

# Accelerated Aging and Cure Kinetics of Butacene® Containing Composite Propellants

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## Abstract

Butacene® (trademark by SNPE, France) with ferrocenyl groups chemically bonded to HTPB backbone leads to high burning rates ( $r_b > 20$  mm/s at 7 MPa) in AP-Al based solid composite rocket propellant (SCRCP) formulations by keeping the pressure exponent ( $n$ ) lower than 0.5. Moreover, one can pre-serve the characteristics (kneading process, mechanical properties, pot-life) of conventional HTPB binder formulations together with less sensitivity regarding formation of pyrophoric iron on inner surfaces of the propellant grain. The behavior of Butacene formulations during accelerated aging is analyzed mainly by DMA and additional results are shared with the current study. The thermo-mechanical analysis (TMA) is used to characterize SCRCP for thermal expansion. But TMA can be used in part complementary to DMA as it is also sensitive to molecular mobility of the different fractions in highly filled elastomeric network. Butacene preserved insensitivity compared to a formulation with HTPB and using other materials as burning catalyst as Catocene™ or iron oxide. The interpretation of SCRCP cure kinetics is important in order to get the final product free of flaws, i.e., cracks, fissures, voids, and further on interphases with adequate mechanical properties. An important point is to be able to define final point of curing and residual post-curing time because the latter interferes with the accelerated aging and would distort the estimation of in-service time. Thus analysis of rheological and thermal cure kinetics during the evolution of liquid to gel to solid phase is investigated. The curing characteristics of such a system can be modelled in several ways in terms of viscosity build-up w.r.t. time, thermally with DSC via Kissinger method, and in Heat Flow Calorimeter (HFC) and Pressure Curing Cells (PCC). Current work comprise cure modelling in PCC with different SCRCP formulations, which allows the investigation of the effect of curing catalyst TPB (triphenyl bismuth), reactivity of formulations containing HTPB and Butacene® versus the formulation based on HTPB binder alone.

**Keywords:** Butacene®, composite propellants, accelerated aging, DMA loss factor, kinetic modelling of curing.

## 1. Introduction and scope

Formulations with Butacene® were prepared and analyzed for the first time using  $\tan\delta$  curves together with mechanical, morphological and burning rate analyses [1]. Quantitative analysis of the  $\tan\delta$  curves of DMA allows to estimate the in-service time and this was already shown to be applicable for HTPB based formulations [2, 3]. These previously developed special procedures and models, comprising so-named BLC (Base Line Correction) of  $\tan\delta$  curve and modelling with EMG (exponentially modified Gauss) distributions [4] were used to define and quantify sub-transition regions in the  $\tan\delta$  curves of Butacene® based SCRP. In order to estimate in-service times of Butacene® formulations both Arrhenius and Generalized van't Hoff (GvH) temperature parameterizations of rate constants were used with the EMG data of  $\tan\delta$  curves and a comparison is provided between the two methods. An aging program for Butacene® containing formulations and a reference formulation with only HTPB was performed at three temperatures (70°C, 80°C and 90°C) with aging times established by assuming  $F=2.5$  in the GvH and applying the principle of thermal equivalent load (TEL) [5]. The results reveal that the van't Hoff parameterization estimates the in-service times more reliable compared to the Arrhenius parameterization, especially at low temperature storage conditions. The reason is that there is a change in activation energy ( $E_a$ ) in going from higher aging temperatures to lower ones. The determination of  $E_a$  values at lower temperatures between 60°C and 30°C is very time extensive because of storage times up to several years. This can be circumvented by using GvH method, because this extrapolation has inherently the characteristic of a two-mechanism behavior. Different oxidation types of HTPB binder with different activation energies ( $E_a$ ) cause the difference in mechanisms. The lower  $E_a$  value dominates the aging at low temperatures. Reduction in intensity of DMA  $\tan\delta$  and % of strain values obtained by tensile tests revealed a strong oxidation behavior during ageing, fostered by the iron of Butacene®.

After the addition of isocyanate in a SCRP formulation, polyurethane forming reaction immediately starts. Up to gel point network the mix can be regarded as viscous liquid and at the gel point a wide polymeric network across the sample is obtained by chemical cross-linking. The gel point defines the time a polyurethane network is established to an extent to sustain a certain load. After that point polymeric network gets denser, Van der Waals bonds between

the pre-polymer are overlapped by covalent bonds. This reduces the effective volume of the molecules, the onset of volumetric cure shrinkage begins and the density of the mixture increases. The higher the temperature the faster the cure shrinkage happens through acceleration of the reaction.

In order to analyze the optimum time-temperature profile during curing in the ovens, the degree of curing conversion w.r.t. time can be modelled as a function pressure decrease occurring in Pressure Cure Cells [6, 7]. This also allows to calculate the volumetric shrinkage for such reactions [8]. The description is based on tracking the isochoric pressure decrease in the confined volume of PCC w.r.t. time due to cure reaction between OH groups of HTPB (functionality more than 2) and NCO groups of isocyanate (functionality=2). DBST sensors from company Micron Instruments, Simi Valley, CA, USA, are used to follow the pressure decrease and temperature course. Details of the PCC configuration and operation principles [6, 8] and applications with HTPB based binder [7] and propellant formulations are published previously. Under the scope of the current study is the analysis of the cure reactions of formulations with and without Butacene® and with curing catalyst TPB (TriPhenyl Bismuth).

## 2. Propellant formulations

Table 1 shows the information on the materials and SCRP formulations. Formulations contain Butacene® (Mn=~13,500 g/mol, hydroxyl value 35 mg KOH/g, Iron content: 8±0.5 mass-%, viscosity ~1000 Poise at 25 °C) together with the standard binder HTPB R45HTLO. Two HTPB types both similar to the HTLO type but with different OH-functionalities were used from two different suppliers. The HTPB / Butacene® (HT/B) mass ratio was always 70/30. This ratio was selected after developing binder formulations with different HTPB/Butacene® ratios. TPB was used as curing catalyst. The SCRP formulation TS-78 with only HTPB binder was produced for comparison purposes. HTPB R45HTLO and Butacene® were dried in rotation-vaporization technique at 60°C and 5 mbar over 16 hours before mixing. AP and Al batches were dried in an air circulating oven at least over 48 hours at 60°C. The equivalent ratio Req of NCO and OH groups was 0.86. All SCRP formulations were prepared in a vertical kneader (Drais T FHG, Germany) having one liter of volume and they were cured in an electrical oven cabinet (company Memmert, Germany) for 5 days at 60°C.

**Table 1.** Compositions in mass-% of the investigated formulations.

Substance	Supplier	TS-66	TS-74	TS-78	TS-92	TS-95	TS-103
HTPB-R45HTLO	Sartomer, USA	7.58	7.58	10.68	7.58	7.58	-
HTPB Polyvest EP HT	Evonik, DE	-	-	-	-	-	7.58
Butacene	SNPE, FR	3.32	3.32	-	3.32	3.32	3.25
HTPB/Butacene ratio	-	70/30	70/30	-	70/30	70/30	70/0
IPDI (diisocyanate)	Evonik, DE	0.77	0.780	0.93	0.77	0.77	0.78
TEPANOL, HX 878	MACH I, USA	0.15	0.15	0.15	0.15	0.15	0.15
DOA (plasticizer)	BASF, DE	6	6	6	6	6	6
Vulkanox BKF (AO)	LANXESS, DE	0.17	0.17	0.24	-	-	
Irganox 565 (AO)	Ciba / BASF	-	-	-	0.17	0.17	0.24
AP, 200 $\mu\text{m}$	SNPE, FR	56	56	56	56	56	56
AP, 45 $\mu\text{m}$	SNPE, FR	12	12	12	12	12	12
Al, 18 $\mu\text{m}$	Powder grade	14	14	14	14	14	14
TPB	ABCR, DE	-	0.02	0.02	0.02	-	0.02
Req = NCO/OH	-	0.867	0.867	0.867	0.867	0.867	0.867

An aging plan based on GvH rule with  $F=2.5$  was started for the formulations at three different temperatures (70°C, 80°C and 90°C), details are given in [9].

### 3. Accelerated Aging

The aging was performed in glass vials with ground stoppers loosely inserted. Therefore, oxygen of air was present. The relative humidity is below 10% in this configuration. The vials were inserted in aluminum block oven with PID temperature control to  $\pm 0.2^\circ\text{C}$ . DMA tests of aged TS-78 formulations are shown in Figure 2, while the trend of TS-74 is given in Figure 3. Comparisons clearly show that Butacene® has strong effect in TS-74 compared to the reference formulation TS-78. The reduction in the intensity of the second peak in TS-78 is much lower than with TS-74. The intensity of the first  $\tan\delta$  peak does not change with TS-78 formulation, whereas with TS-74 a reduction in the first peak intensity is observed. This analyses show how the burning catalyst bonded to HTPB backbone facilitate oxygen attack on the HTPB and by this increasing cross-linking points, increasing  $G'$ , toughness and decreasing strain capability. Low strain capability may lead to beginning of cracks, gap formation and consequently to catastrophic failures during firing of motors.

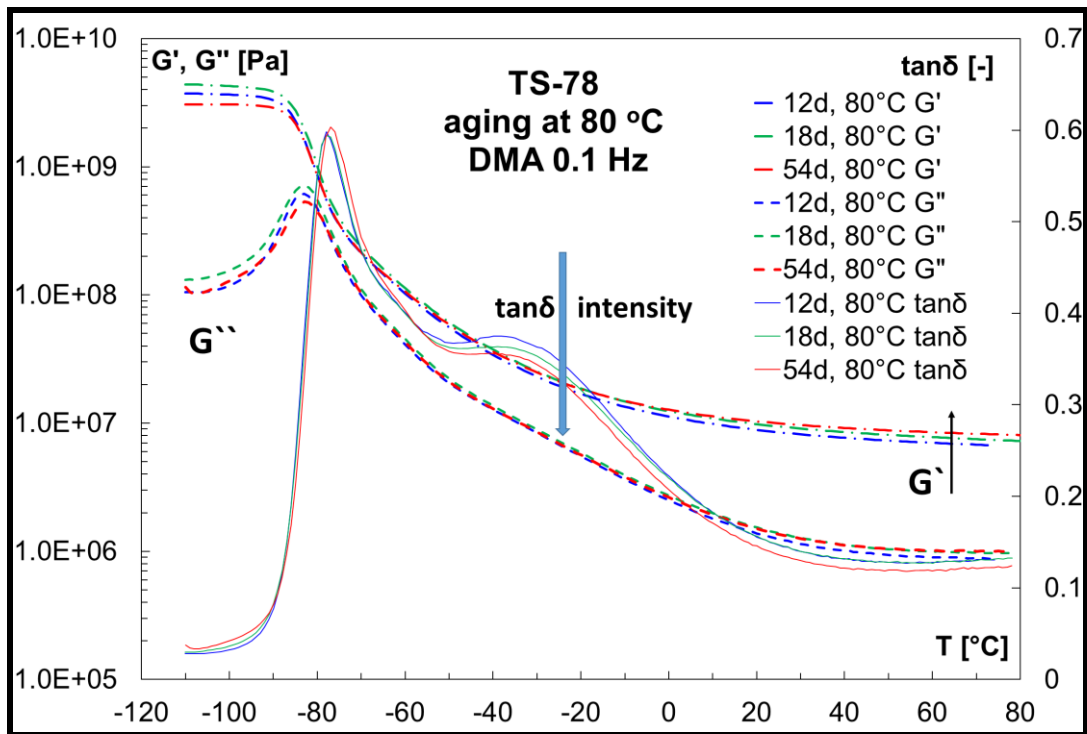


Figure 1. Aging trend in  $\tan\delta$ ,  $G'$ ,  $G''$  of TS-78 at 80°C up to 54 days.

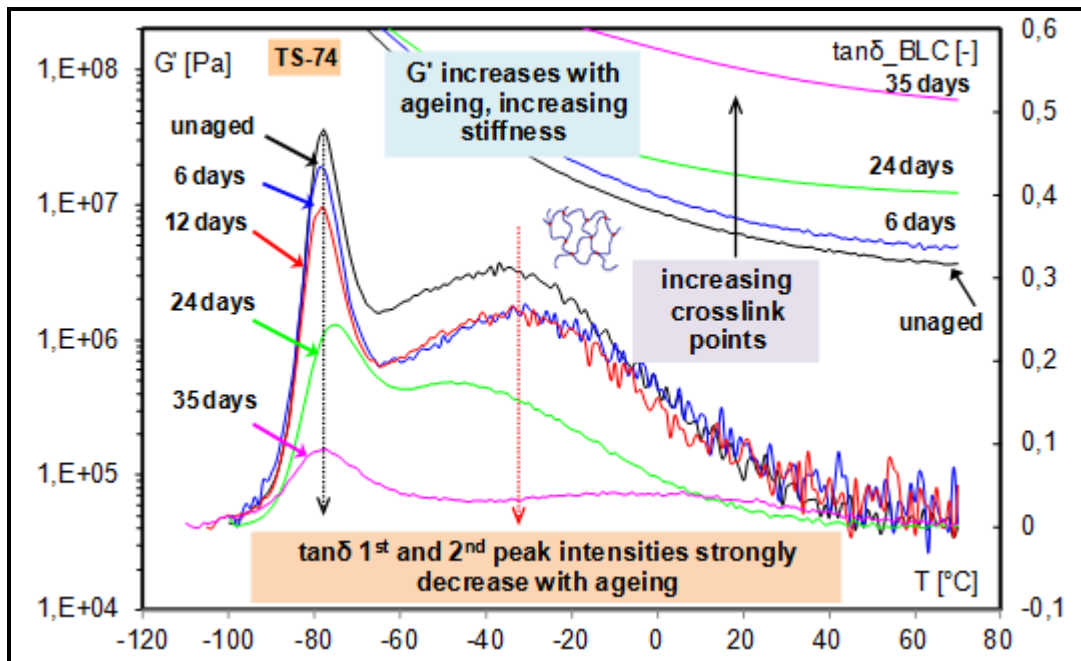
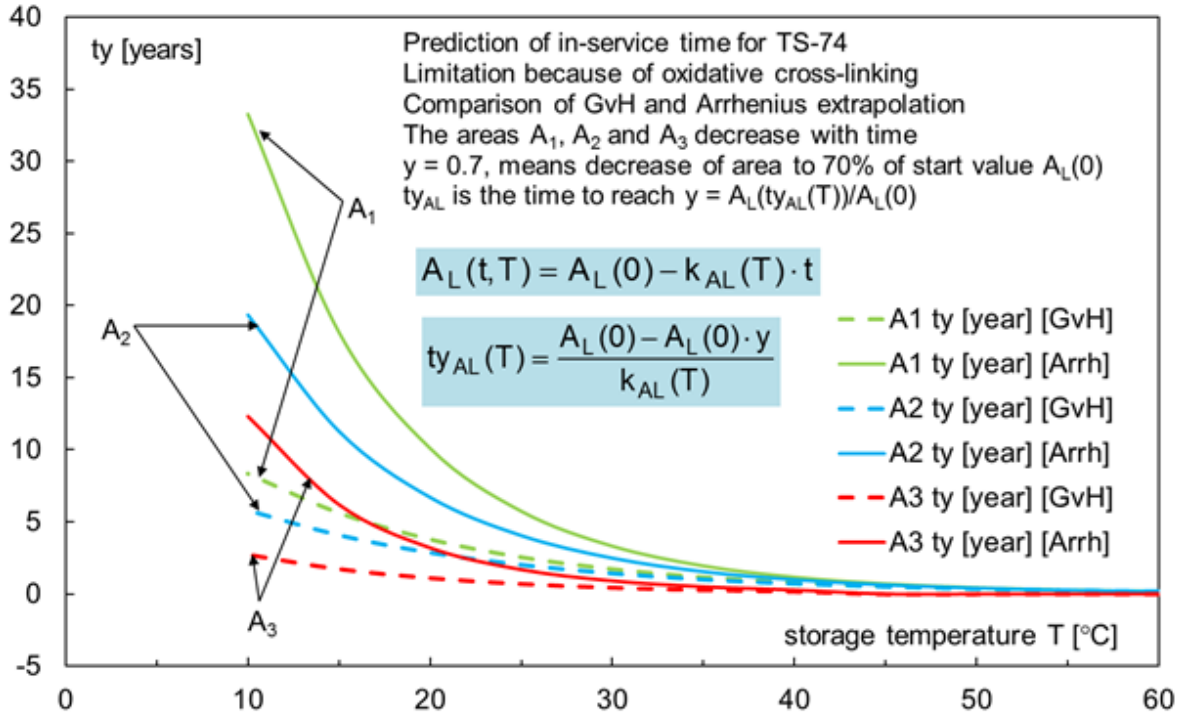


Figure 2. Aging trend in  $\tan\delta$ ,  $G'$ ,  $G''$  of TS-74 (containing Butacene®) at 80°C up to 54 days.

Figure 3 shows the in-service time vs. temperature for the formulation TS-74 calculated both with Arrhenius and GvH parameterization of the rate constants. Details of the calculations are given in [9]. GvH and Arrhenius can differ in providing in-service time estimation. Conservative nature of the GvH can be followed in the Figure 3. The GvH method contains inher-

ently a two mechanistic behaviour, which is found in oxidation processes of HTPB. The Arrhenius method in usual form considers only one mechanism with one activation energy. Two consider a two mechanistic behaviour with Arrhenius methods demands firstly to have both sets of Arrhenius parameters and secondly to apply the correct extrapolation formula for this case, see [5].



**Figure 3.** Estimated in-service times with GvH and Arrhenius parameterization of the rate constant  $k_{AL}$ . GvH method provides much shorter times, because it describes inherently the two mechanistic behavior expected with oxidation processes.

### 3.1 Effect of Aging on Impact and Friction Sensitivity

Table 2 gives the impact and friction sensitivities of the formulations TS-74 and TS-78; aged and unaged, measured in Fraunhofer ICT with BAM drop hammer method and BAM friction methods. According to the international document “Recommendations on the Transport of Dangerous Goods rev.13.4.2 and 13.5.2”, friction sensitivity of a material higher than 80 N is accepted as safe for transport. The limit of the impact sensitivity is given as  $\geq 2$  J.

Ghosh et al. [10] give for the base formulation (composite propellant formulation with HTPB binder only) the impact and friction sensitivity as 5.6 Nm (J) and 110 N, respectively. Landsem et. al. [11] give for friction sensitivity of AP-HTPB composite propellants values of 1.5 to 4 J

(predominance in 3 to 4 J region), and for the impact sensitivity values between 30 to 120 N (predominance in 40 to 50 N range). In the work of Ghosh et al., through addition of Butacene® (70/30=HTPB/Butacene®) the friction sensitivity increases (64 N) and impact sensitivity increases (4.2 J) also somewhat. Oppositely, the current study shows friction and impact sensitivity as 80 N and 15 J respectively for both formulations. This result shows that the addition of Butacene® did not change the sensitivity of the unaged material.

**Table 2.** Friction and impact sensitivity of TS-74 and TS-78, given as limit impact energy and limit friction force

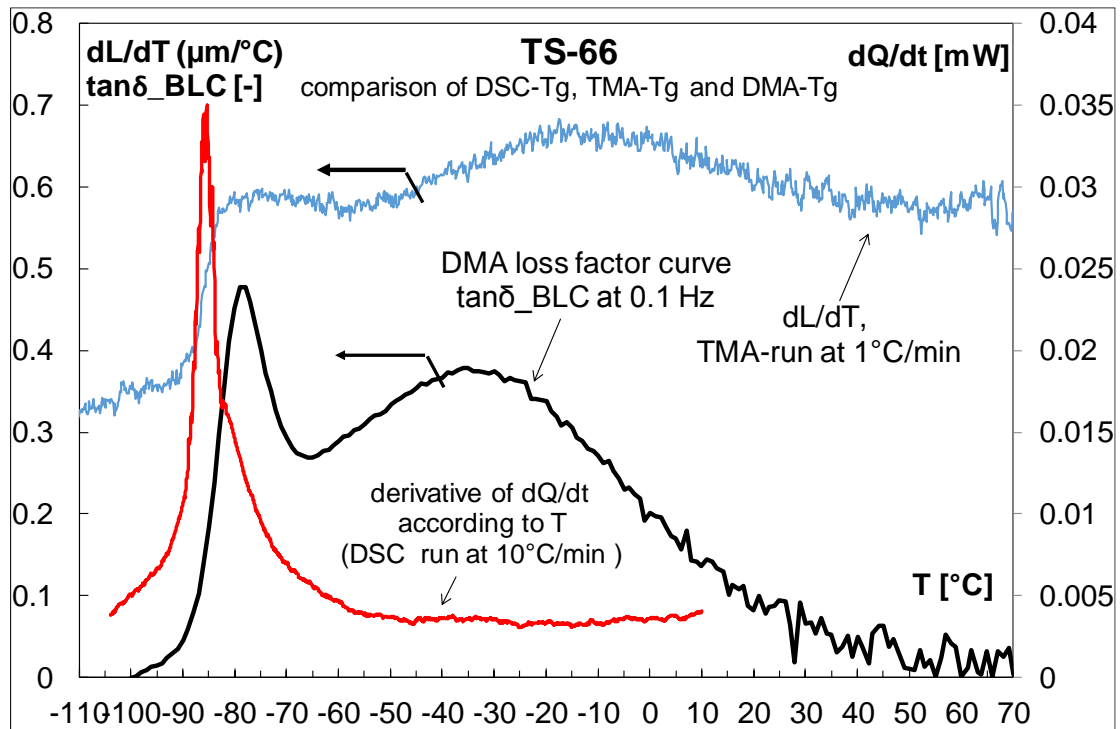
Batch number with aging state	Impact Sensitivity as limit impact energy [J]	Friction Sensitivity as limit friction force [N]
TS-78, unaged	15	80
TS-78, 80°C-35 days	15	120
TS-78, 80°C-60 days	20	240
TS-74, unaged	15	80
TS-74, 80°C-35 days	4.5	80
TS-74, 80°C-48 days	6	80
TS-74, 80°C-60 days	6	80

Through aging, impact sensitivity of TS-74 increases, meaning it gets more sensitive to impact while friction sensitivity does not change by aging up to 60 days at 80°C. Surprisingly, through aging the friction limit force of formulation TS-78 increases, means TS-78 gets more insensitive to friction. Nevertheless, TS-78 aged at 80°C over 60 days showed a spark during the friction test. Impact sensitivity of TS-78 does not change through aging, TS-78 gets more insensitive both in impact and friction, while TS-74 gets more sensitive to impact through aging. This might be attributed to incorporation of Butacene® to the formulation.

### 3.2 TMA, DSC and DMA for Tg measurements

The second main transition in  $\tan\delta$  curve, which is attributed to restricted polyurethane chains by the filler particles, is also detectable by TMA as in  $\tan\delta$  curve of DMA, but with weaker intensity (Figure 4). These results show that the derivative of linear expansion w.r.t temperature measured with TMA supports the shape of  $\tan\delta$  curve detectable with DMA,

while DSC fails to recover this second transition. DSC can detect only the first main transition, which is not changing in maximum temperature with aging. This means relying on the DSC determined glass-rubber transition temperature  $T_g$  alone would mislead in assessing the aging state of the propellant, when looking only for an increase in  $T_g$  value.



**Figure 4.** Comparisons of glass-rubber transition characteristics measured by DMA loss factor curves, DSC and TMA analysis with TS-66.

Figure 5 and 6 show the coefficient of thermal expansion (CTE) measured with TMA from  $-110^{\circ}\text{C}$  to  $+100^{\circ}\text{C}$ . Figure 5 shows the comparison of TS-74 and TS-66, implying TS-66 has a higher second peak resembling what is found in DMA curves. This result of TMA is in accordance with the result obtained with DMA. TMA can be seen as sensitive to molecular level interactions as DMA is, but maybe not in this pronounced extent. Through accelerated aging at  $80^{\circ}\text{C}$  TS-66 (Figure 6) the CTE graph shows that the intensity of second peak is lowered as in the case with DMA, as found with Butacene<sup>®</sup> based formulations. The similarity between DMA and TMA can be used complementary to each other assessing the aging or increasing crosslinks in the propellant network.



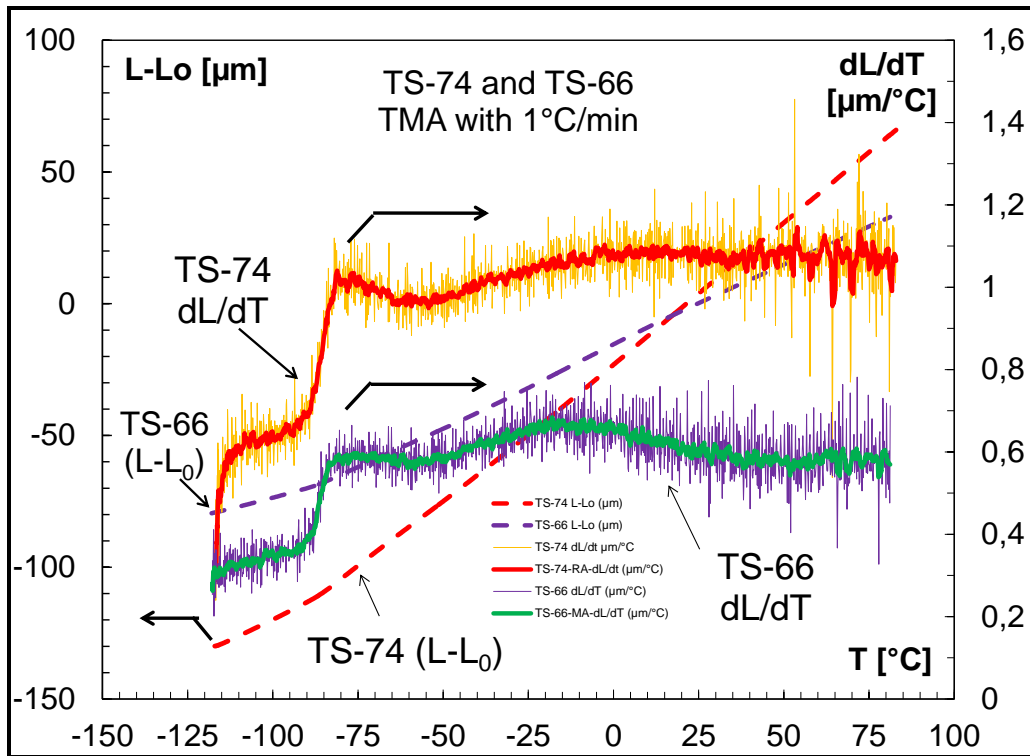


Figure 5. Comparison of CTE of TS-66 and TS-74.

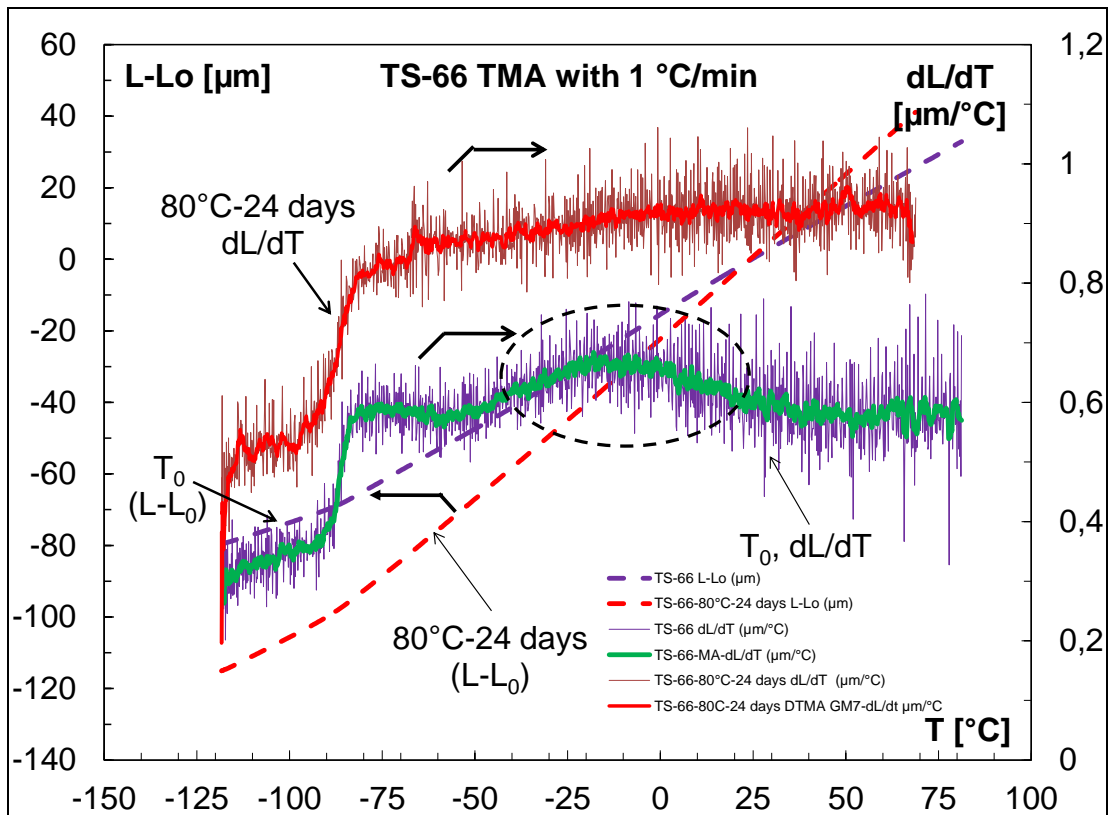


Figure 6. Effect of accelerated aging on the CTE course with TS-66; aging at  $80^{\circ}\text{C}$  for 24 days.

#### 4. Morphological analysis with SEM

SEM (scanning electron microscopy) technique reveals the molecular level bonding (wetting) or de-bonding (de-wetting) mainly between AP particles and the polymeric network. Here the bonding agent TEPANOL HX 878 (obtained from company MACH I, USA) was used in all formulations. TS-103 was prepared with HTPB Polyvest EP HT, which has a higher OH-functionality than HTPB R45HTLO used in TS-92, 2.7 and 2.45, respectively, see [12]. Formulation TS-103 shows differences in terms of coverage/wetting of the AP particles, where both formulations contain Butacene® (Figure 7a, 8a). Wetting of AP particles by the polymeric network is weaker with TS-103 compared to TS-92 (Figure 7b, 8b), which may imply a compatibility problem with different HTLO types. The degree of bonding also depends on processing and the degree of degassing of ammonia ( $\text{NH}_3$ ), which is released due to reaction between TEPANOL HX 878 and AP.

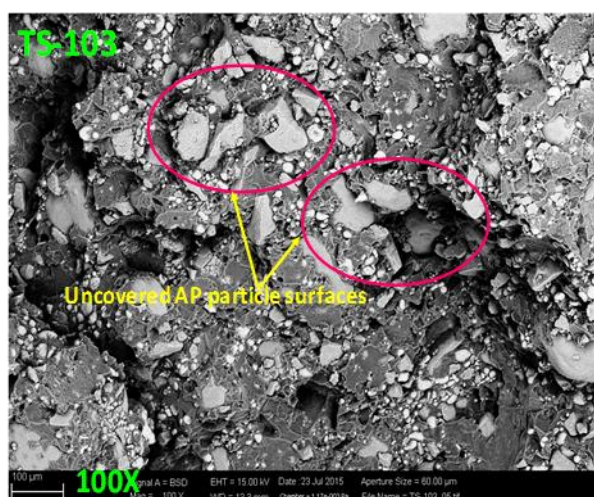


Fig.7a: SEM images of TS-103, F:100X.



Fig.7b: SEM images of TS-92, F:100X.



Fig.8a: SEM images of TS-103, F: 50X.

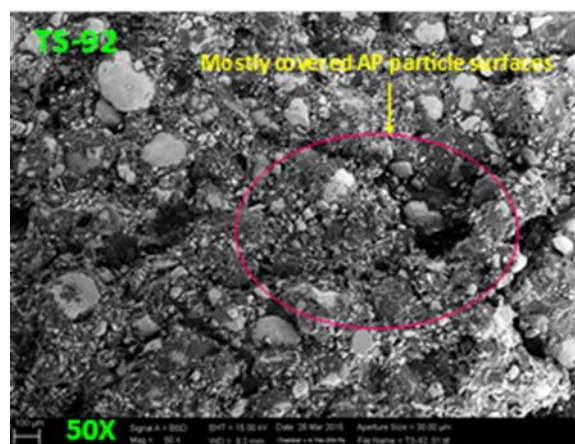
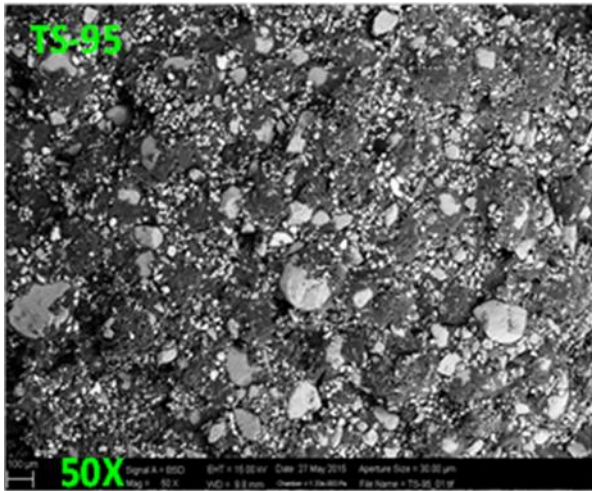
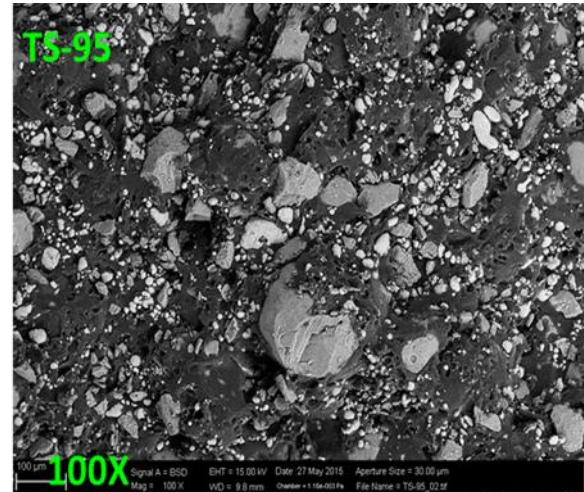


Fig.8b: SEM images of TS-92, F: 50X.



**Fig.9a:** SEM images of TS-95, F: 50X.



**Fig.9b:** SEM images of TS-95, F: 100X.

## 5. Cure Kinetics Investigation with PCC

In order to investigate the cure reaction, the necessary kinetic derivation, which relates pressure decrease as a function of time with a kinetic model, was developed in Fraunhofer ICT by M.A. Bohn [6,7,8], where a bimolecular reaction between HTPB and the isocyanate (IPDI, HDI, ...) is taken, describing the addition reaction of the isocyanate [A] to the OH-groups [B] of HTPB, forming polyurethane [AB] according to following reaction. The reaction is exothermal and shows volume shrinkage.



The reaction in the HTPB+isocyanate mixture confined in a constant volume causes an isochoric density increase, which leads to a pressure decrease, defined by Eq.(2) and Eq.(3). Taking the concentration of isocyanate at the end of reaction time (complete conversion) as 0,  $A(te)=0$ , and defining the conversion of A with Eq.(4), one can obtain Eq.(5). The Eq.(6) is derived from assuming undisturbed second order reaction between OH and NCO groups, the details are given [6, 7, 8].

$$\Delta p(t) \sim \Delta V(t) \sim \Delta A(t) \quad \text{Eq.(2)}$$

$$\frac{p(0) - p(t)}{p(0) - p(te)} = \frac{V(0) - V(t)}{V(0) - V(te)} = \frac{A(0) - A(t)}{A(0) - A(te)} \quad \text{Eq.(3)}$$

$$y_{pr} = \frac{p(0) - p(t)}{p(0) - p(te)} = y_{Ar} = \frac{A(t)}{A(0)} = Ar(t) \quad \text{Eq.(4)}$$

$$p_s(t) - p_s(te) = (p_s(0) - p_s(te)) \cdot Ar(t) \quad \text{Eq.(5)}$$

$$Ar(t) = \frac{(Re q - 1)}{Re q - \exp\left(+\left(\frac{1}{Re q} - 1\right) \cdot k_{2A} \cdot t\right)} \quad \text{Eq.(6)}$$

$$p_s(t) = (p_s(0) - p_s(te)) \cdot \left( \frac{(Re q - 1)}{Re q - \exp\left(+\left(\frac{1}{Re q} - 1\right) \cdot k_{2A} \cdot t\right)} \right) + p_s(te) \quad \text{Eq.(7)}$$

$$\text{where } ABr(t) = 1 - Ar(t) \quad \text{Eq.(8)}$$

$Ar(t)$  normalized concentration of isocyanate,  $Ar(t) = A(t)/A(0)$ ;

$ABr(t)$  normalized concentration of polyurethane;  $ABr = 1 - Ar$

$k_2$  second order reaction rate constant between isocyanate and polyol;

$k_{2A}$  normalized second order reaction rate constant,  $k_{2A} = k_2 \cdot A(0)$ , between isocyanate and polyol;

$p_s(t)$  pressure course during curing in PCC, also  $p(t) = p_s(t)$ ;

$p_e$  final pressure after the curing is completed,  $p_e = p_s(te)$ ;

$p_0$  initial pressure  $p_0 = p_s(0)$ , it is determined by model, not measurable because of time delays up to measurement start;

$Req$  equivalent ratio,  $Req = A(0)/B(0)$ .

Considering pressure data ( $p_s$ ) obtained from PCCs, one uses fitting algorithms with Eq.(7) and calculate the reaction constant  $k_{2A}$  as well as the initial and final pressures. But one must be aware that the curing reaction starts immediately by adding the curing agent to the propellant mix. A careful compiling of times and temperatures must be done up to the point, where the data loggers read the pressure data. These pre-times, reaction kinetically weighted, must be added to the actual logger times in order to describe the curing reaction correctly. This is necessary, because with a second order reaction the initial concentration determines the value of the reaction rate constant. Details of the measurements and the type of calculation the additional times is given [8]. An example of such pre-times is shown in Table 3. The pre-times includes necessary steps from addition of isocyanate until filling the PCC in laboratory and it pre-tempering. The times are re-scaled to the target temperature  $T_M$  (cure temperature) before adding to the sensor time data, which are measured after closing

the PCC. Rescaling of the time-temperature sets can be performed with GvH taking  $F=2.2$ , see Eq.(9).

$$t_M[d] = t_V[\text{min}] \cdot F^{+(T_V - T_M)/\Delta T_F} / 1440 \quad \text{Eq.(9)}$$

**Table 3.** Operational steps beginning from isocyanate addition to locating PCC's in ovens.

Operation step	temperature $T_V$ [°C]	time $t_V$ [min]	$t_M$ in [d] at target temp. $T_M = 60^\circ\text{C}$ , scaled from ( $t_V, T_V$ ) with $F=2.2$
End of kneading without isocyanate	40	4.13	0.002777778
Kneading with isocyanate	50	10.45	0.006944444
Transport to laboratory	48	3.49	0.002083333
Handling-filling the PCC	47	6	0.004166667
Preheating	50	28	0.017361111
Total pre-time $t_p$ at $T_M$ in days	-	-	0.033333333

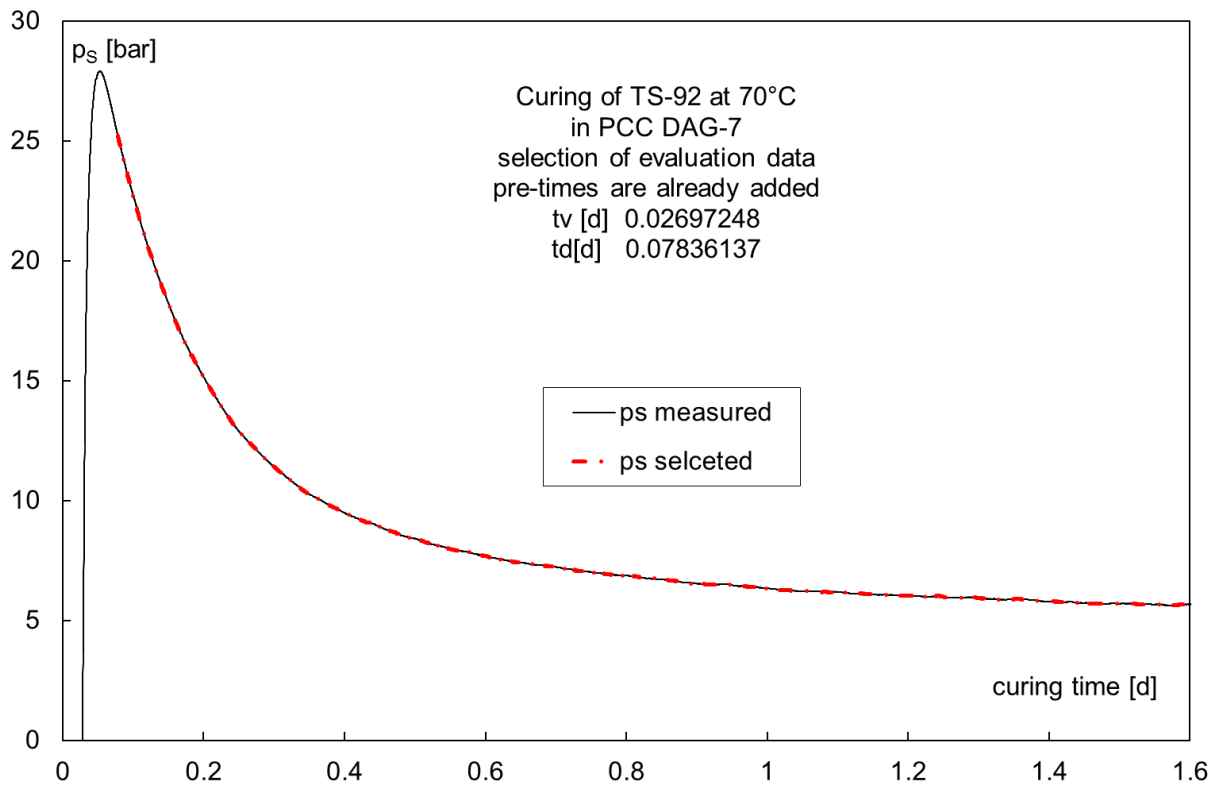
Evaluation of pressure sensor data was performed mainly in three steps.

- Step 1 includes the selection of starting point for pressure measurement with DBST sensor. Figure 10 shows such a step with TS-92 cured at  $70^\circ\text{C}$ .
- Step 2, selected pressure data as a function of time is fitted with Eq.(7) with Origin V7 Programme Code to calculate  $k_{2A}$ ,  $p_s(0)$  and  $p_s(t_e)$  (Figure 11).
- Step 3 includes the use of  $k_{2A}$  to evaluate the degree of curing as a function of time with Eq.(8) (Figure 12).

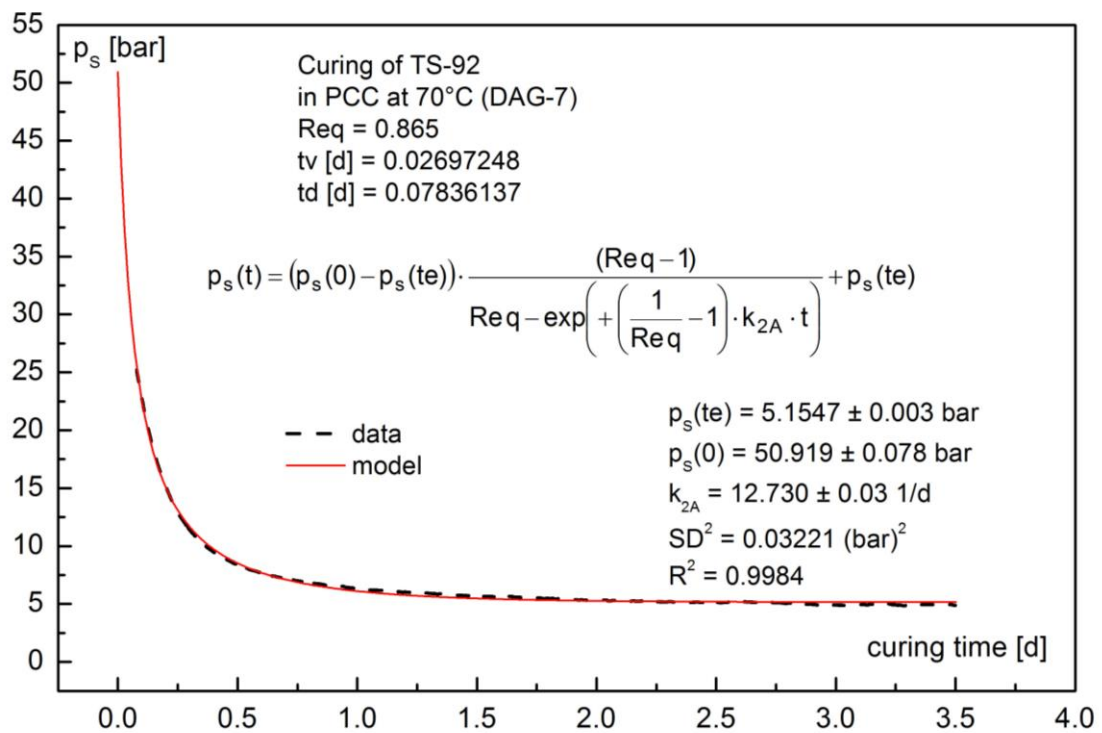
Comparisons of pressure sensor data obtained with TS-92 at  $T=70^\circ\text{C}$  in Figure 11 represents measured data and fitted model. The model equation satisfactorily describes the data with a high correlation coefficient  $R^2 = 0.99$  for each analysis.

Fig. 12 shows pressure course obtained at  $50^\circ\text{C}$  is lower than that of  $60^\circ\text{C}$ . This difference comes from different handling times during experimental preparation which is corrected via the addition of pre-times. Further, because of high bulk modulus the temperature causes higher pressures at  $60^\circ\text{C}$  also with equal amount of filling in both cases. The normalized representation shows conversion of the curing reaction to polyurethane  $1\text{-Ar} = \text{ABr}$ , here the rates are in correct order, showing them as higher with  $60^\circ\text{C}$  compared to  $50^\circ\text{C}$ .

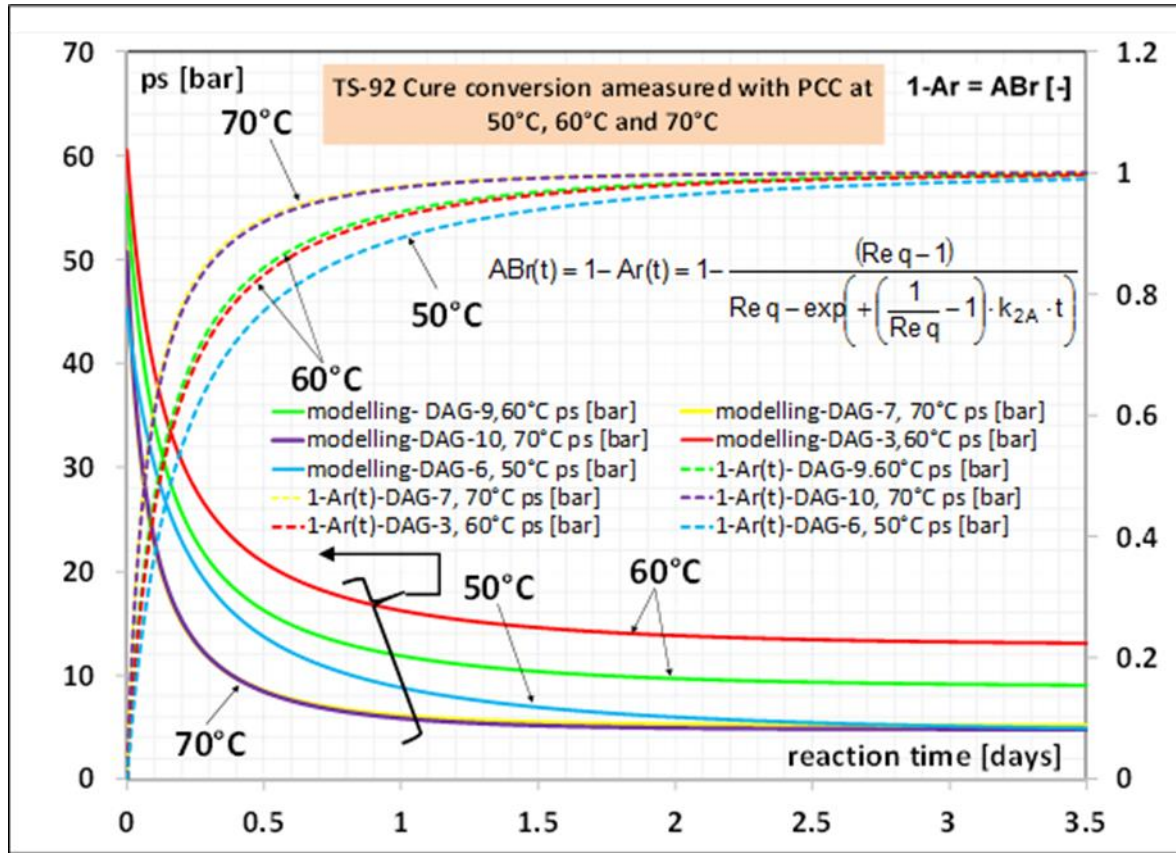




**Figure 10.** Pressure course from DBST sensor, batch TS-92 cured at 70°C and selection of pressure data for evaluation.

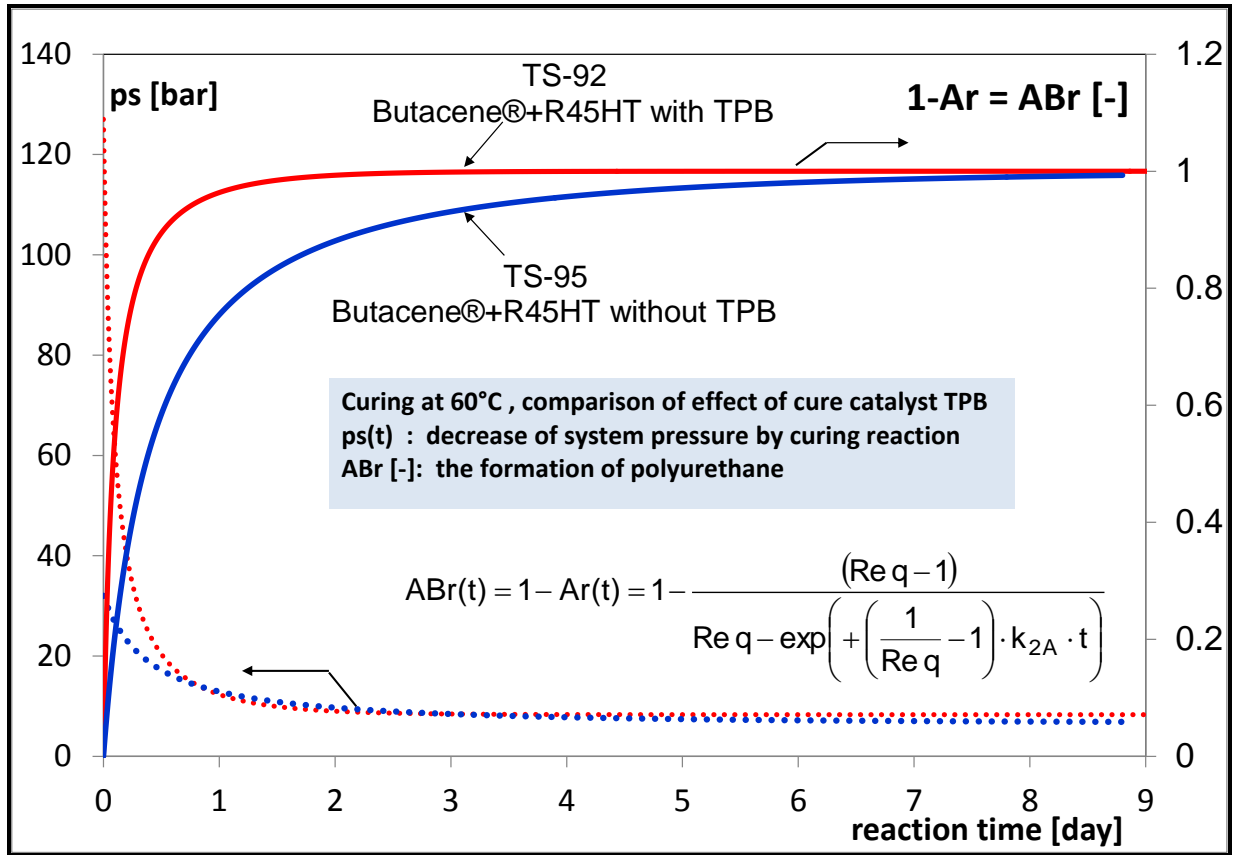


**Figure 11.** Pressure course during curing reaction, fit of model given with Eq.(7), TS-92 cured at 70°C with DAG-7.



**Figure 12.** Pressure course during curing reaction, fit of model for the formation of polyurethane ABr, TS-92 cured at 50°C, 60°C and 70°C.

Figure 13 shows the pressure decrease,  $p_s(t)$ , and degree of conversion w.r.t. time for TS-92 and TS-95. PCC test at 60°C clearly shows fast reaction with TS-92, which has 0.02 % TPB whereas TS-95 has no curing catalyst. While cure reaction has reached a final conversion state in 3 days with TS-92, TS-95 has a complete degree of curing at around 8 days. Interesting to note that final pressure,  $p_e = p_s(t_e)$ , obtained at 60°C with the two formulations are similar, which implies that the degree of volumetric cure shrinkage is same for both formulations. This result shows that the catalyst TPB has an accelerating effect on the curing reaction, which is detectable with PCC and it should have a mild or no effect on the degree of volumetric cure shrinkage.



**Figure 13.** Pressure course through cure reaction, fit of model for ABr, TS-92 and TS-95 cured at 60°C.

In order to relate pressure decrease in PCC to volumetric cure shrinkage, bulk modulus (decompression or resistance to compression) relation to pressure and volume given by Eq.(9) can be used [6, 7, 8]. Derivation of Eq.(9) results Eq.(10) which relates change in volume of reaction mixture to pressure data.

$$\left( \frac{dp_s}{dV_g} \right) \Big|_T = + \frac{K}{V_{PCC}} \quad \text{Eq.(9)}$$

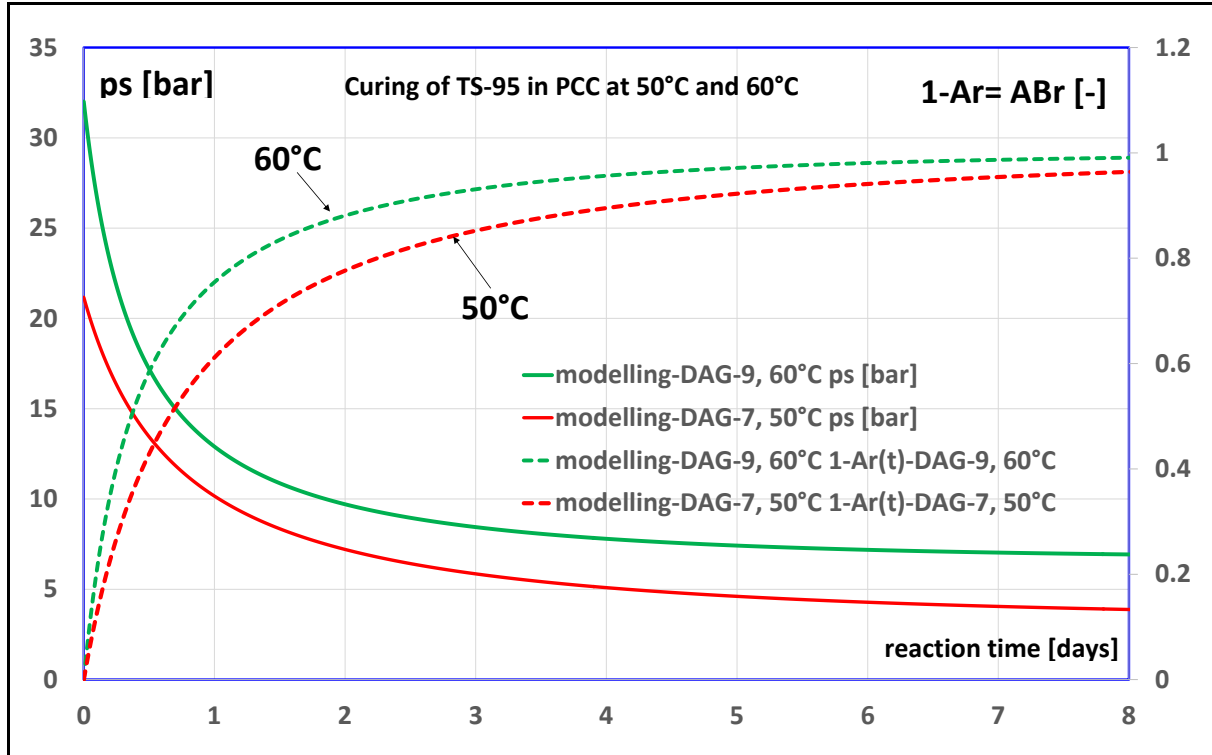
$$\Delta p_s = (p_s(te) - p_s(0)) = + \frac{K}{V_{PCC}} \cdot \Delta V_g \quad \text{Eq.(10)}$$

Where:

- K      bulk modulus or decompression constant,
- $p_s$     the pressure measured in PCC
- $V_g$     total volume of the reaction mixture.
- $V_{PCC}$    volume of the PCC, 10.71 cm<sup>3</sup>



Details of the calculation of volumetric cure shrinkage is given in [8]. Eq.(10) shows the higher  $p_s(t_e)$  or the smaller  $\Delta p_s$ , the lower the volumetric cure shrinkage or change in  $V_g$ . This relation shows dependence of cure shrinkage to bulk modulus and pressure decrease due to reaction progress.  $K$  is assumed as 18000 Pa for HTPB based propellants [3]. Additional analysis might be necessary to calculate bulk modulus rather than making assumptions. Figure 14 shows the PCC runs at two different temperatures with TS-95 at 50°C and 60°C.



**Figure 14.** Pressure course during cure reaction, fit of model for ABr, degree of conversion as a function of time for TS-95 cured at 50°C and 60°C.

Table 4 and Table 5 summarize the cure reaction parameters, the reaction rate constants  $k_{2A}$ , and the Arrhenius parameters activation energy  $E_a$  and pre-exponential factor  $Z$ . These results show that PCC can be used to follow the degree of cure reaction w.r.t. time. Besides the post cure time can be defined to exclude from aging programmes which in turn effects the in-service time of formulations.

The activation energies given in Table 5 are congruent with ones determined with DSC-data evaluated with the Kissinger method [8], obtained from curing in microcalorimeters [8] and values reported in [13], which are also discussed in [8].

**Table 4.** Cure reaction parameters, reaction rate  $k_{2A}$  [1/d], calculated from PCC pressure data.

Batch No	DAG No	T [°C]	ps(te) [bar]	ps(0) [bar]	$k_{2A}$ [1/d]	R <sup>2</sup>	SD <sup>2</sup> [bar] <sup>2</sup>
TS-95	7	50	3.661	21.06 ± 0.04	1.357 ± 0.004	0.95895	0.343
	3	60	7.051	28.14 ± 0.03	1.857 ± 0.004	0.98667	0.114
	9	60	6.93	32.47 ± 0.05	2.332 ± 0.005	0.98462	0.118
TS-92	3	60	12.90	60.49 ± 0.08	6.602 ± 0.02	0.9979	0.0851
	7	70	5.155	50.92 ± 0.08	12.730 ± 0.028	0.9984	0.0322
	10	70	4.780	50.75 ± 0.08	12.077 ± 0.026	0.99844	0.0343
TS-78	1	60	4.13	73.65 ± 0.14	16.54 ± 0.03	0.99782	0.0486
	3	60	2.10	67.90 ± 0.16	17.22 ± 0.04	0.99654	0.0706
	9	70	1.60	57.63 ± 0.24	31.70 ± 0.12	0.99109	0.0608
	7	70	5.45	84.76 ± 0.11	31.49 ± 0.04	0.99896	0.0159
TS-74	1	60	11.90	46.28 ± 0.03	6.318 ± 0.01	0.99979	0.0546
	3	60	10.20	41.27 ± 0.02	6.376 ± 0.01	0.99981	0.006
	7	70	15.60	46.49 ± 0.12	12.064 ± 0.07	0.99856	0.043

**Table 5.** Arrhenius parameters activation energy  $E_a$  and pre-exponential factor  $Z$  of the cure reaction calculated from  $\ln(k)$  versus  $1/T$  [1/K]. The abbreviation  $\lg$  means decadic logarithm.

Batch No	Remark	$E_a$ [kJ/mol]	$\lg(Z$ [1/d])	$Z$ [1/d]
TS-92	with Butacene®, TBP	56.6	9.715	5.185 E+9
TS-74	with Butacene®, TBP	61.4	10.374	2.364 E+10
TS-78	with TPB	59.6	10.572	3.736 E+10

## 6. Conclusions

Pressure curing cells (PCC) were used with different types of propellant formulations to see the measurement sensitivity with regard to composition changes of the system set up. Results reveal precious measurements and experimental procedures are necessary to carry on PCC experiments. Compilation of sensor raw pressure data to investigate cure reaction kinetics contains several steps. As HTPB+isocyanate reaction starts immediately after addition of isocyanate, a blank time passes until the data acquisition can start with the PCC setup and this additional time should be added to evaluation time. This is applied in the current work. A constant and uniform temperature shall be preserved during curing of formulation in the

PCC, since reaction rate is sensitive to temperature changes and especially the pressure course is very sensitive to temperature variations.

PCC experimental results were used to calculate cure kinetic parameters, reaction rate constants  $k_{2A}$ , activation energy  $E_a$  and pre-exponential factor  $Z$ . The evaluation of formulations without cure catalyst TPB showed lower reaction rate constants  $k_{2A}$  compared to the one with catalyst. Volumetric cure shrinkage measurements given in detail [8] can be used to optimize time-temperature profiles of propellant formulations. It is important for the grains formed in optimum time-temperature profiles, where volumetric changes such as expansion and shrinkage should be controlled. Rheological analysis, which includes gel time measurements with parallel plate configurations, shall be useful to optimize such profiles.

In-service times of SCRP formulation TS-74 were computed with GvH and Arrhenius parameterization of the change rate constants of loss factor parameters measured by DMA and analysed by EMG (exponentially modified Gauss) functions. The comparison showed that GvH gives conservative times versus Arrhenius extrapolation. The reason is that GvH covers two competing reactions with different  $E_a$ 's. Assuming a degree of aging of  $\gamma=0.7$  a motor containing 70/30 per mass HTPB/Butacene<sup>®</sup> binder, the propellant would have a chemical in-service time at 20°C of 13 months with GvH, and 38 months with Arrhenius parameterization, if stored with full oxygen access and when changes in area  $A_3$  of the loss factor are considered as service time limiting property. This result show how Arrhenius parameterization can give overestimated in-service time for the motors.

Derivatives with respect to temperature of DSC heat flow curves and TMA linear expansion data show clearly transition regions in the polymeric networks. However, the static characteristic of DSC cannot reveal the second apparent transition peak, which is clearly visible with DMA  $\tan\delta$  and can be identified in part from the TMA curve. TMA analysis recognizes also the first apparent transition, which is attributed to by particles unrestricted polyurethanes chains. Through ageing the free inter-cross-link lengths of these chains get shorter as cross-link points increase and this decreases the elasticity or strain capacity of the polymeric network, which may lead to several failure modes, as crack formation at inner bore, de-bonding from liner, de-wetting from filler particles. The effect of increasing oxidation of the binder

can be followed by quite sensitive changes in DMA loss factor, but is not recognizable with DSC measurements considering only glass-rubber transition temperature  $T_{g,DSC}$ .

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## 9. List of Abbreviations

AO	Antioxidant
AP	Ammonium perchlorate, oxidator, $\text{NH}_4\text{ClO}_4$
Al	Aluminum (powder in CRP), fuel
ARES	Advanced Rheometric Expansion System
BKF	type of antioxidant, Vulkanox® BKF, 2,2'-methylene-bis-(4-methyl-6-tert.-butyl-phenol)
BLC	Base Line Correction of loss factor

BR	burning rate, $r_b$
B-SCRP	Butacene® containing SCRCP
CRP	Composite solid rocket propellant
CTE	Coefficient of thermal expansion
DMA	Dynamic Mechanical Analysis
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
DOA	Dioctyl adipate (plasticizer)
EMG	Exponentially modified Gauss distribution
GvH	Generalized van't Hoff equation
$G^*$ :	Complex shear modulus, $G^* = G' + iG''$ , $ G^*  = \sqrt{G'^2 + G''^2}$
$G'$	Storage shear modulus
$G''$	Loss shear modulus
$\delta$	Phase angle, angle between stress and strain in the dynamical measurement
HFC	Heat Flow Calorimetry (microcalorimetry)
HTPB	Hydroxyl Terminated PolyButadiene (R45HTLO type)
HX 878	Bonding agent for AP
IPDI	Isophorone diisocyanate (isocyanate), has four conformation isomers
NCO	Isocyanate group
OH	Hydroxyl groups
PCC	Pressure Curing Cell (pressure cell curing)
SCRCP	Solid composite rocket propellant
$\tan\delta$	Loss factor (loss tangent); characterisation of the glass-rubber transition; in elastomers or in polymers; $\tan\delta = G''/G' = E''/E'$
TEL	Thermal equivalent load
Tg	Glass-rubber transition temperature, here defined as maximum of the loss factor curve in DMA measurements, $T_{g,DMA}$
TMA	Thermal Mechanical Analyser
TPB	Triphenyl bismuth, curing catalyst.