s(t) = (p_s(t_e) - p_s(0)) \cdot \frac{A(0) - A(t)}{A(0)} + p_s(0) \quad (33)$$

$$\left. \begin{aligned}
 p_s(t) &= (p_s(0) - p_s(t_e)) \cdot \left(\frac{(Re\ q - 1)}{Re\ q - \exp\left(+ \left(\frac{1}{Re\ q} - 1\right) \cdot k_{2A} \cdot t\right)} \right) + p_s(t_e) \\
 V_g(t) &= (V_g(0) - V_g(t_e)) \cdot Ar(t) + V_g(t_e)
 \end{aligned} \right\} \quad (34)$$

Some further relations are shown in the following Eq.(35).

$$\left. \left(\frac{dp_s(t,T)}{dt} \right) \right|_T = -(p_s(0) - p_s(te)) \cdot \left(\frac{dAr(t,T)}{dt} \right) \Big|_T = -(p_s(0) - p_s(te)) \cdot \left. \frac{d \left(\frac{V_g(t,T)}{\Delta V_g} \right)}{dt} \right|_T \quad (35)$$

$$V_g(te) - V_g(0) = \Delta V_g = A(0) \cdot \Delta V_{R,A}$$

3.4 Modification of kinetic expression to include already happened conversion

Eq.(19) describes the course of the heat generation rate $dQ_A(t)/dt$, if the measurement starts really at the time, when the reaction between A and B starts. But this is not achievable with practically any measurement method. The curing reaction starts at the same moment of adding the isocyanate to the mix containing the binder or pre-polymer. After preparing the reactive mix for example in a kneader, one has to transfer the reacting mix to the measurement cells of the microcalorimeter and one has to wait some 10 to 15 minutes for equilibration before starting the active measurement. But mostly even then the first part of the data is not yet usable and one has to discard further portions of the data. Meanwhile a defined conversion is reached in the mix. The data from the microcalorimeter are usable only from a time period on after the real start point. Means one get not the full data on the curing reaction. In other words the quantity $Q_A(te)$ necessary in Eq.(19) is not achievable from the measurements, a quite uncomfortable situation. It is illustrated in Fig. 1. Up to about 0.152777 days = 3.66 hours (without pre-time t_p added, blue solid line) the data are not useable.

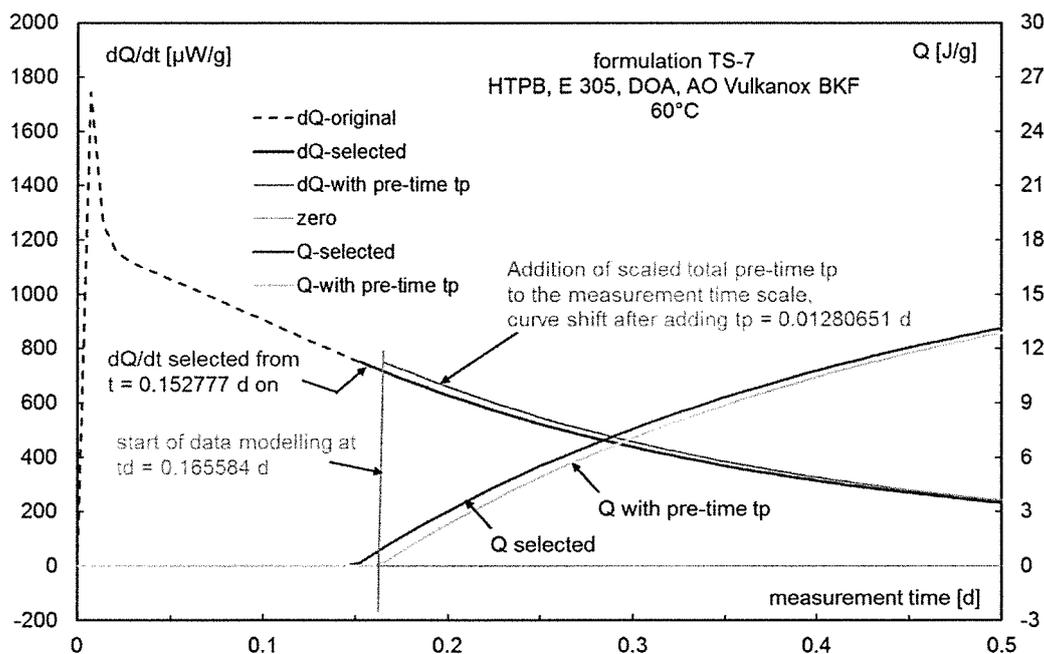


Fig. 3: Illustration of data condition by following the curing reaction with microcalorimetry and data selection for modelling.

The aim is to modify Eq.(19) in such a way to be applicable with the data. From Fig. 3 it can be seen that the reaction heat is in part measured and obtainable from the time t_d to the end of measurement at time t_e . This part of reaction heat (heat generation) is named Q_{Ade} . In addition, one needs the part of reaction heat from time $t=0$, meant is the real start of the curing reaction in the kneader, up to the time t_d . From Eq.(17) we get the Eq.(36), here with introducing that reasonably the quantity $Q_A(0) = 0$, which gives the heat generated from time $t=0$ to any time t . Therewith the Eq.(37) is obtained for the total released reaction heat and this equation reformulated to Eq.(38) gives an expression for $Q_A(t_e)$, which is finally determined by the reaction model, see Eq.(39). This enables to establish the looked for Eq.(40) for modelling of the measured data. The only unknown parameter in this equation is the reaction rate constant k_{2A} .

$$Q_A(t) = \frac{A(0) - A(t)}{A(0)} \cdot Q_A(t_e) \quad (36)$$

$$Q_A(t_e) = Q_{Ade} + \frac{A(0) - A(t_d)}{A(0)} \cdot Q_A(t_e) \quad (37)$$

$$Q_A(t_e) = Q_{Ade} \cdot \frac{A(0)}{A(t_d)} \quad (38)$$

$$Q_A(t_e) = Q_{Ade} \cdot \frac{\text{Re } q - \exp\left(+\left(\frac{1}{\text{Re } q} - 1\right) \cdot k_{2A} \cdot t_d\right)}{(\text{Re } q - 1)} \quad (39)$$

$$\left. \begin{aligned} \frac{dQ_A(t)}{dt} &= k_{2A} \frac{(\text{Re } q - 1)}{\text{Re } q - \exp\left(+\left(\frac{1}{\text{Re } q} - 1\right) \cdot k_{2A} \cdot t\right)} \\ &\cdot \left(\frac{1}{\text{Re } q} - 1 + \frac{(\text{Re } q - 1)}{\text{Re } q - \exp\left(+\left(\frac{1}{\text{Re } q} - 1\right) \cdot k_{2A} \cdot t\right)} \right) \cdot Q_{Ade} \frac{\text{Re } q - \exp\left(+\left(\frac{1}{\text{Re } q} - 1\right) \cdot k_{2A} \cdot t_d\right)}{(\text{Re } q - 1)} \end{aligned} \right\} (40)$$

With the Eq.(34) to describe the pressure decrease no special measures must be applied to this equation, it can be used as it is to determine the start pressure $p_s(0)$ for the extrapolated reaction start and the final pressure $p_s(t_e)$ as well as the reaction rate constant k_{2A} .

3.4 Consideration of handling of the cure mix before the start of measurement

The curing reaction starts with the addition of the isocyanate to the already kneaded pre-mix. The reaction rate of the second order reaction is sensitive to the start condition, see Eq.(5) and Eq.(6), in contrast to a first order reaction. Even if one would make the mix inside the microcalorimeter one has to discard a significant part of the data at begin, because the instrument would be out of measurement equilibrium. Therefore, one has to achieve the 'reconstruction' of the start of the reaction. First one must include all the pre-handling sections, as shown in Table 3.

Table 3: Example of handling sections with times t_v and corresponding handling temperatures T_v before the start of the measurement with the microcalorimeter and their rescaling to the curing (measurement) temperature $T_M = 60^\circ\text{C}$ with the generalized van't Hoff equation. Finally the scaled pre-times are summed-up to the total pre-time t_p .

Operations before measurement	temp. T_v [°C]	time t_v [min]	t_M at target temp. $T_M = 60^\circ\text{C}$, scaled from t_v with $F = 2.2$ [d]
end of kneading without isocyanate	28	0	0
kneading with isocyanate	28	2	0.00011141
transport to laboratory	26	15	0.00071366
handling in laboratory	25	4	0.00017588
pre-heating in microcalorimeter	60	17	0.01180556
total pre-time t_p at T_M in days			0.01280651

The scaled times t_M are the times at measurement temperature T_M , which result in the same conversion achieved at the times t_v at the corresponding temperatures T_v . This consideration needs a scaling of the times t_v to the used measurement temperature T_M , which is done here with the generalized van't Hoff equation, Eq.(41).

$$t_M[\text{d}] = t_v[\text{min}] \cdot F^{+(T_v - T_M)/\Delta T_F} / 1440 \quad (41)$$

These times are added up to the total pre-time t_p . The inclusion of this pre-time is shown in Fig. 3. In Fig. 4 the total situation for modelling is illustrated. The broken black, thick line shows the dQ_A/dt experimental data used in modelling with Eq.(40). The heat generation Q_A corresponding to these dQ_A/dt data is shown as blue dotted line. By modelling, the red, thin curve is established as the total dQ_A/dt curve and the corresponding Q_A curve is the blue full line. The two characteristic times t_p and t_d are shown also.

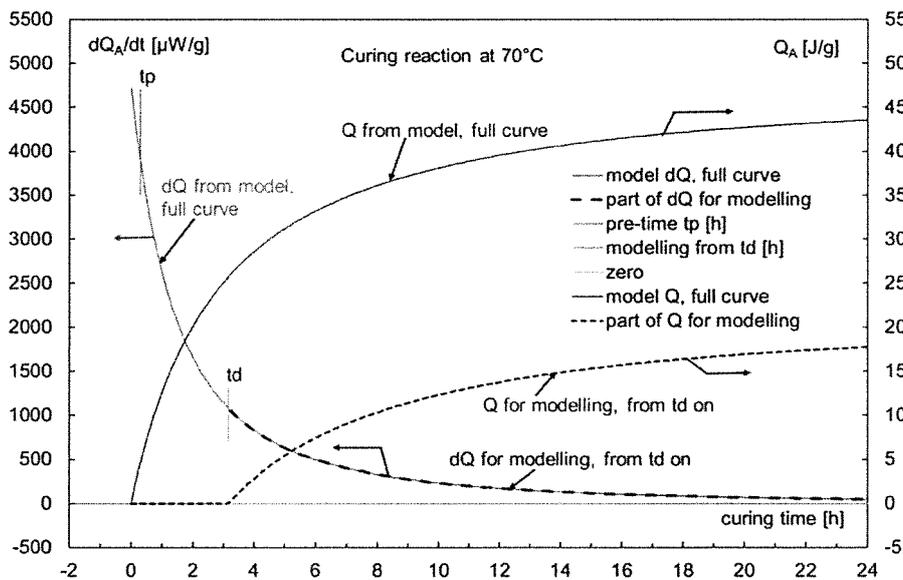


Fig. 4: Situation of data. Accessible and usable data are only the dQ/dt -data from time t_d on. Before determining t_d the pre-time t_p is added to the data. A significant part of reaction heat is not directly achievable, only by extrapolation with the model.

For modelling of the data, the Eq.(42) is used, with the abbreviations $dQ1$ and $dQ2$ given in Eq.(43) and Eq.(44) respectively. Formally only the reaction rate constant k_{2A} is the fit parameter of Eq.(40). There can be a residual reaction producing a small part of heat generation rate not coming from the wished reaction. For compensation, the parameter dQ_{off} can be used.

$$\frac{dQ_A(t)}{dt} = dQ_{off} + k_{2A} \cdot dQ1 \cdot \left(\frac{1}{Re q} - 1 + dQ1 \right) \cdot Q_{Ade} \cdot dQ2 \quad (42)$$

$$dQ1 = \frac{(Re q - 1)}{Re q - \exp\left(+\left(\frac{1}{Re q} - 1\right) \cdot k_{2A} \cdot t\right)} \quad (43)$$

$$dQ2 = \frac{Re q - \exp\left(+\left(\frac{1}{Re q} - 1\right) \cdot k_{2A} \cdot td\right)}{(Re q - 1)} \quad (44)$$

With pressure-time data the similar procedure was made: adding the pre-handling time t_p and then selection of suitable pressure-time data from time t_d on, see Fig. 5. But in contrast to heat generation rate, with Eq.(34) for pressure decrease no special measures must be applied, Eq.(34) can be used as it is to determine the formal start pressure $p_s(0)$ for the extrapolated reaction start. Also $p_s(t_e)$ and the reaction rate constant k_{2A} can be directly obtained with Eq.(34).

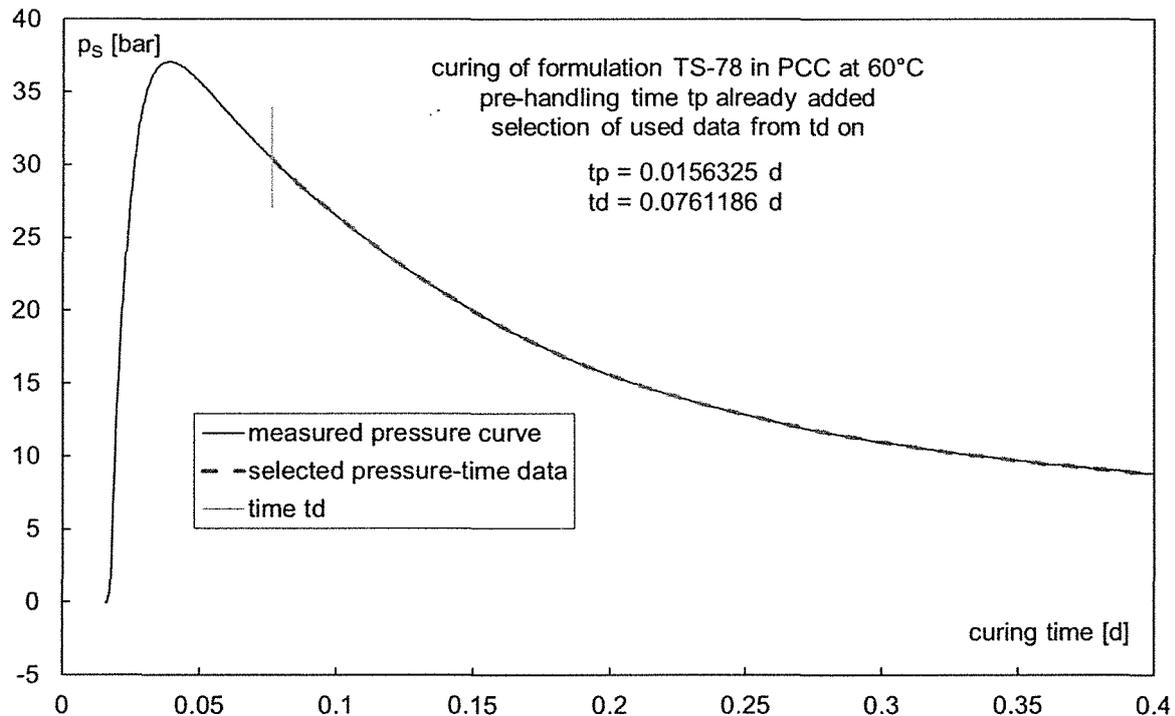


Fig. 5: Typical pressure course during curing in the PCC. The data at begin are not usable for the evaluation, because the temperature of the reaction mix is not yet constant. The data for the kinetic description are used from t_d on.

4. Results of the modelling

4.1 Microcalorimetric measurements

The results of the modelling can be seen in the Fig. 6 to 8 for the three curing temperatures. The graphs show the full curve for dQ_A/dt and the used experimental heat generation rate data for modelling as dashed curve, mainly coinciding with the modelled curve, as well as the heat generation Q_A , which is always the curve going up to the right. All the parameters obtained are collected in Table 4 together with the fit quality data. For comparison of the outcome the normalized representation shown in Fig. 9 is suited. There the conversion to the urethane linkage AB is shown, calculated by Eq.(45). Another possibility is to use the normalized heat generation rate, Eq.(14).

$$ABr(t) = 1 - Ar(t) = \alpha_A(t) = 1 - \frac{(Re q - 1)}{Re q - \exp\left(+\left(\frac{1}{Re q} - 1\right) \cdot k_{2A} \cdot t\right)} \quad (45)$$

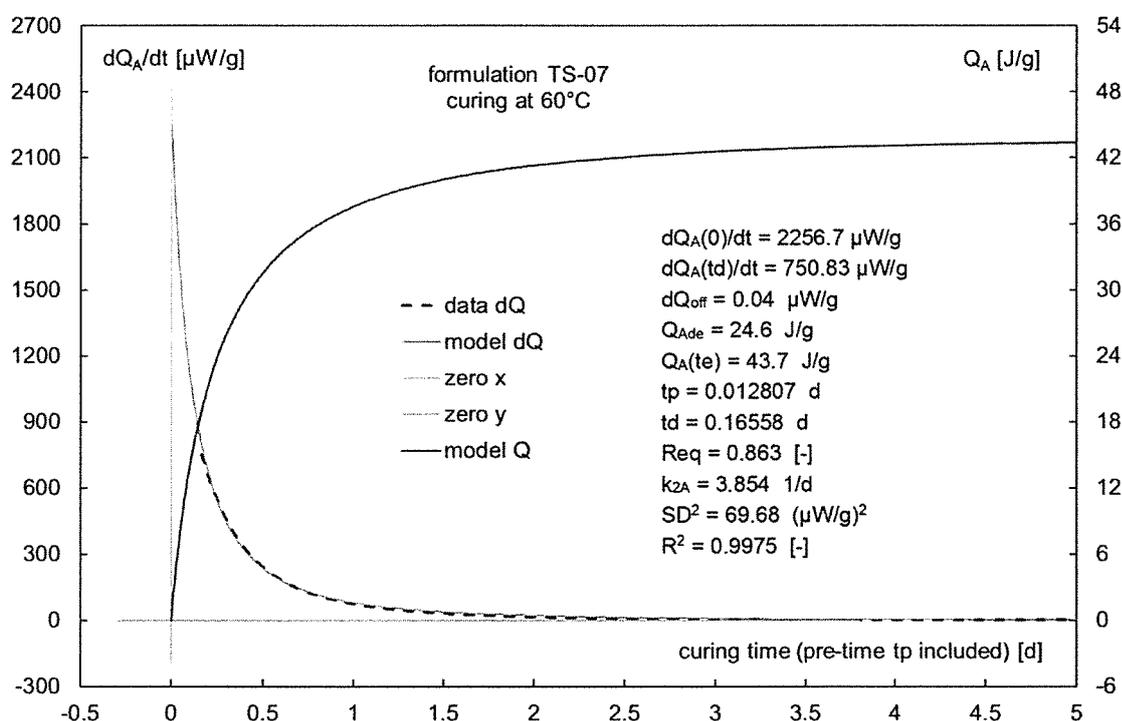


Fig. 6: Modelling of the curing data dQ_A/dt at 60°C with $t_d = 0.16558$ d. The model extrapolates the missing curve from t_d to time zero. Used measurement data are shown as black dashed line. To the measured time data the pre-time $t_p = 0.012807$ d was added before the modelling.

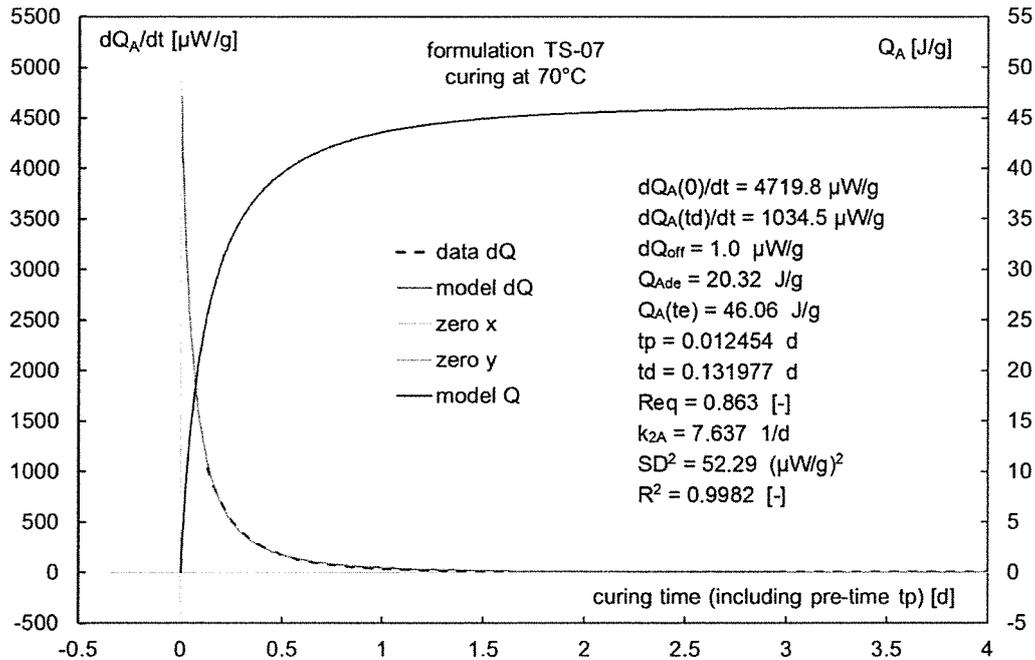


Fig. 7: Modelling of the curing data dQ_A/dt at 70°C with $t_d = 0.131977$ d. The model extrapolates the missing curve from t_d to time zero. Used measurement data are shown as black dashed line. To the measured time data the total pre-time $t_p = 0.012454$ d was added before the modelling.

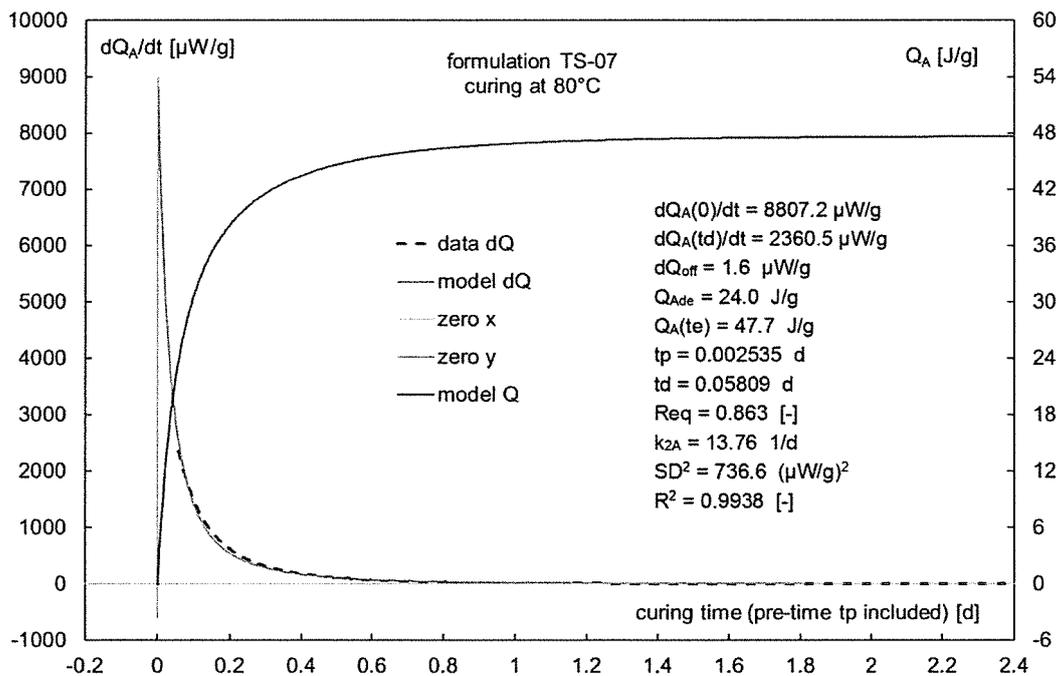


Fig. 8: Modelling of the curing data dQ_A/dt at 80°C with $t_d = 0.05809$ d. The model extrapolates the missing curve from t_d to time zero. Used measurement data are shown as black dashed line. To the measured time data the total pre-time $t_p = 0.002535$ d was added before the modelling.

Table 4: Results of the modelling of the heat generation rates measured during curing of TS-07 samples at three curing temperatures. One column shows the results at 60°C with td (start of modelling) reset to zero.

quantity	unit	60°C, td=0	60°C	70°C	80°C	remark
$dQ_A(0)/dt$	$\mu\text{W/g}$	794.8	2256.7	4719.8	8807.2	from model
$dQ_A(td)/dt$	$\mu\text{W/g}$	750.8	750.8	1034.5	2360.5	experimental
dQ_{off}	$\mu\text{W/g}$	0.02	0.04	1.0	1.6	model input
Q_{Ade}	J/g	25.27	24.6	20.32	24	experimental
$Q_A(te)$	J/g	25.27	43.7	46.1	47.7	from model
tp	d	0.012807	0.012807	0.012454	0.002535	experimental
td	d	0.00	0.16558	0.131977	0.05809	experimental
k_{2A}	1/d	2.345	3.854	7.637	13.76	from model
SD^2	$(\mu\text{W/g})^2$	74.83	69.68	52.29	736.6	from model
$COD-R^2$	-	0.9964	0.9975	0.9982	0.9938	from model

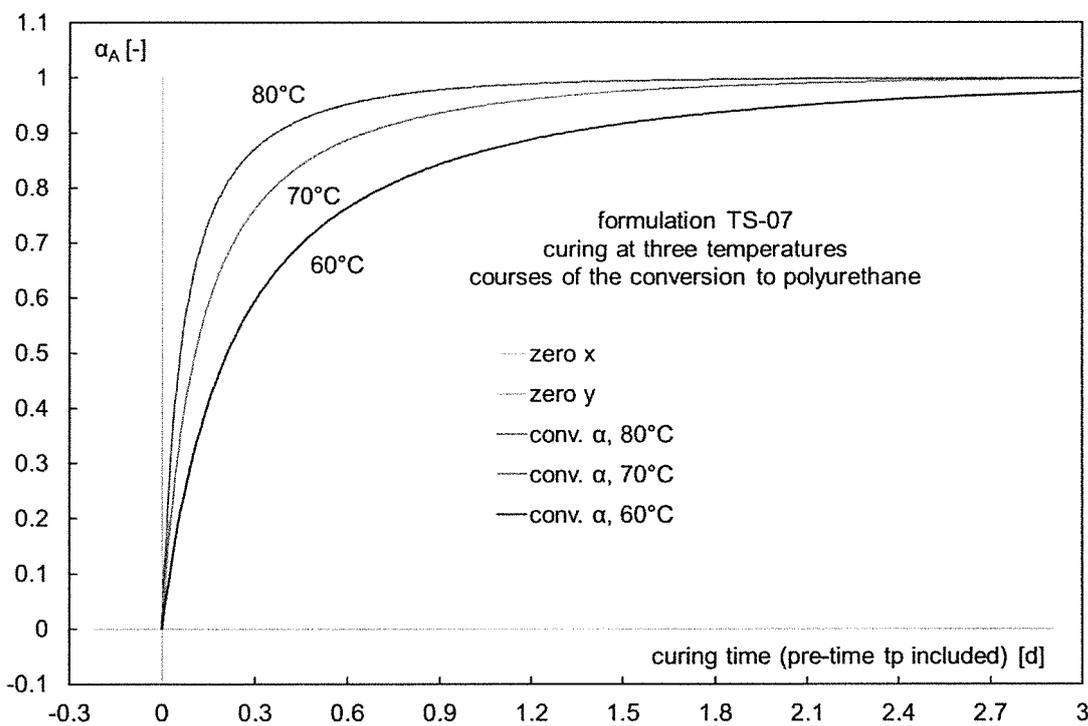


Fig. 9: Conversion of the curing reaction, formation of the urethane compound AB at three curing temperatures.

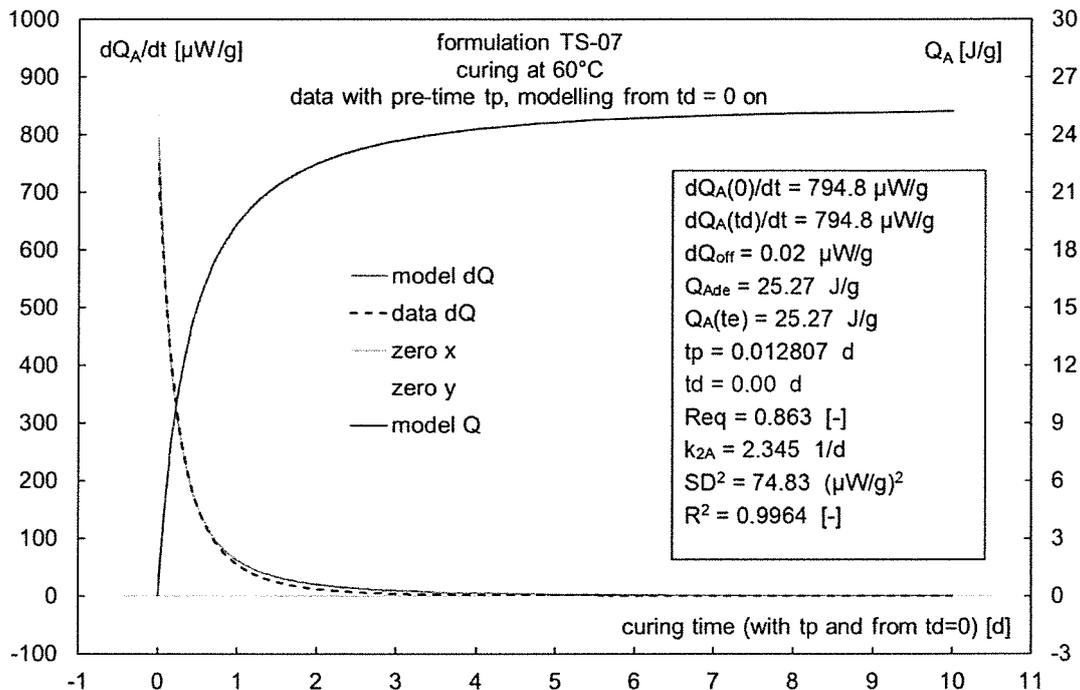


Fig. 10: Modelling of the curing data dQ_A/dt at 60°C with $t_d = 0$, means no extrapolation back to real time zero by the model. Used measurement data are shown as black dashed line. To the measured time data the pre-time $t_p = 0.012807$ d was added before the modelling.

Because of lack of measurement information from begin on of the reaction, one could have the idea to make another way of modelling in that the measurement data are reset to zero from time t_d on. This gives firstly the wrong heat of reaction and secondly it provides with incorrect Arrhenius parameters and incorrect values of reaction rate constants. In Fig. 10 such a modelling is illustrated with the curing at 60°C . The obtained modelling parameters are also given in Table 4 and can be compared with the ones of the correct modelling.

4.2 Pressure measurements

The results of the modelling of the pressure decrease curves are exemplarily shown in Fig. 11 and Fig. 12. In principle, the procedure is the same as with heat generation rate. First, the pre-handling times have to be considered, scaled to the applied curing temperature. Then data must be analysed with respect to the usable start time t_d . Then the modelling is performed with mainly k_{2A} and $p_s(0)$ as fit parameters. The final pressure $p_s(t_e)$ was found by trial. Both initial and final pressure depend on the temperature during the filling of the PCC, which is always lower than the used curing temperature. By temperature increase in the oven, the overpressure is obtained [6].

Fig. 13 shows the formation of the urethane compound AB at two curing temperatures, but as double measurements. Shown are also the pressure decrease curves, which are quite individual, means they do not coincide for the same temperature, but calculated to conversion the two curves at each temperature coincide perfectly. The reason is the different filling temperatures applied, which result in different pressurization.

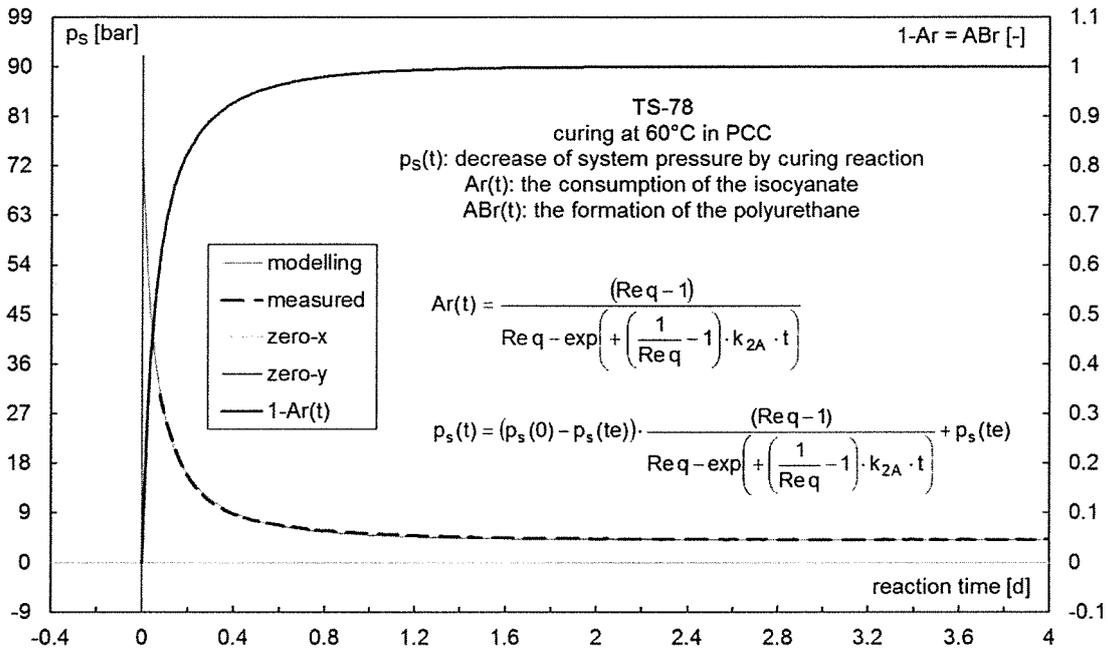


Fig. 11: Modelling of the curing data obtained as system pressure $p_s(t)$ at 60°C in PCC-1 with $t_d = 0.076119$ d. The experimental start pressure was about 34 bar. The model extrapolates the missing curve from t_d to time zero. Used measurement data are shown as black dashed line. To the measured time data the total pre-time $t_p = 0.0156325$ d was added before the modelling.

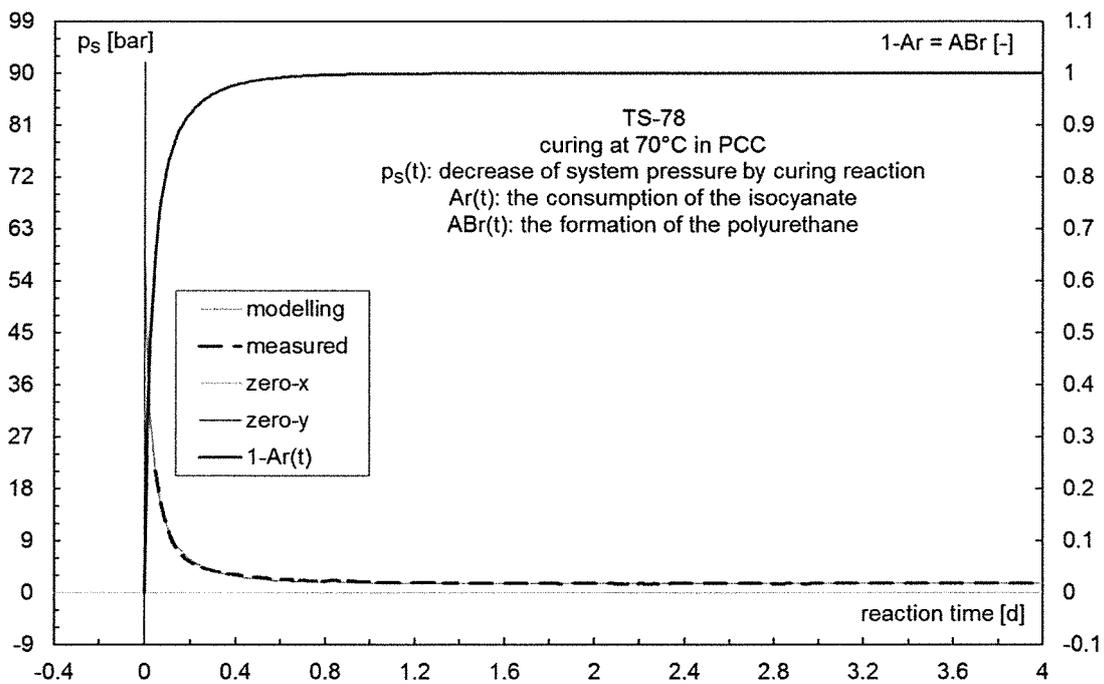


Fig. 12: Modelling of the curing data obtained as system pressure $p_s(t)$ at 70°C in PCC-9 with $t_d = 0.0480106$ d. The experimental start pressure was about 23 bar. The model extrapolates the missing curve from t_d to time zero. Used measurement data are shown as black dashed line. To the measured time data the total pre-time $t_p = 0.0091217$ d was added before the modelling.

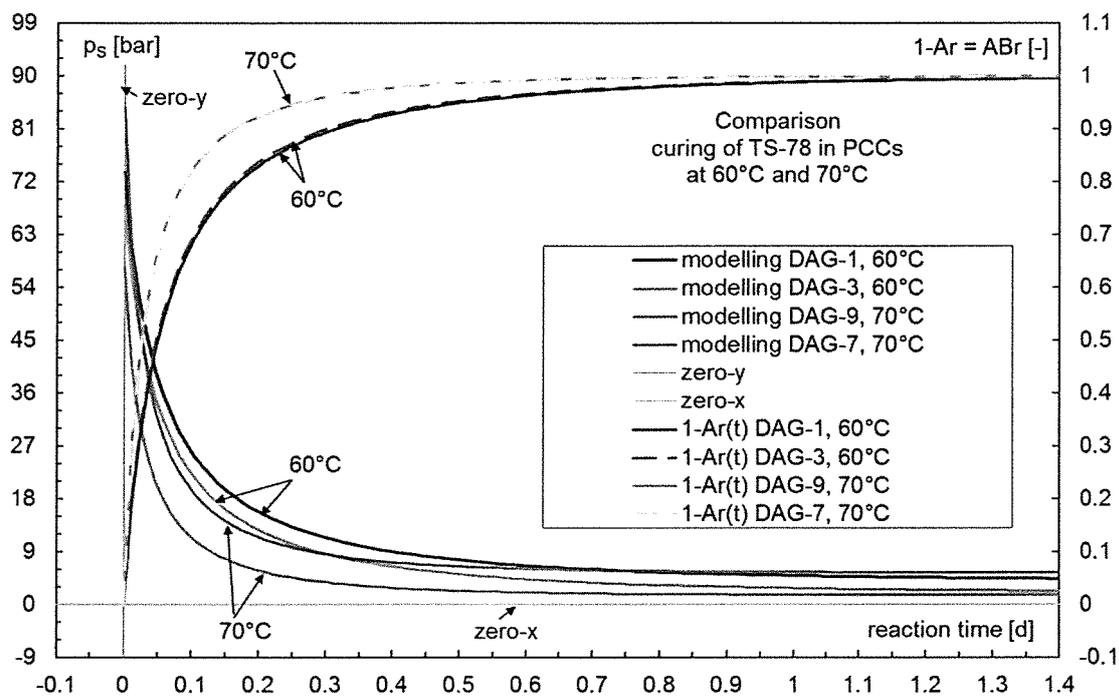


Fig. 13: Conversion of the curing reaction, formation of the urethane compound AB at two curing temperatures, but as double measurements. Shown are also the pressure decrease curves, which are quite individual, means they do not coincide for the same temperature, because of individual filling of the PCCs at slightly different temperatures at filling. But calculated to conversion the two curves at each curing temperature coincide perfectly.

Table 5: Results of the modelling of the pressure decrease by volume shrinkage of formulation TS-78 at two curing temperatures. At each curing temperatures two measurements were performed. The final pressure $p_s(t_e)$ was determined by trial.

quantity	unit	60°C, PCC-1	60°C, PCC-3	70°C, PCC-7	70°C, PCC-9	remark
$p_s(0)$	bar	73.653 ± 0.14	67.897 ± 0.16	84.760 ± 0.11	57.625 ± 0.24	from model
$p_s(t_d)$	bar	30.445	27.716	32.664	21.119	experiment
$p_s(t_e)$	bar	4.13	2.10	5.45	1.60	from model
t_p	d	0.0156325	0.0155612	0.0089227	0.0091217	experiment
t_d	d	0.076119	0.069103	0.0446866	0.0480106	experiment
k_{2A}	1/d	16.542 ± 0.03	17.225 ± 0.04	31.485 ± 0.04	31.703 ± 0.12	from model
SD^2	(bar) ²	0.04856	0.0706	0.01589	0.06089	from model
$COD-R^2$	-	0.9978	0.9965	0.9990	0.9911	from model

5. Discussion

Besides reaction rate constants from heat generation rates determined with microcalorimetry also the heat (enthalpy) of reaction is obtainable with this method. In Table 6 the way from heat generation $Q_A(t_e)$ to the heat of reaction is shown. All three values of $Q_A(t_e)$ and $\Delta H_{R,A}$ are compiled in Table 7 together with some

statistical parameters. The average enthalpy of reaction is found as 100.2 ± 4 kJ/mol. The Arrhenius parameters found with the two types of modelling are listed in Table 8 and the Arrhenius graphs are shown in Fig. 14 and 15. The modelling with td set to zero gives wrong Arrhenius parameters and wrong heats of reaction.

Table 6: Calculation of heat (enthalpy) of reaction related to the conversion of one NCO group. Because the addition reaction between NCO and OH is not changing the gas amount during the reaction, the heat of reaction and the enthalpy of reaction are equal by value.

$Q_A(te)$ [J/g]	45.8	Related to total mass of formulation (average value)
$Q_A(te)$ [J/(g PI)]	305.33	in J/g, related to the mass of polyisocyanate
$Q_A(te)$ [J/(mol-eq PI)]	100179.86	J/mol-eq, related to the mol-eq of polyisocyanate
$\Delta Q_{R,NCO}; \Delta H_{R,NCO}$	100.2	in kJ per mol-eq of polyisocyanate
$\Delta Q_{R,NCO}; \Delta H_{R,NCO}$	100.2	in kJ/mol, per NCO group

Table 7: Compilation of by modelling obtained $Q(te)$ values of TS-07 at the applied three curing temperatures and the corresponding heats (enthalpies) of reaction $\Delta H_{R,NCO}$ with regard to one NCO group. The used curing agent Desmodur™ E305 has an equivalent mass of 328.1 g/mol-NCO.

Curing temp. [°C]	$Q_A(te)$ [J/g]		Curing temp. [°C]	$\Delta H_{R,NCO}$ [kJ/mol-eq]
60	43.7		60	95.6
70	46.1		70	100.8
80	47.7		80	104.3
average [J/g]	45.8		average [kJ/mol-eq]	100.2
std dev [J/g]	1.64		std dev [kJ/mol-eq]	3.57
std dev [%]	3.6		std dev [%]	3.6
Min-dev [%]	4.6		Min-dev [%]	4.6
Max-dev [%]	4.1		Max-dev [%]	4.1

Such values of reaction heats are reported also in literature. In another work [9,10] the exothermal molar heat of reaction ($-\Delta H_R$) was determined to 93 ± 5 kJ/mol for the reaction of one mol-equivalent NCO with one mol-equivalent OH, but in a system HTPB R45M with IPDI. In [11] 108.8 kJ/mol are given and in [12] a value of 100.4 kJ/mol is reported. But also much smaller values can be found in literature, between 77.5 and 104.7 kJ/mol [13], or even only 60.3 kJ/mol [14] and as less than 23.7 kJ/mol-eq, [15], in a range up to 50 kJ/mol-eq, with an average value of 38.4 ± 7.4 kJ/mol-eq [15]. To some extent the molecular structure of the reactants and the used medium have influence on the enthalpy of reaction. But such a wide span indicates some principle problems in determining the correct heat or enthalpy of reaction for the isocyanate addition reaction with alcohols to urethane. Especially the data from [15] suffer because of limited sensitivity of DSC and that the start of the reaction was quite before the start of recordable heat flow in the DSC thermogram.

Table 8: List of the obtained Arrhenius parameters of TS-07 and TS-78 with the modelling using td not zero (correct modelling). With TS-07 a modelling using td set formally to zero and heats of reaction was made.

quantity	TS-78 in PCC td not zero (correct modelling)	TS-07 in microcal. td not zero (correct modelling)	TS-07 in microcal. rescaling of time axis with td set to zero
E_{aA} [kJ/mol]	59.6 ± 2	62.3 ± 1.6	51.5 ± 0.8
Z_A [1/d]	$3.707E+10$	$2.257 E+10$	$2.816 E+8$
$\lg(Z_A$ [1/d])	10.569 ± 0.3	10.354 ± 0.25	8.450 ± 0.12
COD- R^2	0.9979	0.9993	0.9998
$Q_A(te)$ [J/g]	-	45.8 ± 1.6	24.8 ± 2.5
$\Delta H_{R,NCO}$ [kJ/mol-eq]	-	100.2 ± 3.6	54.2 ± 5.5
Remarks	with curing cat. TPB curing with IPDI	no curing catalyst curing with E 305	

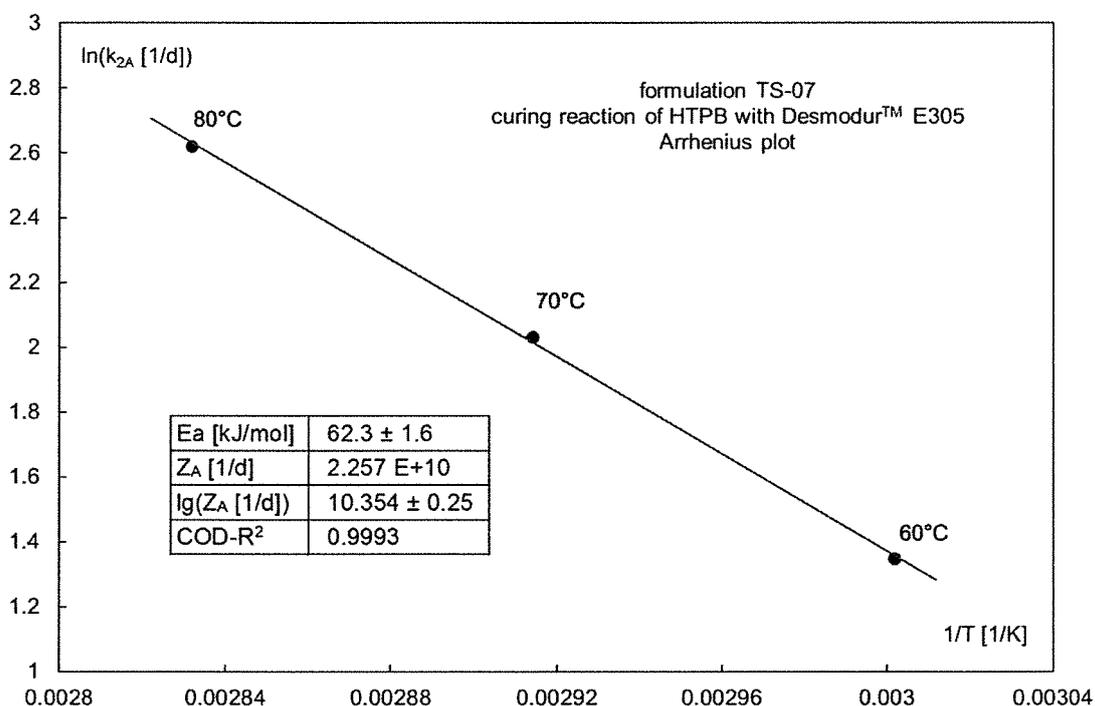


Fig. 14: Arrhenius plot of the reaction rate constants of the curing reaction of TS-07. Determination by modelling with the experimental data with added pre-time t_p and starting from td not re-set to zero (correct modelling).

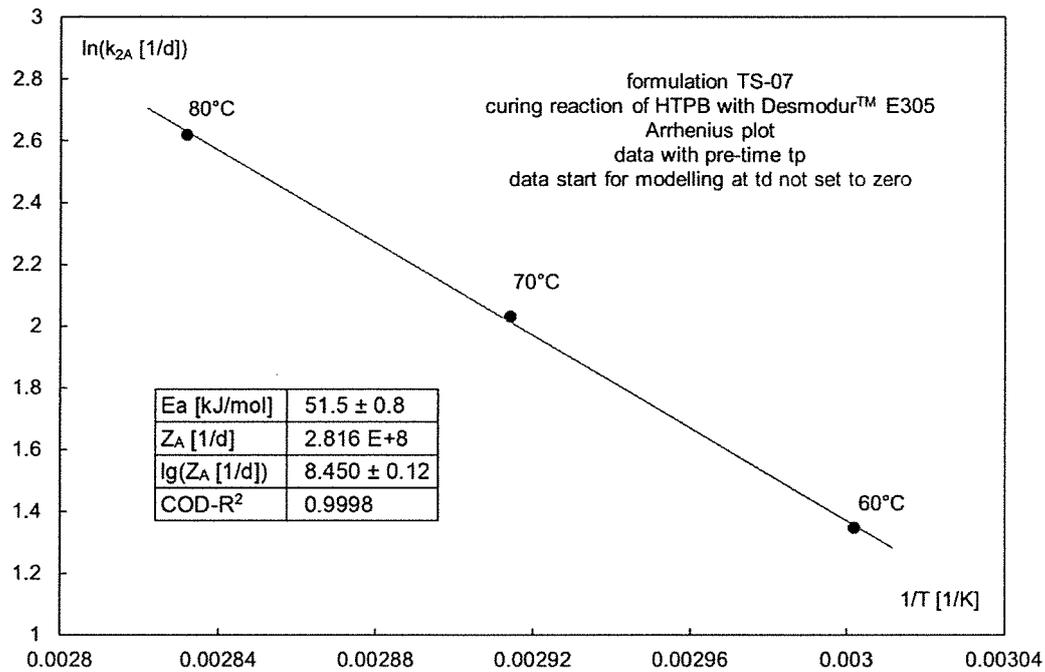


Fig. 15: Arrhenius plot of the reaction rate constants of the curing reaction of TS-07. Determination by modelling with the experimental data with added pre-time t_p and starting from t_d re-set to zero. Different Arrhenius parameters are obtained in comparison to the procedure used with t_d not set to zero.

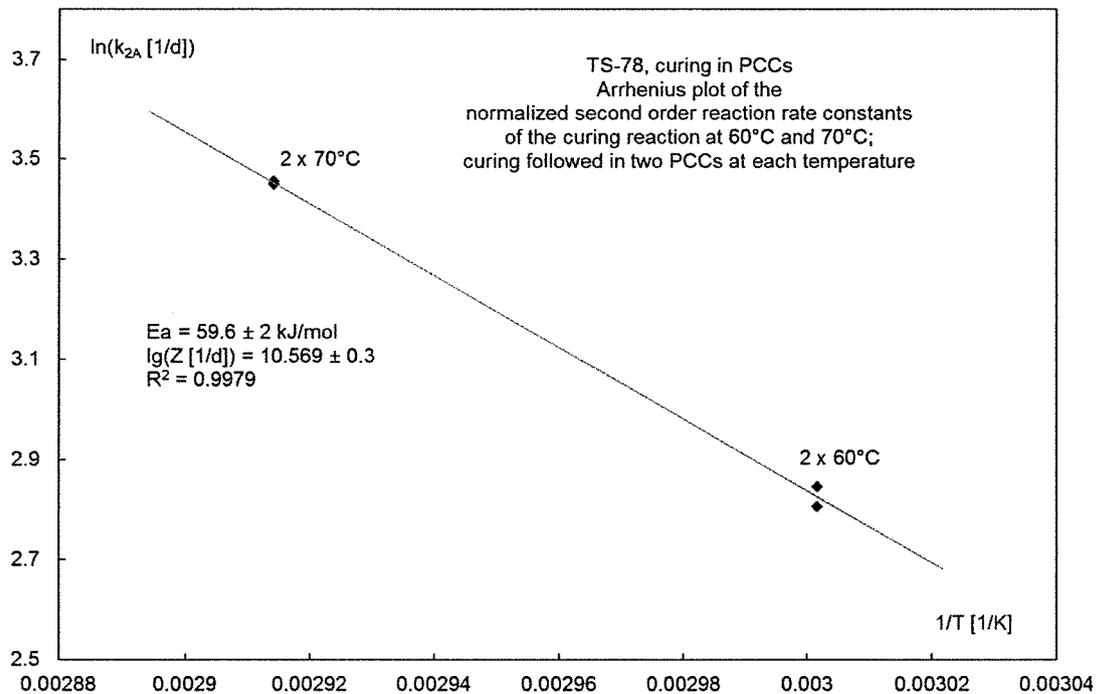


Fig. 16: Arrhenius plot of the reaction rate constants of the curing reaction of TS-78 in PCCs. Determination by modelling with the experimental data with added pre-time t_p and starting from t_d not re-set to zero (correct modelling).

The results from the tracking of the volume shrinkage by decrease of system pressure in PCCs are shown in Fig. 16 as Arrhenius plot. The obtained Arrhenius parameters are congruent with the other data obtained and also found in the literature. The comparison of the reaction behaviour of the pure binder formulation TS-07 and the propellant formulation TS-78 is presented in Fig. 17. The curing of TS-78 proceeds much faster than that of the binder TS-07. The reason is seen in the added curing catalyst TBP in TS-78. But the activation energies are quite similar. Means here the catalyst acts also by increasing the pre-exponential factor. Also the difference in chemical structures of the isocyanates can have an influence.

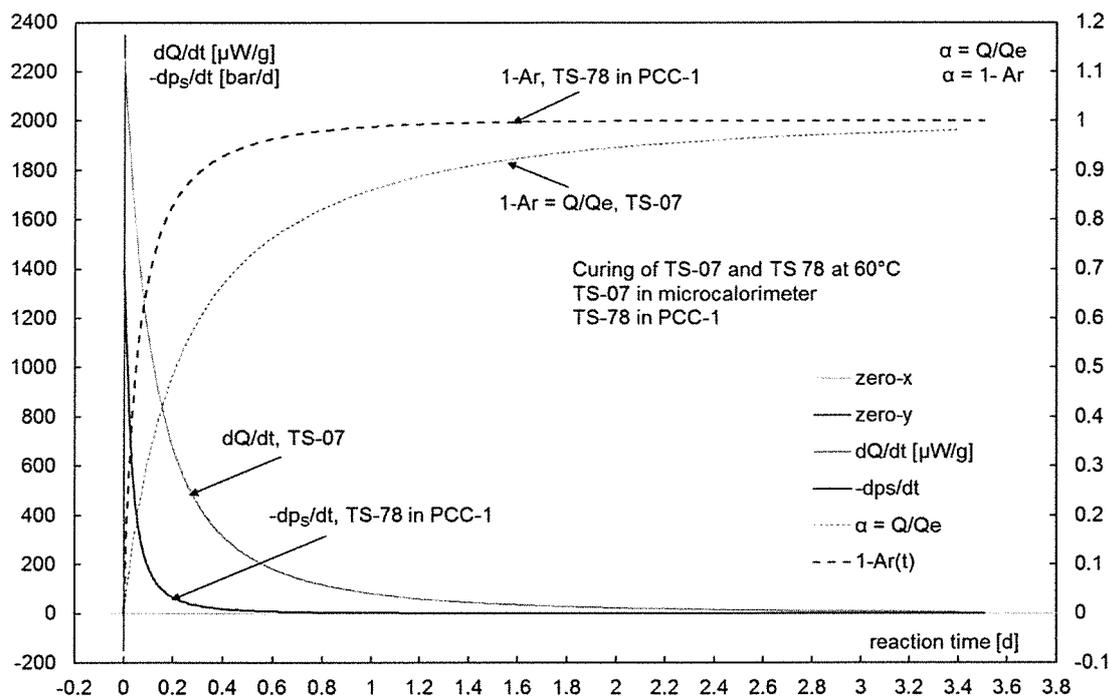


Fig. 17: Comparison of curing behaviour of binder TS-07 (contains no fillers, curing agent E305) and formulation TS-78 (containing AP and Al, curing agent IPDI) at 60°C. The curing of TS-78 proceeds much faster than the one of the binder TS-07.

From the data of the PCCs one should get also the molar reaction volume $\Delta V_{R,A}$ of TS-78 with regard to one molar conversion of the NCO-groups. The data to calculate it are compiled in Table 9. The volumes of the PCCs are set equal to 10.71 cm³ and the 'decompression constant' K is estimated as 18000 bar, the average of the two values given in [9]. The final pressure differences $\Delta p_s = p_s(te) - p_s(0)$ are obtained from Table 5. The final volume difference for the total formulation is calculated from Eq.(30). In average, it is -0.0403 cm³ means about 0.38 % shrinkage in the PCCs. With regard to the reaction mixture HTPB+IPDI the volume must be scaled by the factor 8.614 given in Table 9. It is just the amount scaling to 100% of HTPB+IPDI in the formulation. The shrinkage with regard to only the binder HTPB+IPDI is -0.35 cm³ or -3.24 %. With the molar volume sum of HTPB and IPDI per equivalent and the start concentration of IPDI in equivalent numbers, one gets as molar reaction volume for one NCO equivalent the value of -41.6 cm³/mol-eq in average from all four measurements. The molar volume shrinks by about 3 % caused by the addition reaction. These values depend on the value of the constant K. The results of two further calculations are shown in Table 9 with the values in brackets. From molecular dynamics calculations also values of volume shrinkage can be derived [16].

Table 9: Calculation of the molar reaction volume $\Delta V_{R,A}$ with regard to one molar NCO conversion from the data of the PCCs for the curing of formulation TS-78.

	60°C, PCC-1	60°C, PCC-3	70°C, PCC-7	70°C, PCC-9	average
V_{PCC} [cm ³]	10.71	10.71	10.71	10.71	-
K [bar]	18000	18000	18000	18000	-
$\Delta p_s = p_s(te) - p_s(0)$ [bar]	-69.52	-65.8	-79.31	-56.03	-
$\Delta V_g = V_g(te) - V_g(0)$ [cm ³] per total formulation	-0.041364	-0.039151	-0.047189	-0.033338	-0.040261
$\Delta V_g/V_{PCC}$ [%]	-0.39	-0.37	-0.44	-0.31	-0.38
factor [g/g]	8.614	8.614	8.614	8.614	-
ΔV_{g-sc} [cm ³] per HTPB+IPDI only	-0.3563	-0.3372	-0.4065	-0.2872	-0.3468
$\Delta V_{g-sc}/V_{PCC}$ [%] per HTPB+IPDI only	-3.33	-3.15	-3.80	-2.68	-3.24
V_{mol} [cm ³ /mol-eq] HTPB+IPDI only	1373.14	1373.14	1373.14	1373.14	-
NCO equiv.-nu. [mol-eq]	0.00834315	0.00834315	0.00834315	0.00834315	-
$\Delta V_{R,A}$ [cm ³ /mol] per NCO (with K = 14000 bar)	-42.7	-40.4	-48.7	-34.4	-41.6
(with K = 21000 bar)	(-54.9)	(-52.0)	(-62.6)	(-44.3)	(-53.4)
(with K = 21000 bar)	(-36.6)	(-34.7)	(-41.8)	(-29.5)	(-35.6)
$\Delta V_{R,A}/V_{mol}$ [%] per NCO (with K = 14000 bar)	-3.1	-2.9	-3.6	-2.5	-3.0
(with K = 21000 bar)	(-4.0)	(-3.8)	(-4.6)	(-3.2)	(-3.9)
(with K = 21000 bar)	(-2.7)	(-2.5)	(-3.0)	(-2.2)	(-2.6)

The Arrhenius parameters obtained are compiled in Table 10 and compared with literature data. Data from curing catalyst containing systems and without catalyst are given. The chemical structures of two typical curing catalysts can be seen in Fig. 18 and Fig. 19.

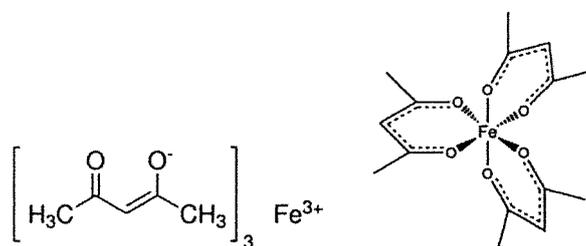


Fig. 18: Chemical structure of FeAA, iron(III) acetylacetonate or tris(acetylacetonato) iron(III).

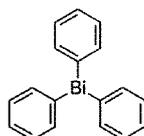


Fig. 19: Chemical structure of triphenylbismuth(III).

The agreed mechanism of a curing catalyst is that it first reduces the activation energy and /or second enhance the pre-factor. This is well illustrated by the work in [15] and some selected data are given in Table 10. For a substance to be named as catalyst one criterion is that it should be effective in small concentrations. The consequence is that a limiting value of reduced activation energy E_a is reached with increasing catalyst concentration. This can be seen in the Fig. 20 and Fig. 21. The data of [15] are taken and described with two parametric models. The first model is a sum of two exponentials, Eq.(45), which can describe nearly always such data course behaviour as shown by the catalyst action on the activation energy reduction. With this description, the low limit for E_a is found as 58.7 kJ/mol. The other model is shown in Eq.(36). It is related to the expression of a second order reaction and gives a more reasonable behaviour of the E_a course for higher catalyst concentrations. The limit value for E_a is found as 60.8 kJ/mol.

Table 10: List of Arrhenius parameters of the urethane formation under different conditions and from different formulations, TS-07, AV00, TS-38, TS-44, TS-78.

E_a [kJ/mol]	$\lg(Z[1/d])$	temp. range [°C]	curing catalyst, conc. [mass-%]	system	reference
63.3 ± 1.6	10.354 ± 0.25	Isothermal in HFMC 60, 70, 80	-	HTPB-E305	This work TS-07
61.4 ± 4.4	10.081 ± 4.1	Isothermal in HFMC 70, 80, 90	TBP, 0.04	HTPB-IPDI	[9] AV00
62.8 ± 2.7	10.468 ± 0.37	Dynamic by DSC 22 to 220°C	TPB, 0.02	HTPB-IPDI	[1] TS-38
63.0 ± 0.46	10.552 ± 0.06	Dynamic by DSC 22 to 220°C	TPB, 0.02	HTPB-IPDI	[1] TS-44
59.6 ± 2.0	10.569 ± 0.3	PCC 60°C, 70°C	TPB, 0.02	HTPB-IPDI	This work TS-78 [5]
73	12.024	Dynamic by DSC, 5°C/min 22 to 200°C	-	HTPB-IPDI	[15]
63.0	12.024	Dynamic by DSC, 5°C/min 22 to 200°C	FeAA, 0.02	HTPB-IPDI	[15]
61.1	12.024	Dynamic by DSC, 5°C/min 22 to 200°C	FeAA, 0.2	HTPB-IPDI	[15]
60.2	12.024	Dynamic by DSC, 5°C/min 22 to 200°C	FeAA, 0.5	HTPB-IPDI	[15]

Other DSC evaluations were performed with the binder formulations TS-38 and TS-44 [1], based on HTPB-IPD, DOA as plasticizer and the antioxidant Vulkanox™ BKF. As curing catalyst, TPB was used in both formulations. The evaluations were achieved with a generalized Kissinger equation. This Eq.(47) correlates peak maximum temperature T_p (in Kelvin), conversion α_p up to peak maximum and heat rate h with the rate expression for a reaction of n th order, using the Arrhenius expression for the rate constant, Eq.(48).

Only the peak maximum temperature T_P is considered a function of heat rate h . Generally, the Kissinger evaluation can be applied, when ‘simple’ reactions are considered, means reactions with only one reaction step. The results are shown in Fig. 22 and Fig. 23 as Kissinger plots. From Table 10, one recognizes that the catalysed curing reactions of HTPB-IPDI all have activation energies in a narrow value range. The pre-exponential factors differ between the groups (this work and [15]). The cause could be the interference of the kinetic compensation effect, which was quite pronounced in the data of [15]. Some correction were made but probably the Z-factor is still too high. The uncatalyzed curing of TS-07 has a relatively low activation energy compared with the assigned value of 73 kJ/mol in [15]. A reason may be the different isocyanate types.

$$Ea(c) = A + B1 \cdot \exp(-k1 \cdot c) + B2 \cdot \exp(-k2 \cdot c) \quad (45)$$

$$Ea(c) = \frac{Ea(0) - Ea(ce)}{1 + k \cdot c} + Ea(ce) \quad (46)$$

$$\ln\left(\frac{h}{T_P(h)^2}\right) = \ln\left(n \cdot (1 - \alpha_p)^{(n-1)} \cdot \frac{R}{Ea} \cdot Z\right) - \frac{Ea}{R \cdot T_P(h)} \quad (47)$$

$$\frac{d\alpha(T)}{dt} = Z \cdot \exp\left(-\frac{Ea}{R \cdot T}\right) \cdot (1 - \alpha(T))^n \quad (48)$$

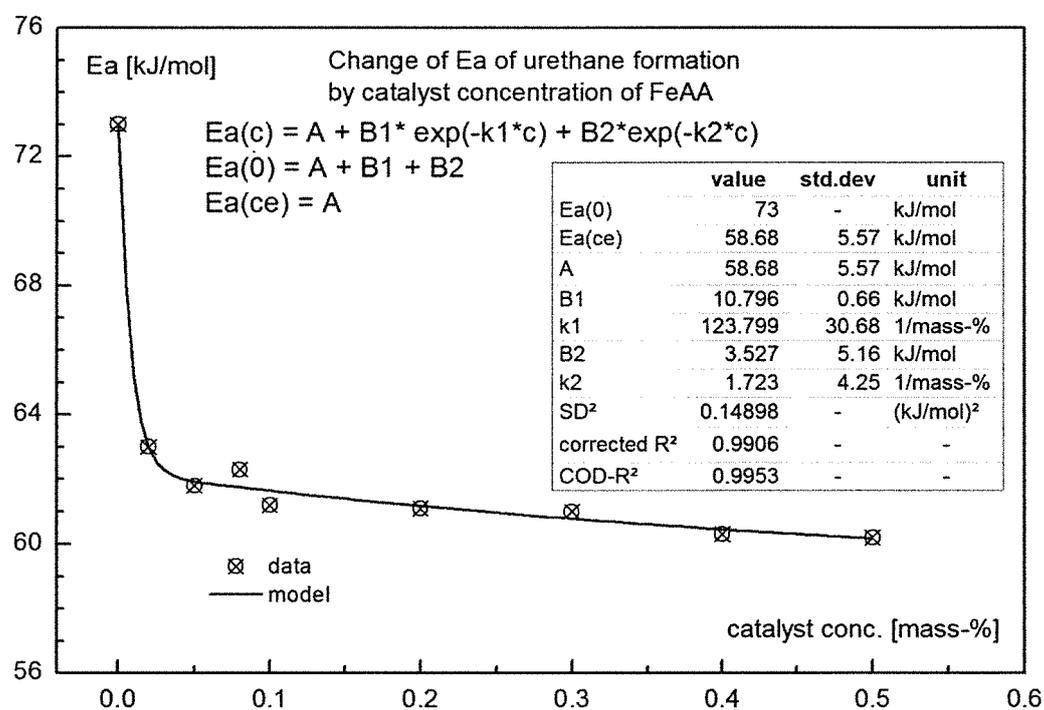


Fig. 20: Course of activation energy of the urethane formation as function of the concentration of curing catalyst FeAA. Parametric description is made by a double exponential function. Data from [15].

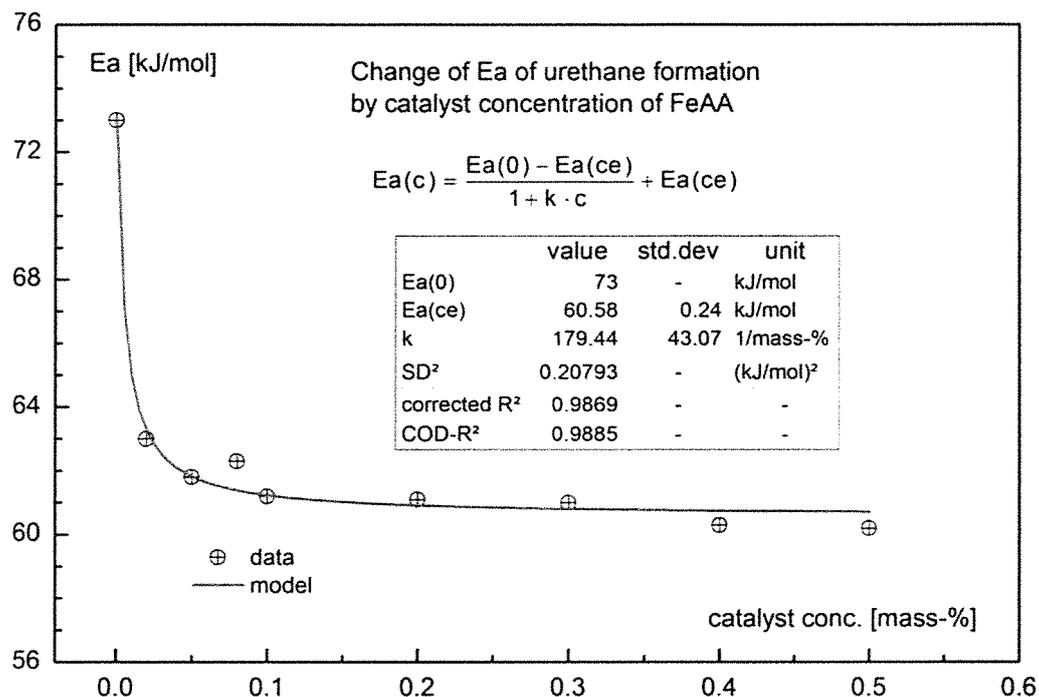


Fig. 21: Course of activation energy of the urethane formation as function of the concentration of curing catalyst FeAA. Parametric description is made by an equation for a formal reaction of second order. Data from [15].

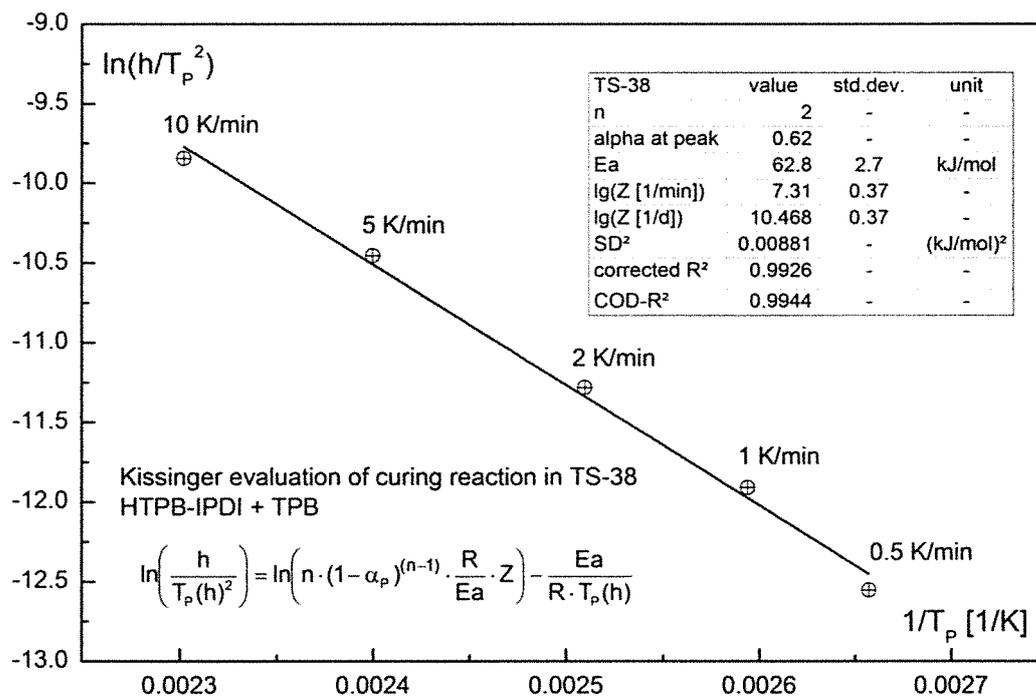


Fig. 22: Generalized Kissinger evaluation of curing reaction of binder formulation TS-38 [1] using DSC thermograms obtained at five different heat rates. Reaction of second order and conversion at peak maxi-

mum $\alpha_p = 0.62$. TS-38 comprises of HTPB-IPDI (Req = 0.869), 25 mass-% DOA, 1.53 mass-% Vulkanox™ BKF and 0.02 mass-% (phr) TPB.

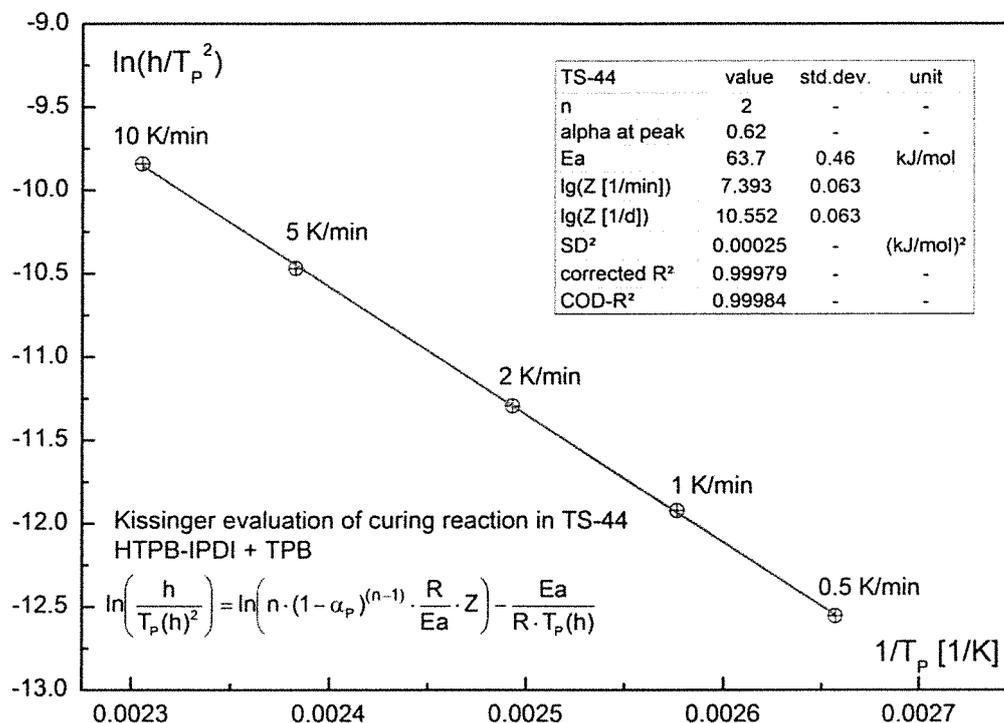


Fig. 23: Generalized Kissinger evaluation of curing reaction of binder formulation TS-44 [1] using DSC thermograms obtained at five different heat rates. Reaction of second order and conversion at peak maximum $\alpha_p = 0.62$. TS-44 comprises of HTPB-IPDI (Req = 0.869), 25 mass-% DOA, 1.53 mass-% Vulkanox™ BKF and 0.02 mass-% (phr) TPB.

6. Summary and conclusion

The curing reaction between pre-polymer HTPB and isocyanate, which forms a polyurethane, is a bimolecular reaction or a reaction of second order between the OH groups of HTPB and the NCO groups of the isocyanate. Here the isocyanate was Desmodur™ E305, which is a chain-elongated HDI. This means both isocyanate groups are equal and have equal reactivity. Also the OH groups of HTPB can be treated as of equal reactivity, most of them are primary HO-CH₂ groups [17]. Because the reaction is straight forward, the basic second order reaction with the corresponding rate equation is used, whereby a difference in start concentration between NCO and OH groups is incorporated, which corresponds to the most real cases in formulating rocket propellants. The normalized reaction rate constant of a second order reaction depends on the initial concentration of the leading reactant (minor component), here the NCO concentration. The curing reaction of HTPB-isocyanate starts immediately after adding the isocyanate to the polyol component – this is the case with every second order reaction also as epoxide curing. The curing reaction can increase in complexity by high heat output and / or by autocatalytic effects and / or by side reactions of the curing agent. With the urethane formation, no autocatalysis happens. But the unreacted isocyanate can react with the urethane group to form allophanate species and these can further react with isocyanate to biuret. These reactions take place if one uses normal alcohols. It is assumed that with polymeric alcohols as HTPB these consecutive side reactions are of minor importance, especially when NCO is the minor component.

On the one hand curing reaction was followed by heat flow microcalorimetry, which determines the heat generation rate dQ/dt . The kinetic model has to be developed to describe directly this quantity. A problem with second order reaction is that the start time of the reaction and the one of usable measurement data is firstly in most cases not coinciding and secondly the begin of usable measured data is often delayed, because of equilibration effects or of the time necessary to homogenize the reaction mixture. Further preparation times may add before the measurement can even be started. Microcalorimetry is a good method to follow curing, because one gets firstly the kinetic information and secondly the thermodynamic one as heat or enthalpy of reaction. It is sensitive enough to obtain also at lower temperatures useful data with high signal to noise ratio. However, because of the always present difference between start of the measurement and start of the curing reaction the information on the reaction heat is incomplete. Moreover, even the kinetic parameters may be determined wrongly, if not special precautions are taken to include by reconstructing the lost part of the reaction in the beginning. Indeed, a solution was found, which makes it possible to reconstruct from the measured course the missing part of the dQ/dt curve. Moreover, the pre-handling before the measurement can be included, which resets the start of the modelling to the point, where the isocyanate is added to the pre-mix.

The kinetic data obtained from the modelling of the curing of the binder formulation TS-07 deliver an activation energy of about 63 kJ/mol. This is in agreement with DSC measurements at several heat rates to follow the curing of similar binder formulations, on the base HTPB-IPDI. The heat of reaction was determined to about 100 kJ/mol. This is in agreement to former investigations and also with literature data. But in comparing literature data, special care must be taken to find out, if the measurement has included the complete curing and what measurement method was used. For example in following the isocyanate curing reaction with DSC, a lot of the reaction has already happened before any recordable signal in the DSC thermogram is occurring. This means that DSC investigations have determined mostly to small values for the heat of reaction. In using the so-named Kissinger evaluation one should take the generalized form, means the one, which considers the reaction order. The usual Kissinger expression is valid only for a simple reaction of first order.

Another method to follow the cross-linking reaction between polyol and polyisocyanate is based on the volume shrinkage caused by this reaction. The reaction mixture is filled in a closed volume under slight overpressure and the system pressure decreases with the conversion of the reaction. The reaction kinetic results fit well to the ones obtained with the thermoanalytical methods.

Acknowledgements

Dr. Tijen Seyidoglu is thanked for her post-doctoral work at Fraunhofer ICT and providing with many rocket propellant based formulations, their characterizations and insights in their behaviour. Dipl. Ing. Günter Mußbach has constructed the PCC in the frame of his PhD work at Fraunhofer ICT and made all the not trivial measurement operations with it.

7. Appendix

7.1 Reaction types of isocyanate

The following Fig. A1 to A2 show schematically the reactions of isocyanate with an OH-compound to urethane, from there to allophanate and from there further to biuret. In Fig. A1 also the formation of the complex AB* between NCO-group and alcohol is shown. The kinetic formulation is shown in Eq.(A1) to Eq.(A3). The corresponding reaction rate systems are given in Eq.(A4) up to allophanate and in Eq.(A5) up to biuret. If one would use such extended modelling to describe the curing, then one needs the experimental

information on the time courses of A, B and AB or even up to AAB to apply Eq.(A5). This solving is achievable only by numerical integration and to get the reaction rate constants as fit parameters the full data information on A, A and AB is needed. Obviously, this is not always achievable and with measurements like heat generation rate, which are 'global' or summing-up over all reactions, only a simplified description or modelling is possible.

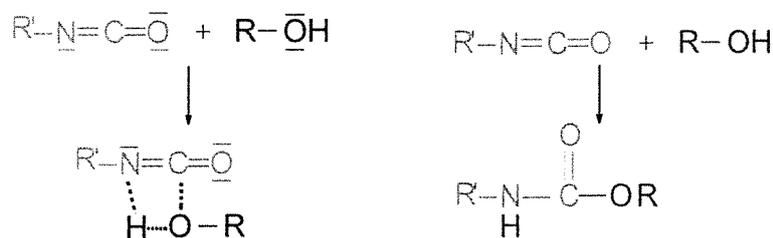


Fig. A1: Left. Complex formation between alcohol and NCO group. Right: Urethane formation by addition of isocyanate to alcohol.

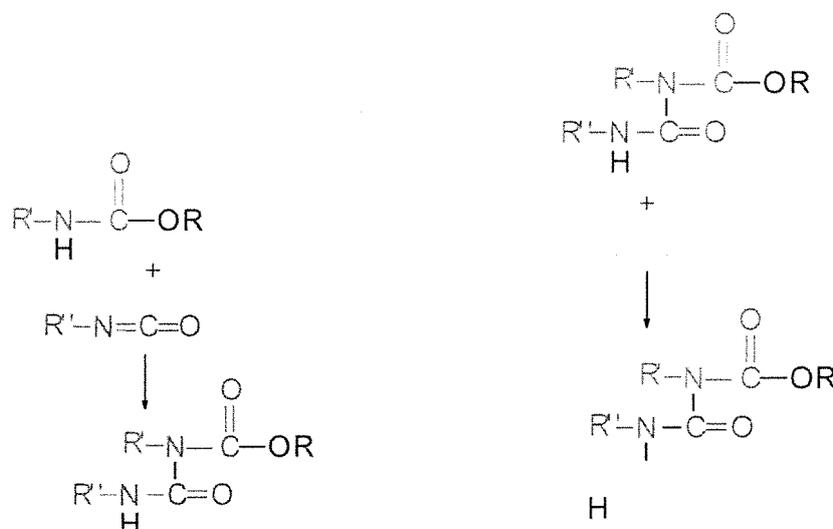


Fig. A2: Left: Allophanate formation by addition of isocyanate to urethane. Right: Addition of isocyanate to allophanate forms biuret.

7.2 Reaction schemes with consecutive isocyanation

In the following equations, the reactant symbols have the meanings:

A = NCO

B = OH

AB = urethane

AAB = allophanate

AAAB = biuret

AB* = complex between R-NCO and R'-OH





Sometimes the reaction scheme comprising Eq.(A1) and Eq.(A2) are named autocatalytic. This is wrong. To have a real autocatalytic reaction course the second reaction, here Eq.(A2), would have to form the same product again, which has opened this reaction. This is not the case here. The character of this reaction system is consecutive, not autocatalytic.

Without reaction Eq.(A3):

$$\left. \begin{aligned} \frac{dA(t)}{dt} &= -k_{21} \cdot A(t) \cdot B(t) - k_{22} \cdot A(t) \cdot AB(t) \\ \frac{dB(t)}{dt} &= -k_{21} \cdot A(t) \cdot B(t) \\ \frac{dAB(t)}{dt} &= +k_{21} \cdot A(t) \cdot B(t) - k_{22} \cdot A(t) \cdot AB(t) \\ \frac{dAAB(t)}{dt} &= +k_{22} \cdot A(t) \cdot AB(t) \end{aligned} \right\} \quad (A4)$$

All three reactions Eq.(A1) to Eq.(A3):

$$\left. \begin{aligned} \frac{dA(t)}{dt} &= -k_{21} \cdot A(t) \cdot B(t) - k_{22} \cdot A(t) \cdot AB(t) - k_{23} \cdot A(t) \cdot AAB(t) \\ \frac{dB(t)}{dt} &= -k_{21} \cdot A(t) \cdot B(t) \\ \frac{dAB(t)}{dt} &= +k_{21} \cdot A(t) \cdot B(t) - k_{22} \cdot A(t) \cdot AB(t) \\ \frac{dAAB(t)}{dt} &= +k_{22} \cdot A(t) \cdot AB(t) - k_{23} \cdot A(t) \cdot AAB(t) \\ \frac{dAAAB(t)}{dt} &= +k_{23} \cdot A(t) \cdot AAB(t) \end{aligned} \right\} \quad (A5)$$

7.3 Reaction schemes with intermediate complex AB*

In the literature the reaction scheme Eq.(A6) + (A7) can be found. The alcohol or OH component is activating the NCO group by forming an addition complex. Then a second alcohol molecule is finally reacting with the NCO group to urethane and the first alcohol molecule is released. One can reduce this reaction scheme to the one shown in Eq.(A9) + (A10) which shows only the intermediate complex AB*. The analytical integration of Eq.(A8) is not achievable. The reaction rate equation system Eq.(A11) can be integrated, but the solution is not handsome, because it contains integrals to be solved numerically for AB and AB*. The solution of A is the same as given above in Eq.(7). This means one has also in this case a reaction of second order.





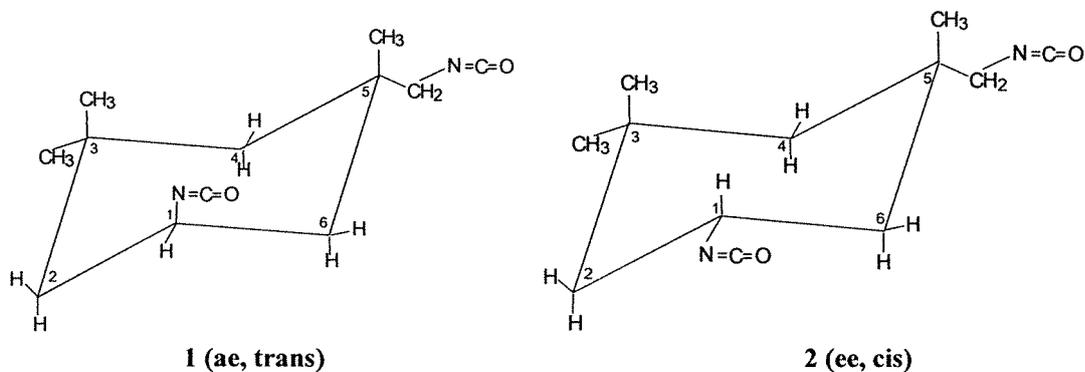
$$\left. \begin{aligned} \frac{dA(t)}{dt} &= -k_{21} \cdot A(t) \cdot B(t) \\ \frac{dB(t)}{dt} &= -k_{21} \cdot A(t) \cdot B(t) \\ \frac{dAB^*(t)}{dt} &= +k_{21} \cdot A(t) \cdot B(t) - k_{22} \cdot B \cdot AB^*(t) \\ \frac{dAB(t)}{dt} &= +k_{22} \cdot B(t) \cdot AB^*(t) \end{aligned} \right\} \quad (A8)$$



$$\left. \begin{aligned} \frac{dA(t)}{dt} &= -k_{21} \cdot A(t) \cdot B(t) \\ \frac{dB(t)}{dt} &= -k_{21} \cdot A(t) \cdot B(t) \\ \frac{dAB^*(t)}{dt} &= +k_{21} \cdot A(t) \cdot B(t) - k_{22} \cdot AB^*(t) \\ \frac{dAB(t)}{dt} &= +k_{22} \cdot AB^*(t) \end{aligned} \right\} \quad (A11)$$

7.4 Further aspects to be considered

The situation is further complicated, in that the polyisocyanate may have NCO groups of different reactivity and also of different sterical arrangements and therefore sterical hindrance. The often used IPDI (isophorone diisocyanate) has such complications in that the two NCO sites have different reactivity, see Fig. A3.



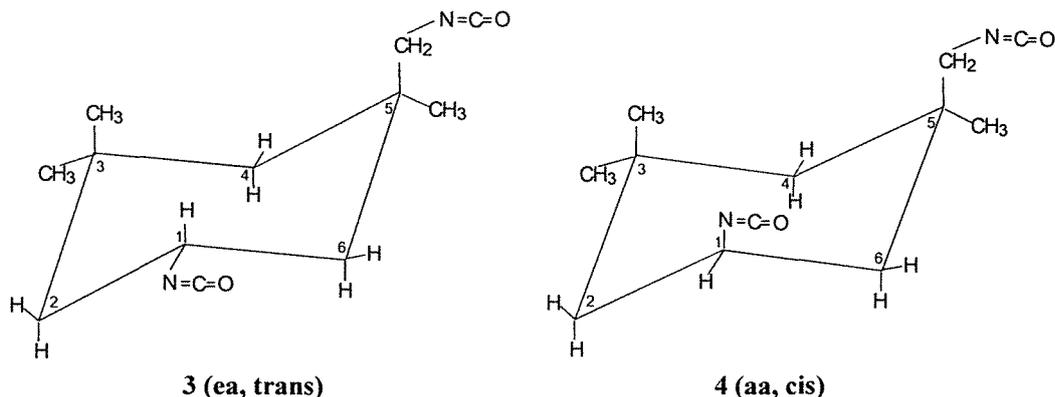


Fig. A3: Four conformers of IPDI (isophorone diisocyanate) resulting from different conformational positions (a = axial, e = equatorial) of the two NCO groups. In commercial IPDI mostly conformers 2 and 3 are present in a ratio 75:25 [18]. The uncatalyzed reactivity ratio of the two NCO groups is about 5.5 for ring-NCO to CH₂-NCO. With catalysts, the reactivity can be equalized or even reverted [18].

Further, with IPDI one has formally to consider four sterical conformations, but in practice only two are present in the product. HDI (hexane diisocyanate) is symmetrical; both NCO groups have the same reactivity. But if one NCO group has reacted the other may be reduced in reactivity by reduced diffusional mobility.

For isophorone diisocyanate one can use the following reaction kinetic description. Start is the description of the reaction of the two isocyanate groups, Eq.(A12). The reactivity of all OH groups of the polyol is seen equal. Each NCO group forms an own urethane. Note that not the formation of the network is followed by the kinetic methods, but the formation of urethane groups. Because the two NCO groups are fixed together in one molecule, the relations Eq.(A13) to A(15) hold. The formation of total urethane groups is according to Eq.(A16).



$$A_1(0) = A_2(0) \quad (A13)$$

$$A(0) = A_1(0) + A_2(0) \quad (A14)$$

$$\text{Req} = \frac{A(0)}{B(0)} = \frac{A_1(0)}{B(0)} + \frac{A_2(0)}{B(0)} = 0.5 \cdot \frac{A(0)}{B(0)} + 0.5 \cdot \frac{A(0)}{B(0)} \quad (A15)$$

The total number of urethane groups is obtained by Eq.(A16):

$$AB(t) = A_1B(t) + A_2B(t) \quad (A16)$$

$$\begin{array}{l}
 B(t) = B(0) - (A_1(0) - A_1(t)) - (A_2(0) - A_2(t)) \\
 B(t) = B(0) - A(0) + A_1(t) + A_2(t)
 \end{array}
 \quad \left. \vphantom{\begin{array}{l} B(t) = B(0) - (A_1(0) - A_1(t)) - (A_2(0) - A_2(t)) \\ B(t) = B(0) - A(0) + A_1(t) + A_2(t) \end{array}} \right\} \quad (A17)$$

The formulation of the model follows the way described above. Two reaction rate equations are obtained, see Eq.(A18). They are coupled via their competition on the polyol B, here already substituted by the relation between A_1 , A_2 and B, given in Eq.(A17). These two rate equations cannot be integrated to an analytical expression for $A_{1,r}(t)$ and $A_{2,r}(t)$. They must be solved by numerical integration and subsequent fit to the experimental data in order to determine the two rate constants. For this, both the concentration decreases of the two NCO groups must be measured.

$$\left. \begin{aligned} \left(\frac{dA_{1,r}(t)}{dt} \right) \Big|_T &= -k_{A1} \cdot A_{1,r}(t) \cdot \left(\frac{2}{\text{Req}} - 2 + A_{1,r}(t) + A_{2,r}(t) \right) \\ \left(\frac{dA_{2,r}(t)}{dt} \right) \Big|_T &= -k_{A2} \cdot A_{2,r}(t) \cdot \left(\frac{2}{\text{Req}} - 2 + A_{1,r}(t) + A_{2,r}(t) \right) \end{aligned} \right\} \quad (\text{A18})$$

Additionally when the viscosity gets higher, the bimolecular reactions become diffusion controlled, at least from the so called gel point on. The gel point is best determined by a liquid state rheometer in oscillatory mode. It is defined as the crossing of storage shear modulus G' and loss shear modulus G'' with curing time.

8. Abbreviations

Al	aluminum
AO	antioxidant
AP	ammonium perchlorate
BKF	antioxidant Vulkanox™ BKF, Bayer Material Science, Germany
DAG	Druckaushärtegefäß, same as PCC
DBST	Dual bond stress and temperature sensor; measuring pressure and temperature; product of Micron Inc., Simi Valley, CA, USA
DOA	dioctyl adipate, plasticizer
DSC	Differential Scanning Calorimetry
E305	NCO curing agent based on HDI elongated by short polyether chain; Desmodur™ E305, Bayer Material Science, Germany
HDI	NCO curing agent, hexamethylene diisocyanate or hexane diisocyanate
HFMC	Heat Flow MicroCalorimetry; the instruments of type TAM™ are such devices to measure heat generation rate at relatively low temperatures
HTPB R45 HTLO	hydroxyl-terminated polybutadiene, type R45 HTLO
HTPB R45 M	hydroxyl-terminated polybutadiene, type R45 M
HX 878	bonding agent for AP, from company MACH I
IPDI	isophorone diisocyanate, NCO curing agent
Irganox™ 565	antioxidant
phr	parts per hundred rubber; means to a basic composition with already; 100 mass-% of several ingredients are given; some additives are added in mass-%; the total composition adds then up to more than 100 mass%
PCC	Pressure curing cell, same as DAG
Req	equivalent ratio NCO/OH in equivalents with regard to functional groups; $\text{Req} = A(0)/B(0)$
TPB	triphenyl bismuth, curing catalyst

TS-07	investigated formulation manufactured at ICT [1]
TS-38	investigated formulation manufactured at ICT [1]
TS-44	investigated formulation manufactured at ICT [1]
TS-78	investigated formulation manufactured at ICT [1, 5]
Vulkanox™ BKF	antioxidant, same as BKF
TAM™	Thermal Activity Monitor, heat flow microcalorimeter (HFMC), trade-mark of TA Instruments, Newcastle, Delaware, USA;
$(-\Delta H_{R,A})$	molar enthalpy of reaction; negative sign converts exothermal values to positive ones, with respect to molar conversion of reactant A
$\Delta V_{R,A}$	molar volume of reaction, molar reaction volume, with respect to molar conversion of reactant A
α_A	degree of conversion of reactant A
α_P	degree of conversion at peak maximum in DSC thermograms
$\Delta Q_{R,A}$	molar heat of reaction; in value very nearly equal to enthalpy of reaction for polyaddition reaction, with respect to molar conversion of reactant A
$A(0)$	start concentration (molar) of isocyanate
$B(0)$	start concentration (molar) of OH
dQ/dt	generated heat rate or heat generation rate (HGR), in $\mu W/g$ here originating from the reaction between R-NCO and R'-OH
dQ_{off}	heat generation rate not originating from investigated reaction
E_a	activation energy in Arrhenius expression
h	heat rate applied in DSC
k_2	bimolecular reaction rate constant in 1/time/concentration
k_{2A}	normalized bimolecular reaction rate constant in 1/time
$\lg(x)$	decadic logarithm of x (logarithm to base 10)
n	reaction order of simple reactions (means not composed reactions)
Q	heat generation, obtained by integration of dQ/dt over time
$Q(te)$	generated heat at the end of measurement at time t_e in J/g
Q_{de}	generated heat from time t_d to time t_e
R	general gas constant; $R = 8.31441 \text{ J/mol/K}$
R^2	standard correlation coefficient (COD, coefficient of determination)
SD^2	squared standard deviation
T	temperature in Kelvin
t_d	start time for data used in modelling
t_e	end time of measurement or data evaluation; ideally time t_e is so long that not further changes in data is observed
T_p	temperature at peak maximum in DSC thermograms, in Kelvin
t_p	total pre-handling time, before start of the measurement
Z	pre-exponential factor in Arrhenius expression

9. References

[1] Tijen Seyidoglu, post-doctoral stay at Fraunhofer ICT, April 2014 to July 2015. Manufacturing of all formulations of type TS-xx and their characterization. TS greatly acknowledges the grant from the Scientific and Technological Research Council of Turkey (TÜBİTAK) under the name of 2219-International Post Doc Fellowship Programme, which enabled the research in Fraunhofer ICT.

[2] Datasheet of Desmodur™ E305. Coatings, Adhesives & Specialties, Bayer Material Science AG. D-51368 Leverkusen, Germany. **2011**.

[3] Seyidoglu, T.; Bohn, M.A.: *Modelling of Loss Factor Curves Obtained by Torsion-DMA of HTPB and GAP Based Binders manufactured with Different Curing Agents and Plasticizers*. Paper 118, pages 118-1 to 118-26 in Proc. of the 46th International Annual Conference of ICT on ‘Energetic Materials – Performance, Safety and System Applications’, June 23 to 26, 2015, Karlsruhe, Germany. ISSN 0722-4087. Fraunhofer-Institut fuer Chemische Technologie (ICT), D-76318 Pfinztal, Germany. **2015**.

[4] Bohn, M. A.: *Safety analysis of a single base propellant for automotive use with heat generation rate*, Proceed. of 41st Int. Ann. Conference of the Fraunhofer ICT, paper 116, pages 116-1 to 116-26. Karlsruhe, Germany, June 29 to July 2, **2010**.

[5] Seyidoglu, T.; Bohn, M.A.: *Effect of Butacene[®] on ageing of composite propellants*. Proceedings of 19th Seminar on “New Trends in Research of Energetic Materials”, pp 904-925. ISBN (print) 978-80-7395-976-0; ISBN (CD) 978-80-7395-977-7; 2016. University of Pardubice, Pardubice, Czech Republic, April 20-22, **2016**.

[6] Mußbach, G.; Bohn, M. A; Tussiwand, G.: *Monitoring of the curing reaction of composite rocket propellants by pressure measurements in closed vessels*. Paper 62, pages 62-1 to 62-6, in Proc 43rd International Annual Conference of Fraunhofer ICT on ‘Energetic Materials – Synthesis, Characterisation, Processing’, June 26 to 29, 2012, Karlsruhe, Germany. ISSN 0722-4087. Fraunhofer-Institut für Chemische Technologie (ICT), D-76318 Pfinztal. Germany. **2012**.

[7] Sutton, G. P.; Biblarz, O.: *Rocket Propulsion Elements*, 7th Edition, p. 454, **2001**.

[8] Mußbach, G.; Tussiwand, G. S.; Buswell, J.: *Assessing the ageing-state of solid propellant grains in case bonded rocket motors by measuring bondline stresses*. Paper 61, pages 61-1 to 61-5, in Proc. 43rd International Annual Conference of Fraunhofer ICT on ‘Energetic Materials – Synthesis, Characterisation, Processing’, June 26 to 29, 2012, Karlsruhe, Germany. ISSN 0722-4087. Fraunhofer-Institut für Chemische Technologie (ICT), D-76318 Pfinztal. Germany. **2012**.

[9] Mußbach, G.; Bohn, M. A.: *Tracking of the curing of binders for composite rocket propellants by heat flow microcalorimetry and pressure-temperature sensors*. Paper 71, pages 71-1 to 71-12 in Proc of the 44th International Annual Conference of Fraunhofer ICT on ‘Energetic Materials – Characterization and Modelling of Ignition Process, Reaction Behavior and Performance’, 25 to 28 June 2013, Karlsruhe, Germany. ISSN 0722-4087. Fraunhofer-Institut fuer Chemische Technologie (ICT), D-76318 Pfinztal. Germany. **2013**.

[10] Mußbach, G.; Bohn, M. A.: *Impact of ageing on the loss factor of composite rocket propellants and interpretation of changes considering post-curing*; Proceedings of 16th Seminar on “New Trends in Research of Energetic Materials”, pages 280-293, University of Pardubice, Pardubice, Czech Republic, April 10-12, **2013**

[11] Saunders, J. H., Frisch K. C., *Polyurethanes, Chemistry and Technology*, Part I, Interscience, New York, **1962**; *ibid.*, Part II, p. 622, **1964**.

[12] Aneja, A.: *Structure-Property Relationships of Flexible Polyurethane Foams*; PhD thesis, Virginia Polytechnic Institute and State University, Blacksburg, USA, **2002**.

- [13] Lovering, E. G., Laidler K. J.: *Thermochemical studies of some alcohol-isocyanate reactions*; Can. J. Chem. 40, pages 26-30, **1962**.
- [14] Lipshitz, S. D., Macosco, C. W.: *Kinetics and Energetics of a Fast Polyurethane Cure*; J. Applied Polymer Science 21, **1977**, 2029-2039.
- [15] Catherine, K. B.; Krishnan, K.; Ninan, K. N.: *DSC study on cure kinetics of HTPB-IPDI urethane reaction*. J. Therm. Anal. Cal. 59, **2000**, 93-100.
- [16] Nardai M.; Bohn, M.A.: *Cohesive zone model parameterization by molecular dynamics*. Proceedings of 19th Seminar on "New Trends in Research of Energetic Materials", pp 231-241. ISBN (print) 978-80-7395-976-0; ISBN (CD) 978-80-7395-977-7; 2016. University of Pardubice, Pardubice, Czech Republic, April 20-22, **2016**.
- [17] Kaiser, M.; Diz, B; Dörich, M.; Bohn M.A.: *Characterization of several HTPB binder samples by NMR, GPC and OH number*. Paper 55, pages 55-1 to 55-?, in Proc. of the 47th International Annual Conference of ICT on 'Energetic Materials – Synthesis, Characterization, Processing', June 28 to July1, **2016**, Karlsruhe, Germany. ISSN 0722-4087. Fraunhofer-Institut fuer Chemische Technologie (ICT), D-76318 Pfinztal. Germany.
- [18] Lomölder, R.; Plogmann, F.; Speier, P.: *Selectivity of Isophorone Diisocyanate in the Urethane Reaction Influence of Temperature, Catalysis, and Reaction Partners*. Journal of Coatings Technology, Vol 69, **1997**, 51-57.