Ageing behaviour of composite rocket propellant formulations investigated by DMA, SGA and GPC

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Motivations and Objectives

Aims

- Correlation of natural ageing of rocket motor propellants with laboratory results on accelerated ageing in order to achieve and perform the ageing prediction

- Ageing conditions and some properties can be monitored using embedded and attached sensors (bond stresses, temperatures, vibration, oxidation, humidity)

Objectives

- Study of nano-Al behaviour on the mechanical properties and ageing mechanisms of composite propellants

- Use of several techniques (DMA, SGA, GPC) to obtain a more detailed molecular interpretation of the propellant ageing behaviour

DMA: dynamic mechanical analysis
SGA: sol-gel analysis
GPC: gel permeation chromatography

Material formulations and ageing procedures

- Formulations: HTPB/AP/Al propellants, binder = 16 m.-%, solid load = 84 m.-%
- Thermal accelerated ageing programme was developed by applying the TEL (Thermal Equivalent Load) principle and using the generalised van't Hoff rule
- van't Hoff scaling factor F=2.5 is used to correlate the in-service loads (t_E, T_E) with the accelerated ageing loads (t_T, T_T)
- Ageing of the surface layer of SRPs: at 60°C to 90° C in air (RH<10%)

From generalised van't Hoff rule one has

$$t_E[\text{years}] = \frac{t_T[\text{days}] \cdot F^{(T_T - T_E)/\Delta T_F}}{365.25}$$

<u>van't Hoff rule with F = 3.0 describes</u>:
ageing processes with E_a values between 80 and 120 kJ/mol in the temperature range 20°C to 90°C

<u>Advantage of the van't Hoff extrapolation</u>:

It is able to cover two-step mechanistic ageing processes. At lower temp. smaller Ea is found

Accelerated ageing plan

Applied accelerated ageing conditions (temperatures and times) to simulate an in-service time of up to 30 years at 25℃.

The given ageing times are rounded up.

Natural or in-service ageing						
In service temperature T_E [°C]	In-service time t_E [year]					
25	5	10	15	20	25	30
Accelerated ageing conditions based on TEL principle using van't Hoff with F = 2.5						
Ageing temperature T_T [°C]	Ageing time t_T [day]					
90	5	10	15	20	25	30
85	7.5	15	22.5	30	37.5	45
80	12	24	36	48	60	72
70	30	60	90	120	150	180
60	75	150	225	300	375	450

Details of the investigated HTPB-IPDI /Al/AP propellant formulations named as: AV03, AV04, AV05, AV06

AV-odd numbered
16 m-% binder
6 m-% Al
78 m-% AP

AV-even numbered
16 m-% binder
12 m-% Al
72 m-% AP

AV03: 18 µm

AV05: Alex

AV04: 18 µm

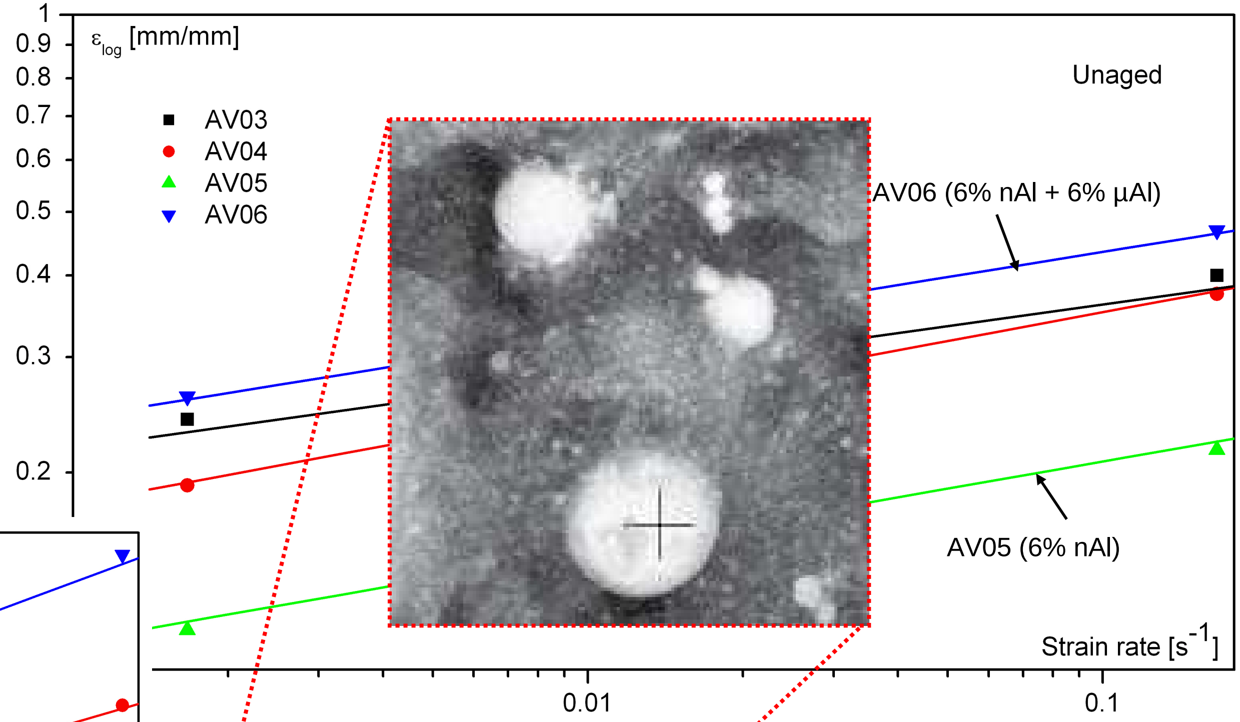
AV06: 6 m-% Alex
6 m-% 18 µm

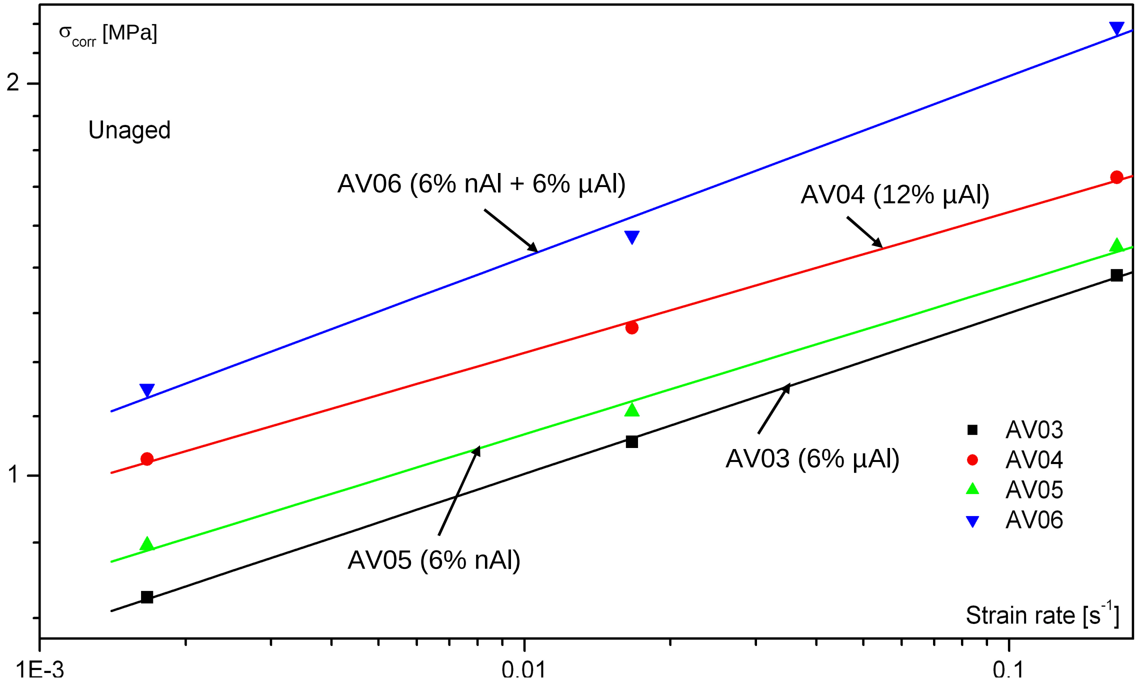
- Study of the influence of the different **individual filler contents** (total solids: 84 m.-%)
- Study of the influence of the **particle size,** micro-Al and nano-Al (100-200nm, EEW)
- Three modal AP filling, with bonding agent forming primary bonds to both sides

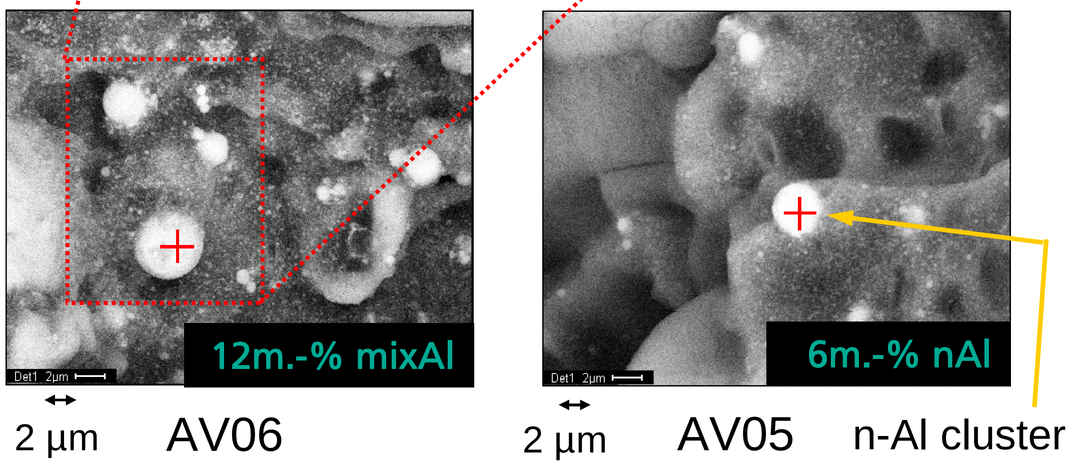
The propellant samples have been manufactured by Dr. Klaus Menke at ICT

Effect of the Al mass fraction and Al particle size on the mechanical properties

- Effect of the Al content
- Effect of the Al particle size: total or partial replacement of micro-Al with nano-Al
- µ-Al and n-Al act as active fillers
- Formulation containing only nano-Al shows the lowest strain capability







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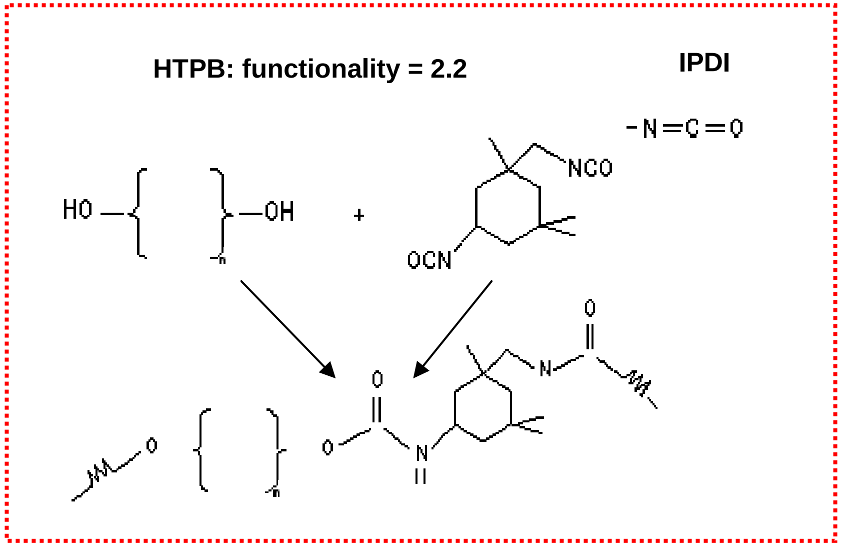
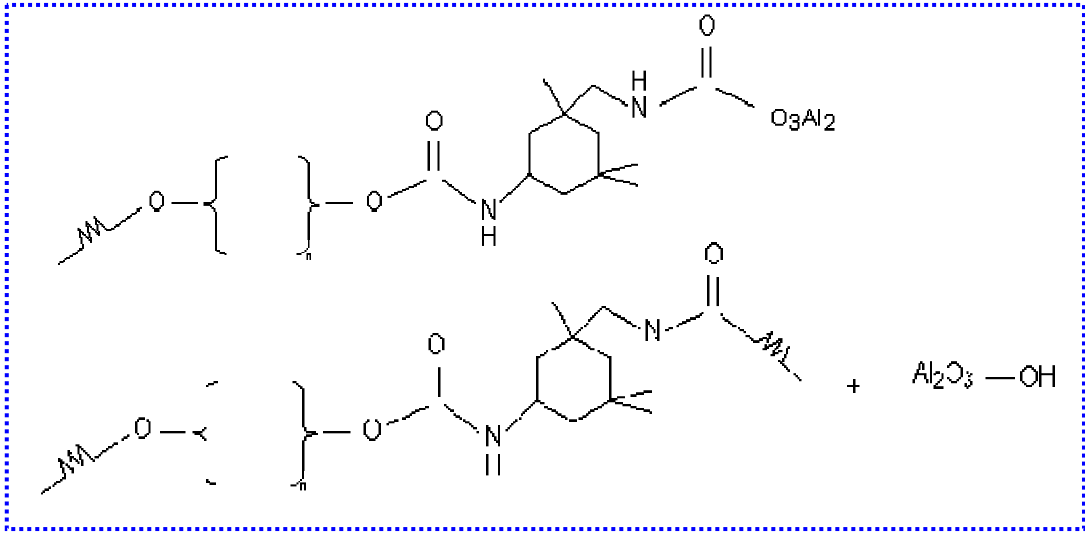
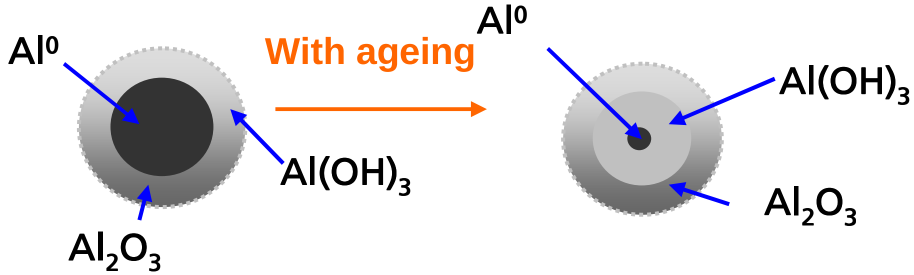
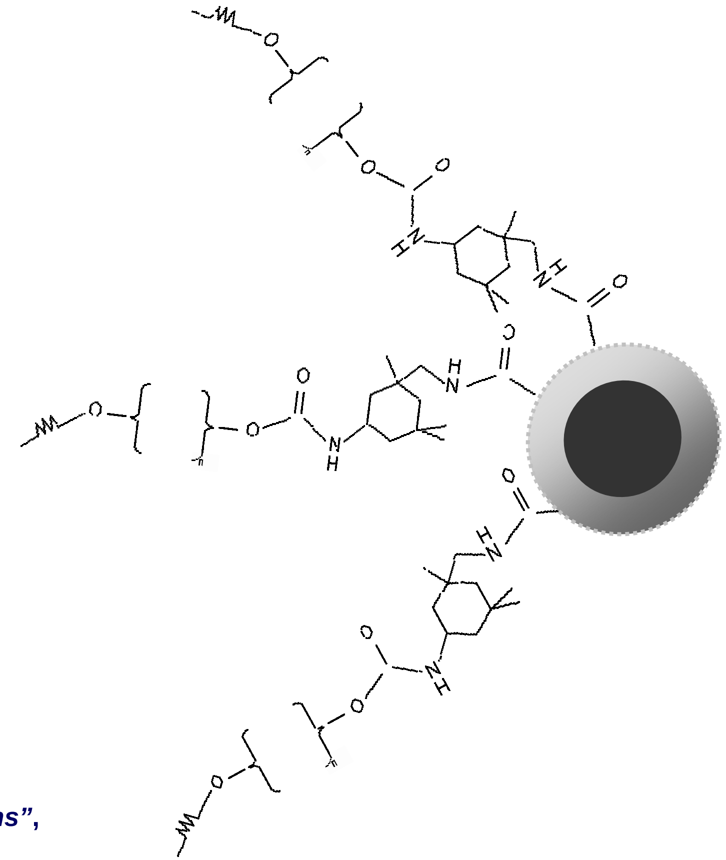
Interaction of nano-Al with the curing process





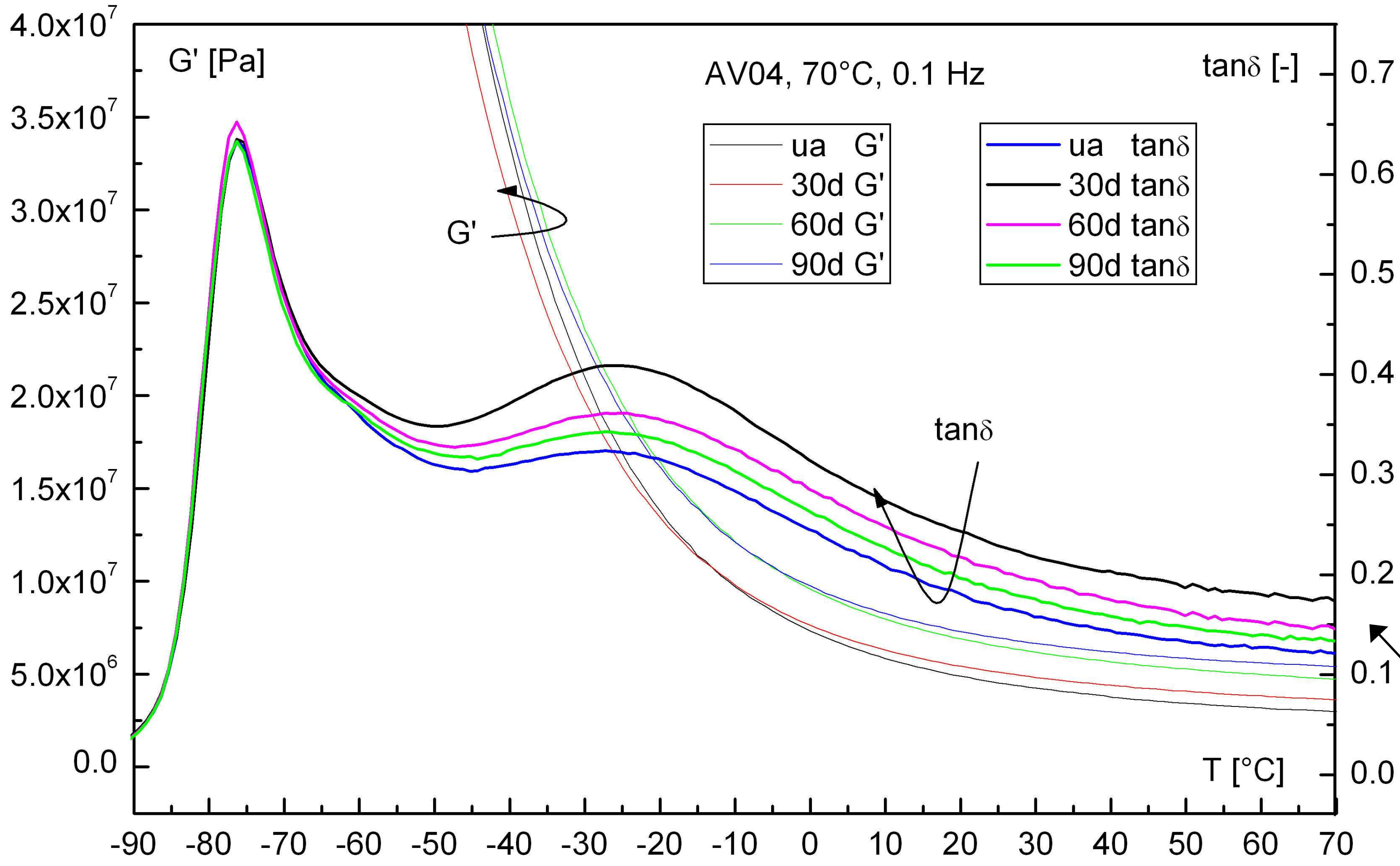


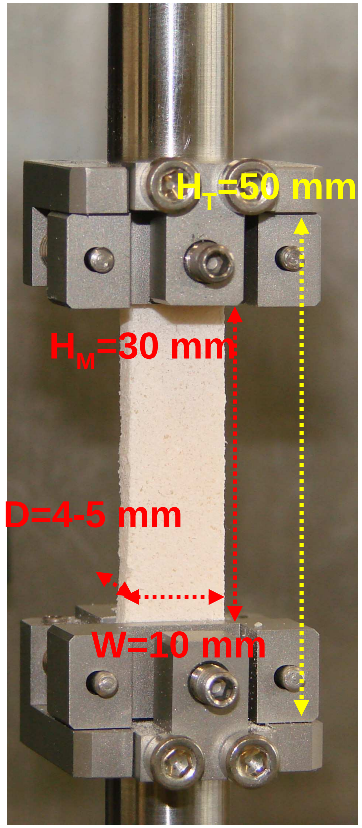


Borsus J.M., Merckaert P., Jérôme R., Teyssié P.H.,
"Enhancement of Adhesion between Filler and Polymer in Alumina-Filled Rigid Polyurethane Foams",
Journal of Applied Polymer Science, Vol. 29, pp. 1857-1863, 1984

DMA – Peak shape and change trend of tan(δ) with ageing

- Loss factor curves tan(δ) = G''/G' of un-aged and aged material show the presence of 2 peak ranges
- **First peak:** shows similar behaviour in the unaged and aged conditions (T_g is called $T_g^{unrestricted}$)
- **Significant changes of the area of the second peak** and on the value of T_g, here called $T_g^{restricted}$





Base line offset by dissipative effects

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DMA - Extracting information on molecular mobility level from the tan(δ) curves

- The energy used up in the sample during the glass transition has two main parts:

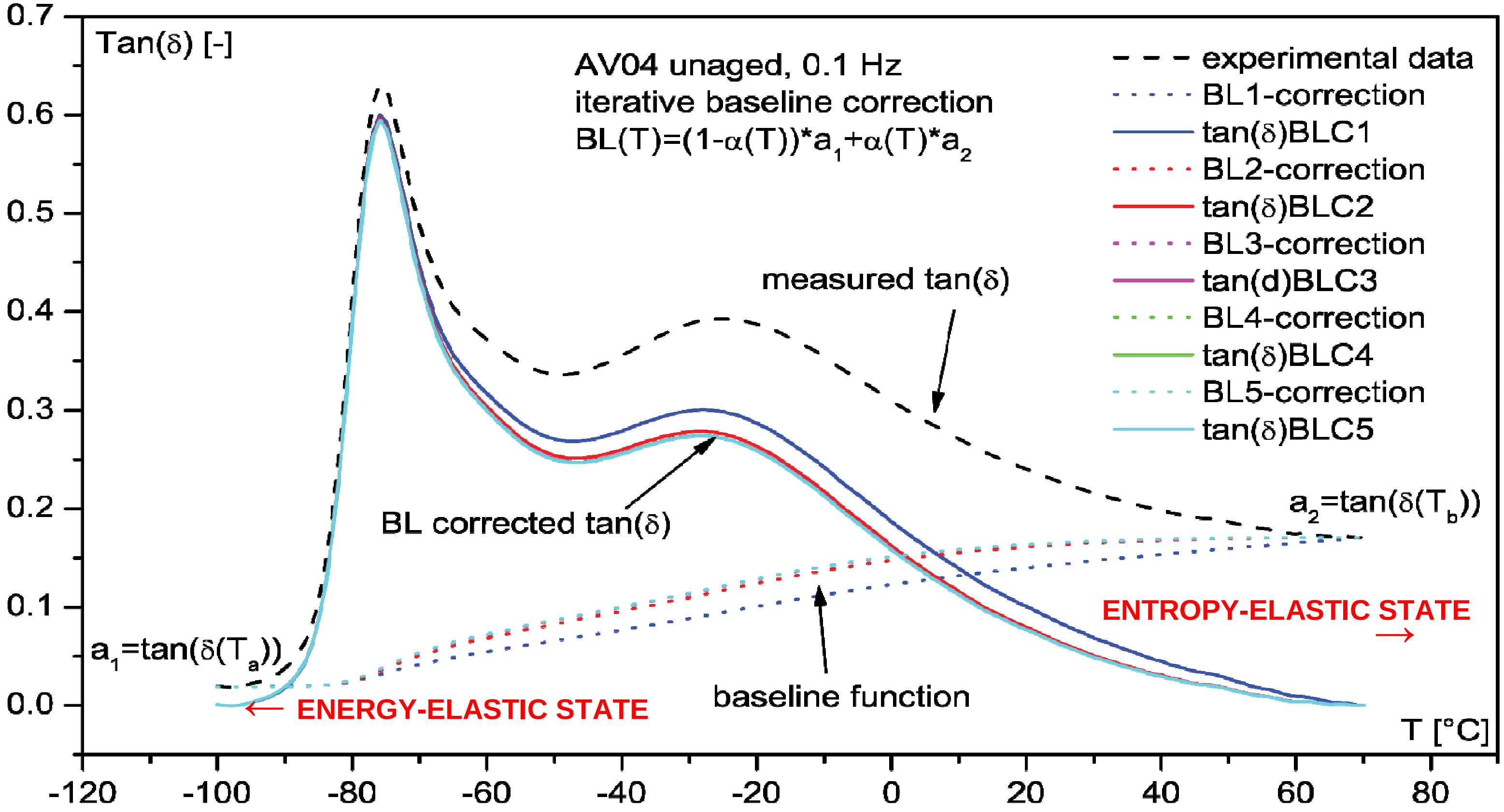
  - a purely dissipative one, the energy is transformed to heat by frictional effects

  - an internal energy optimizing one, the energy is used for molecular rearrangement work to proceed from the energy elastic to the entropy elastic state of the elastomer or vice versa

- For the evaluation of the tan(δ) - distribution function with regard to the molecular rearrangement parts, the dissipative part must be separated

  This is achieved by applying a suitable iterative baseline correction (BLC) using a cumulative partition variable α(T)

DMA - Procedure of the baseline correction of the tan(δ) curves



BL(T)	base line correction function between T_A and T_B
α(T)	cumulative partition variable of tanδ(T)-function
T_A	lower baseline setting temperature [°C]
T_B	upper baseline setting temperature [°C]
T	actual measurement temperature between T_A and T_B [°C]
tanδ(T_A)	value of tanδ(T) at temperature T_A
tanδ(T_B)	value of tanδ(T) at temperature T_B

$$BL(T) = (1-\alpha(T)) \cdot \tan(\delta(T_A)) + \alpha(T) \cdot \tan(\delta(T_B))$$

$$\alpha(T) = \frac{\int_{Ta}^{T} tan(\delta)dT}{\int_{Ta}^{Tb} tan(\delta)dT}$$

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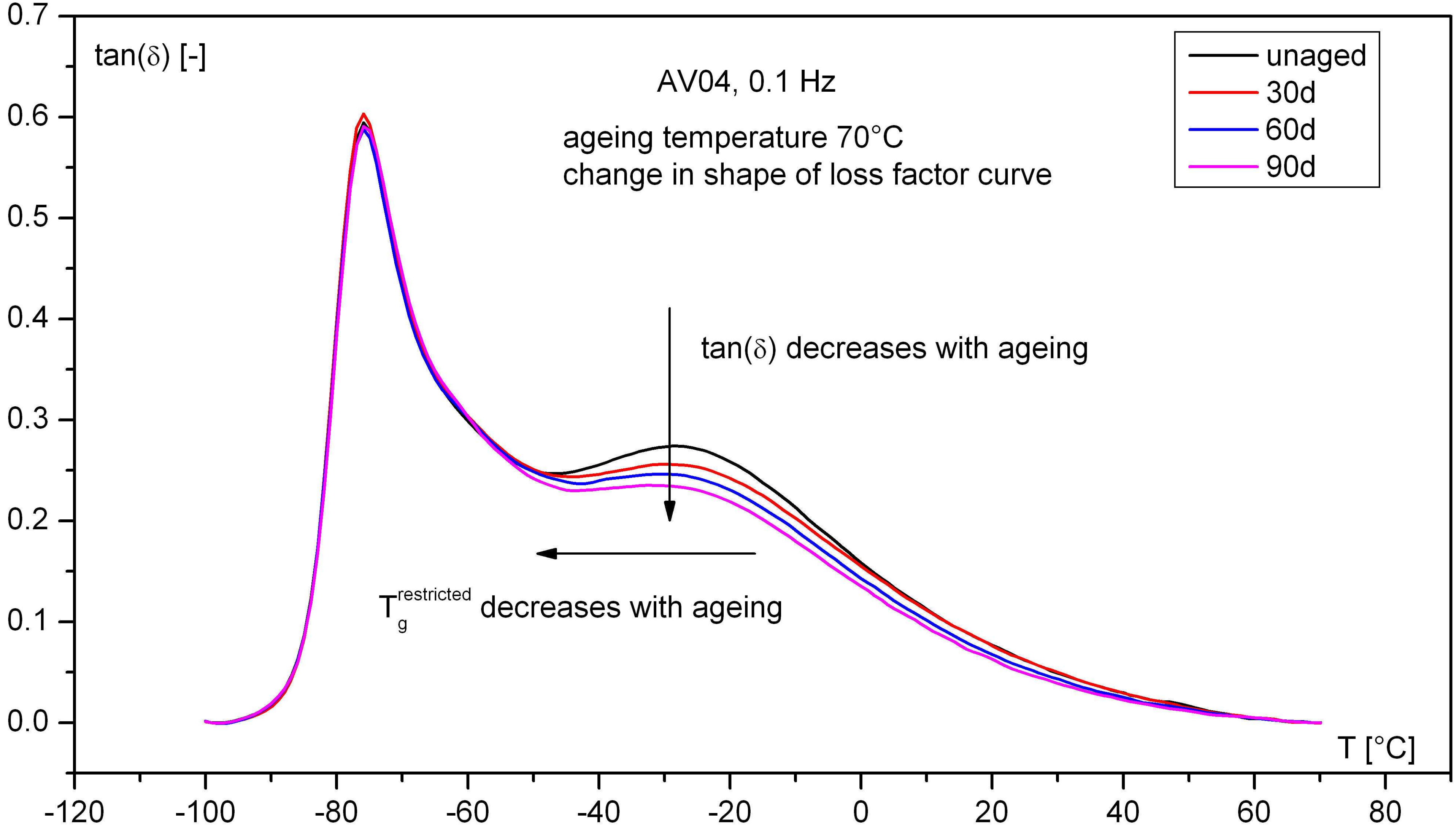
DMA - Comparison of BL-corrected tan(δ) curves with uncorrected ones



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DMA - Modelling of the loss factor curve with the EMG functions

EMG: outcome of a convolution between Gauss distribution and an exponential function

$$\tan(\delta)_{BLC} = td_0 + \sum_{i=1}^{N} \frac{A_i}{\tau_i} \cdot \frac{1}{2} \cdot \exp\left[0.5 \cdot \left(\frac{w_i}{\tau_i}\right)^2 - \frac{T - Tc_i}{\tau_i}\right] \cdot \left\{1 - \operatorname{erf}\left[-\frac{1}{\sqrt{2}} \cdot \left(\frac{T - Tc_i}{w_i} - \frac{w_i}{\tau_i}\right)\right]\right\}$$

T	measurement temperature	[°C]
$\tan(\delta)_{BLC}$	value of $\tan(\delta)$ after the baseline correction (BLC) as function of T	[-]
A_i	peak areas of the EMG peaks, also equivalent of area of the Gauss peak alone	[°C]
w_i	half peak width at half height of only Gaussian part	[°C]
Tc_i	temperature at peak maxima of Gaussian part of EMG (not the peak maxima of EMG)	[°C]
τ_i	relaxation parameter in exponential part of EMG	[°C]
td_0	offset in $\tan(\delta)$ data (for the evaluations here the value was fixed equal to 0)	[-]
N	number of EMG fitting functions	

erf in EMG equation means the error function

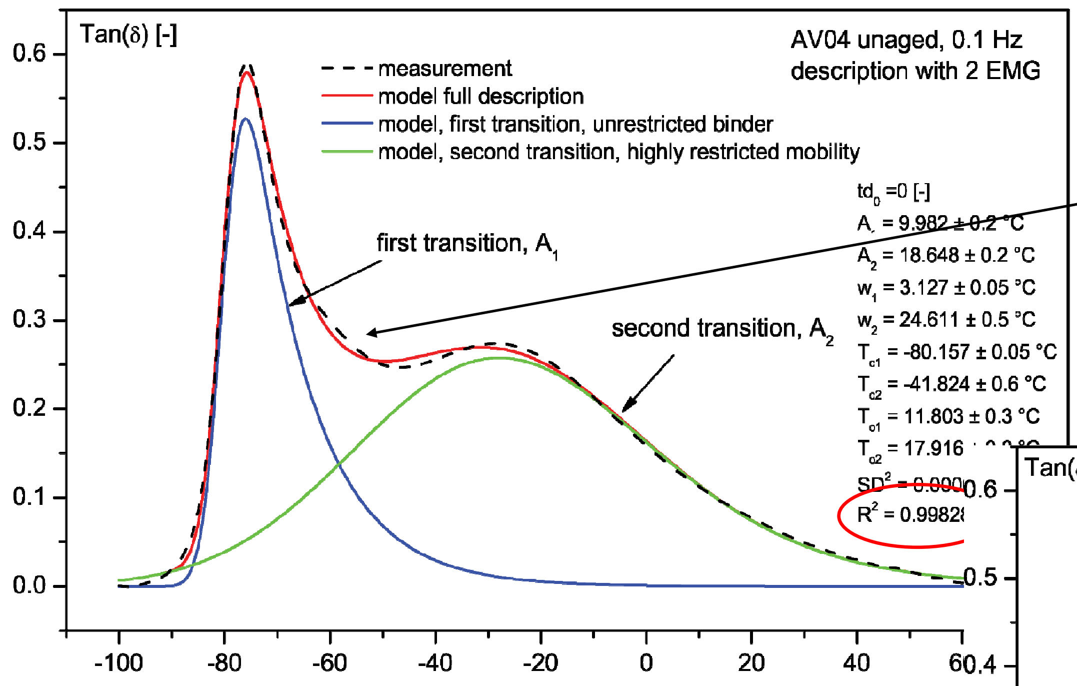
Gauss distribution

$$f_G(T) = \frac{A}{w \cdot \sqrt{2\pi}} \cdot \exp\left[-0.5 \cdot \left(\frac{T - Tc}{w}\right)^2\right]$$

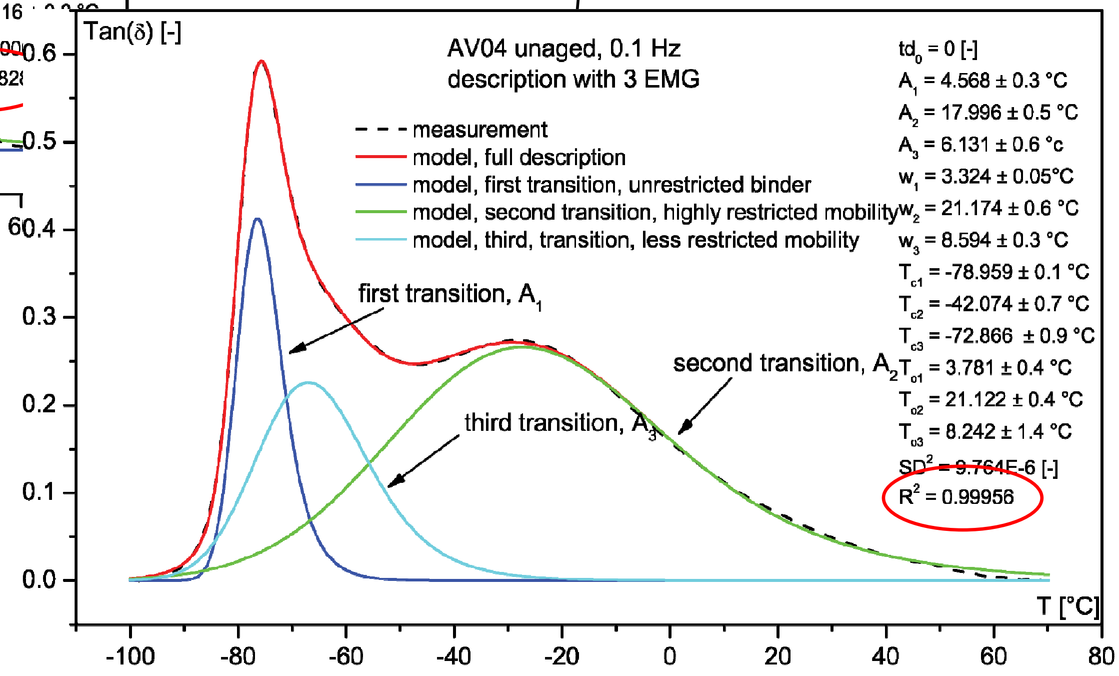
Exponential decay

$$f_E(T) = \exp\left(-\frac{T}{\tau}\right)$$

DMA - Differences in the description of the tan(δ) using 2 or 3 EMGs

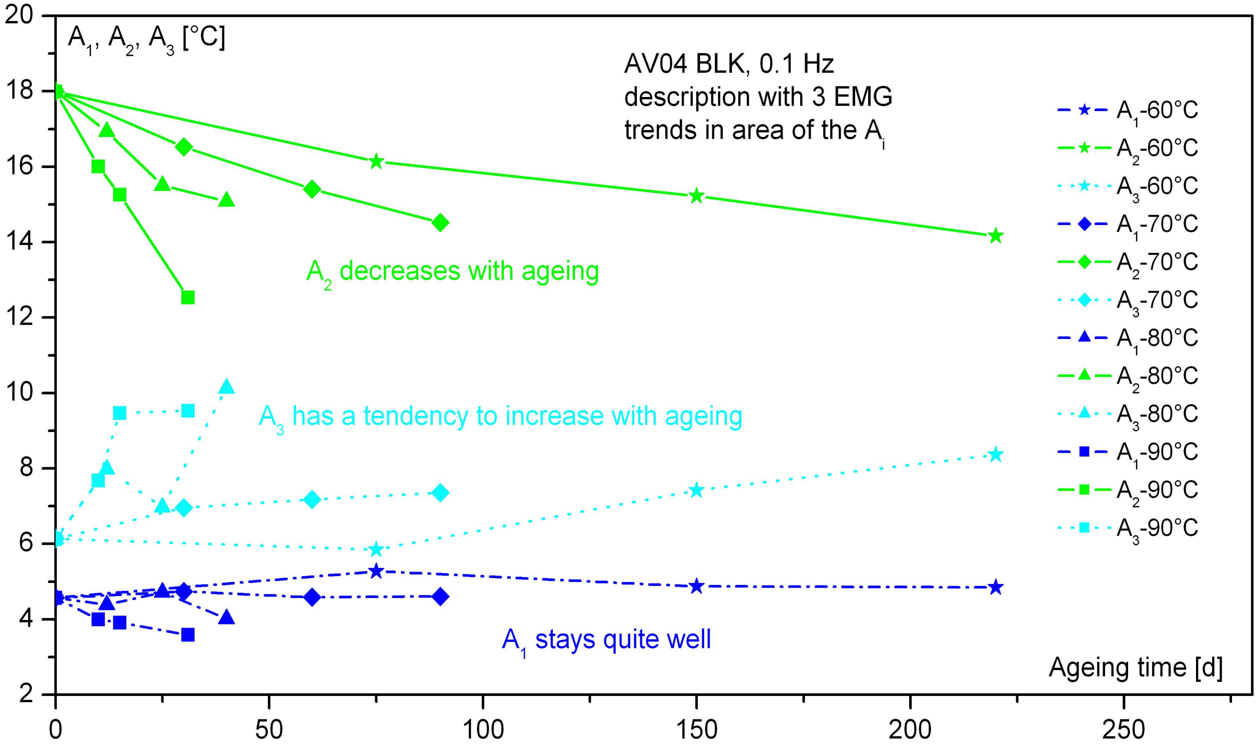


Better description of the valley region in spite of an already high coefficient of correlation (R^2)



- Main transition of the HTPB chains (~-78℃)
- Second transition assigned to restricted mobility of the chains caused by the urethane groups (~-25℃) and binder-filler interaction
- Third transition caused by binder-filler interactions (~-66℃)

DMA - Trend of the areas A_1, A_2, A_3 with ageing time



Peak area **A_2 decreases** and **A_3 increases** linearly with ageing time.
A_1 is nearly constant with time.

Description of the decrease/increase by formal rate constant k_{Ai} (has the dimension peak area/d, actually ℃/d)

By plotting $\ln(k_{Ai})$ vs 1/T it is possible to obtain $E_a(A_i)$
$k_{Ai}=Z(A_i)\cdot\exp(-E_a(A_i)/R\cdot T)$

	Area A_2			Area A_3		
Formulation	**E_a [kJ/mol]**	**Lg(Z [℃/d])**	**R^2**	**E_a [kJ/mol]**	**Lg(Z [℃/d])**	**R^2**
AV03	70.1	9.223	0.9914	69.3	9.128	0.9873
AV04	77.8	10.458	0.9971	95.0	12.769	0.9791
AV05	76.1	10.356	0.9921	72.3	9.167	0.8659

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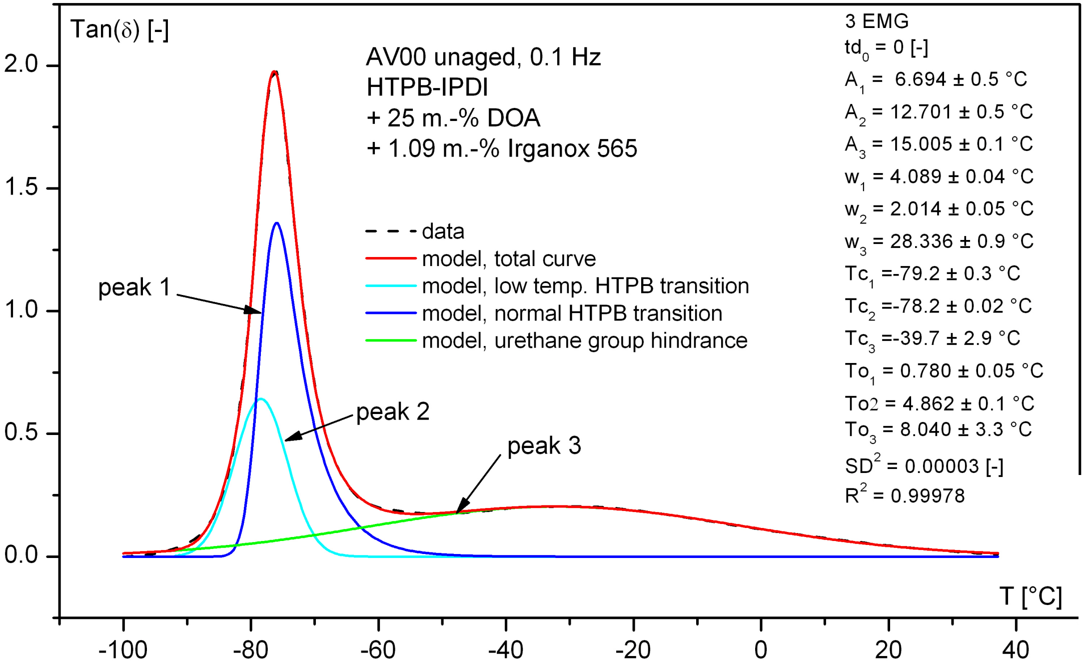
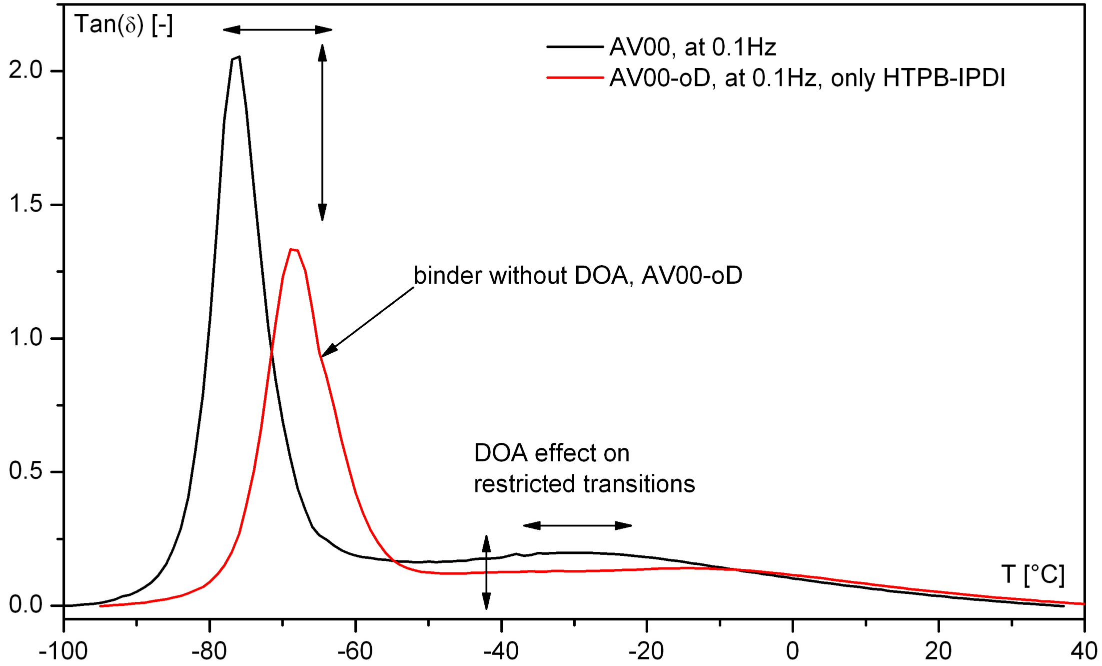
DMA - Loss factor curve of the unaged binder

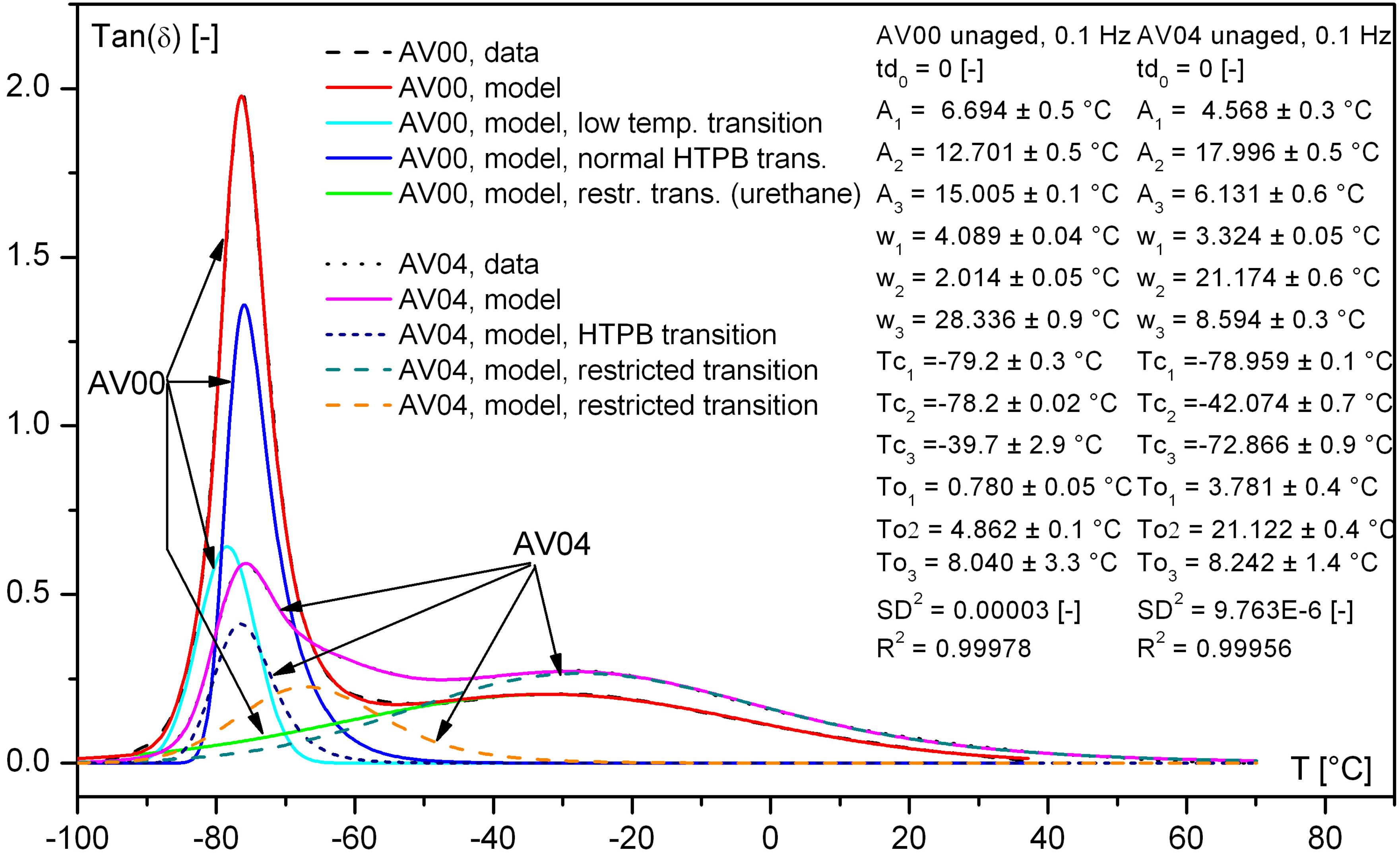


- Apparent main transition peak composed of 2 sub-regions
- Exponential decay part quite low for one of the main transitions, only little frictional movements
- Third transition at high T, broader but well symmetrical associated with the urethane group hindrance

- DOA shifts both T_g –values to lower T and increases the intensity of the main peak (significantly) and the second peak
- Increase of the free volume of HTPB chains
- Pure HTPB-IPDI shows a faint second transition: high mobility restrictions around the urethane cross-linking sites



DMA - Comparison of the loss factor curves: binder vs. propellant



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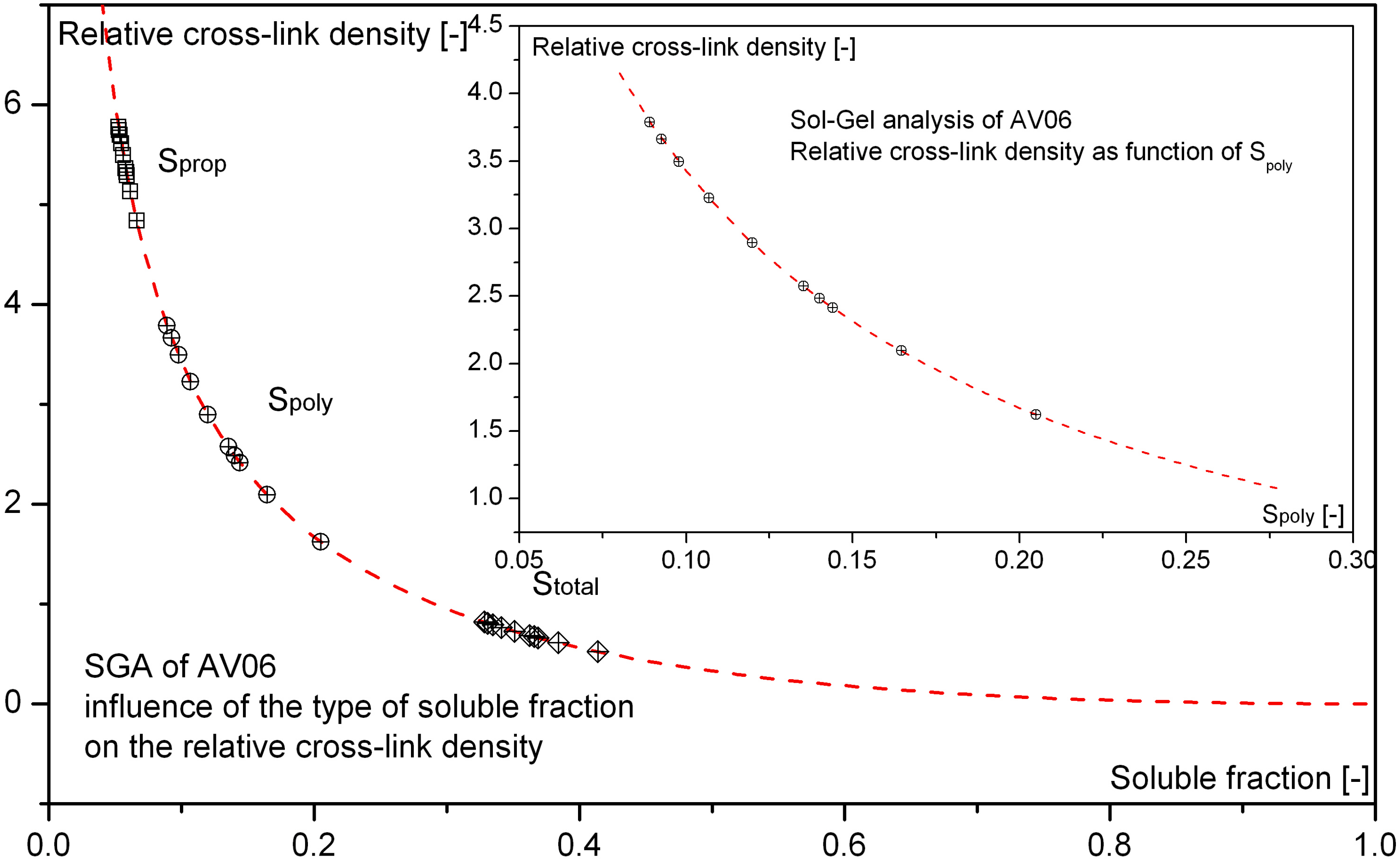
SGA - Evaluation of the soluble parts of the polymeric binder

In STANAG 4581 the procedure is given using the formula $S_{prop} = \frac{E_{total}}{A}$

E_{total}: total extract

A: weighed in amount



Modification of the STANAG formula for the evaluation of the soluble part; - taking into account the presence of other components (DOA and Irganox) in the propellant extracts.

Here is used $S_{poly} = \frac{E_{total} - A \cdot P_{DOA} - A \cdot P_{AO}}{A \cdot (1 - P_{Al} - P_{AP} - P_{DOA} - P_{AO})}$

relat. cross-link density $C = \frac{(1 - S_{poly}) \cdot \left[2 - (S_{poly} + \sqrt{S_{poly}})\right]}{(S_{poly} + \sqrt{S_{poly}})}$

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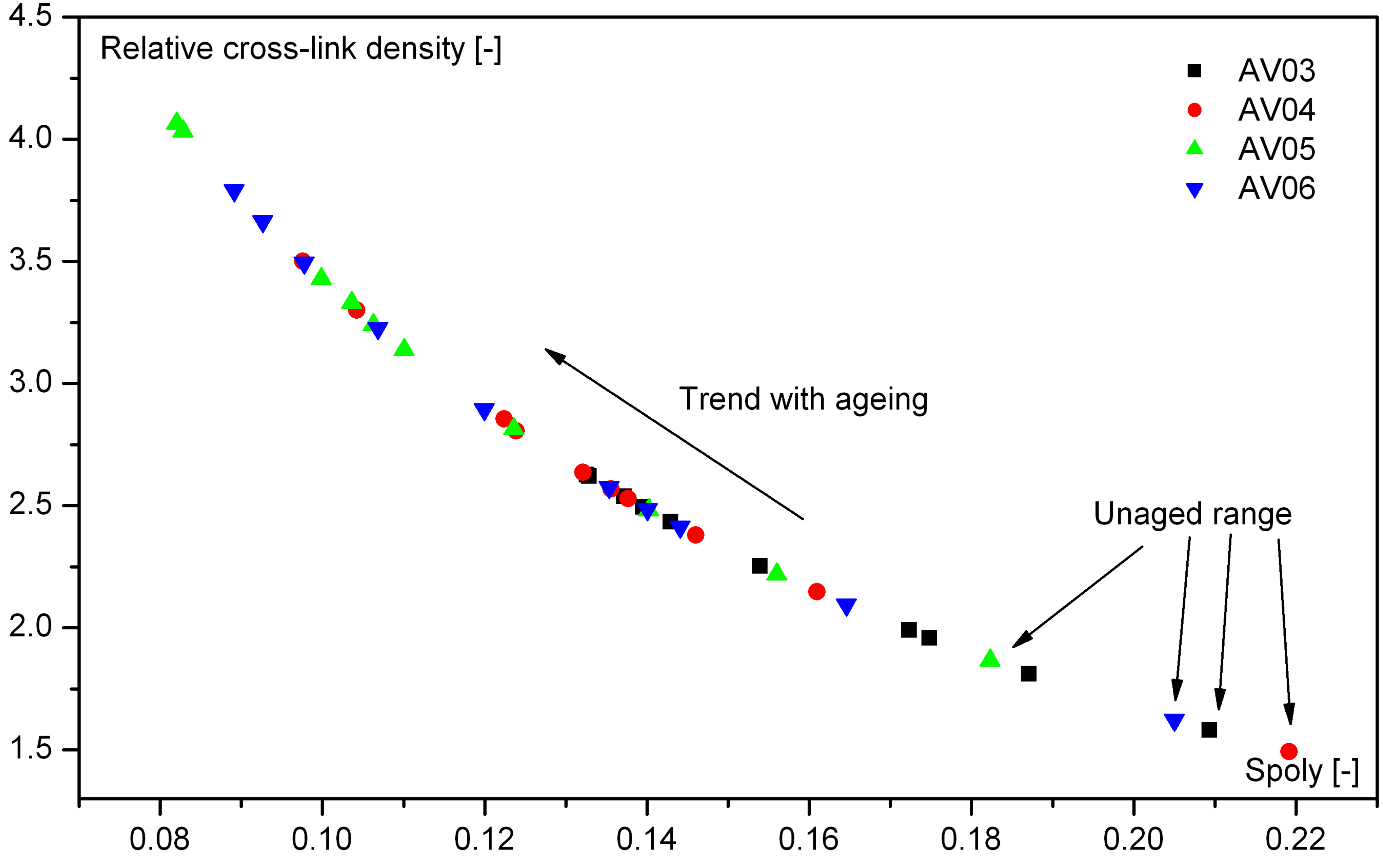
SGA – evaluation of ageing behaviour of the propellants using S_{poly}

Extracted part S_{poly} is ageing time and temperature dependent



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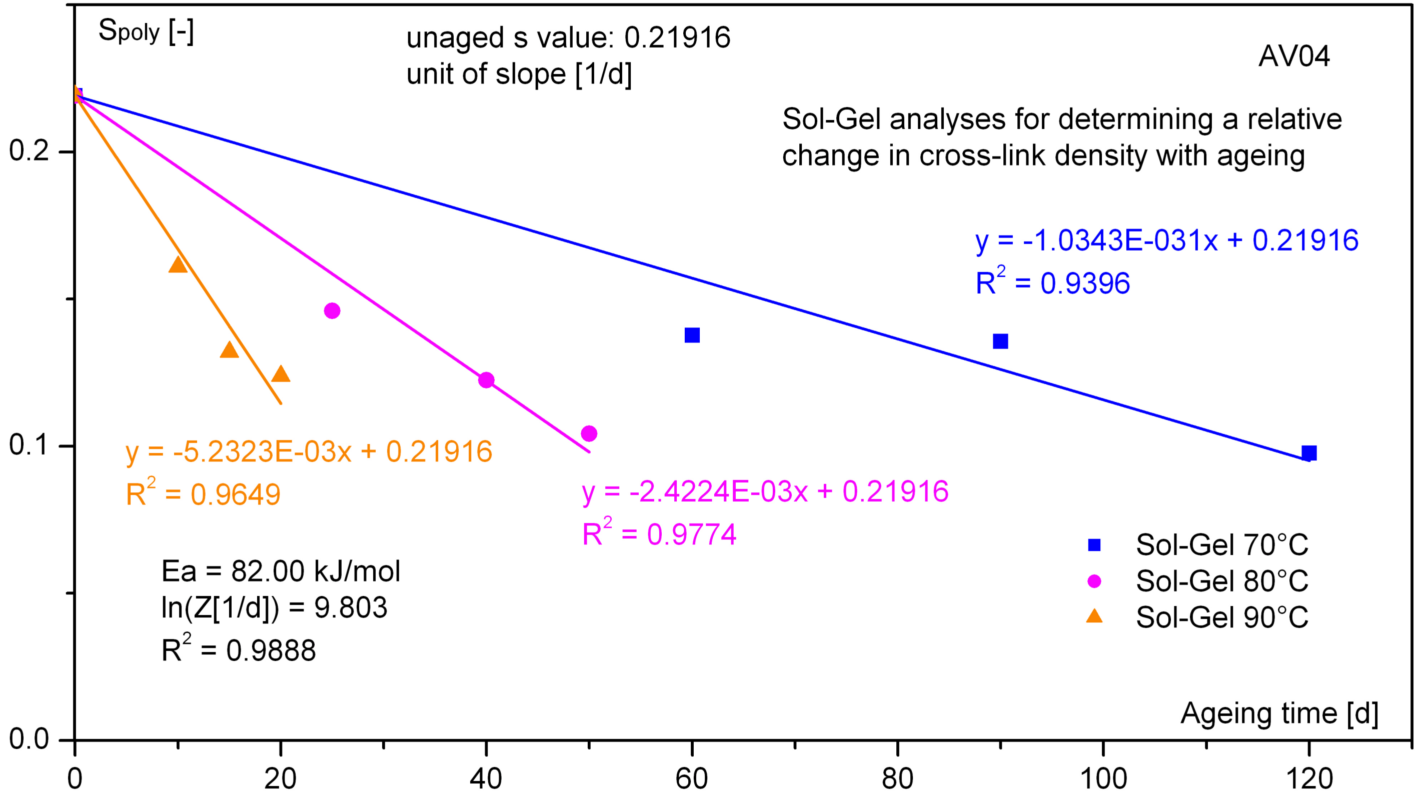
SGA - Evaluation of activation energies E_a from the change rates of S_{poly}



	AV03	AV04	AV05	AV06
$E_a(S_{poly})$ [kJ/mol]	85.1	82.0	72.3	101.5
Log(Z(S_{poly}) [℃/d])	9.794	9.803	7.967	12.373
$R^2(S_{poly})$	0.9984	0.9888	0.9989	0.9976

Used model for decrease of S_{poly}

$$\frac{dS_{poly}}{dt} = k_{Spoly}$$

$$= Z_{Spoly} \cdot \exp\left(-\frac{Ea_{Spoly}}{RT}\right)$$

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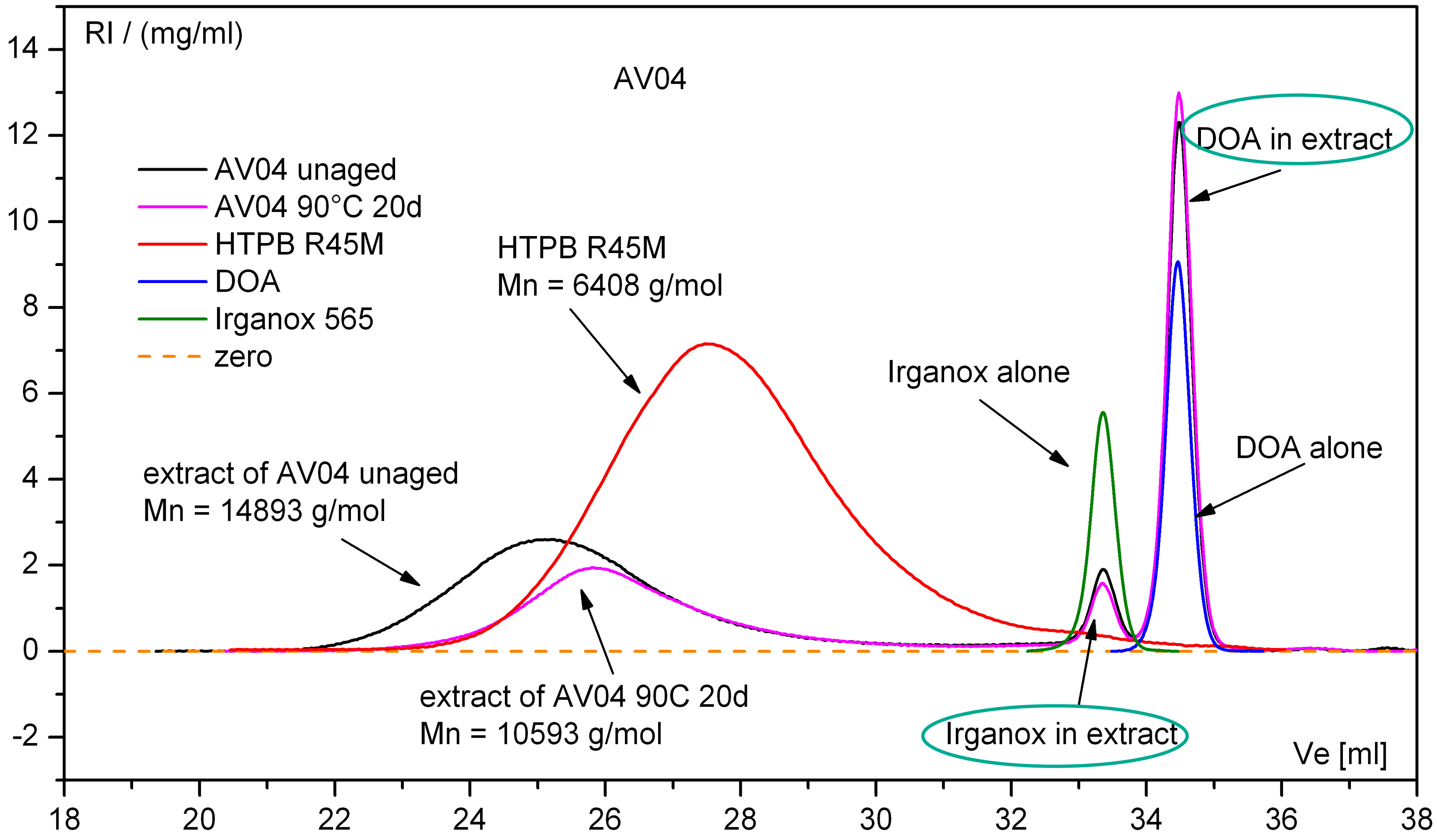
GPC analysis of propellant extracts – overview by elugrams



GPC elugrams showing polymeric part of extract and components DOA and Irganox

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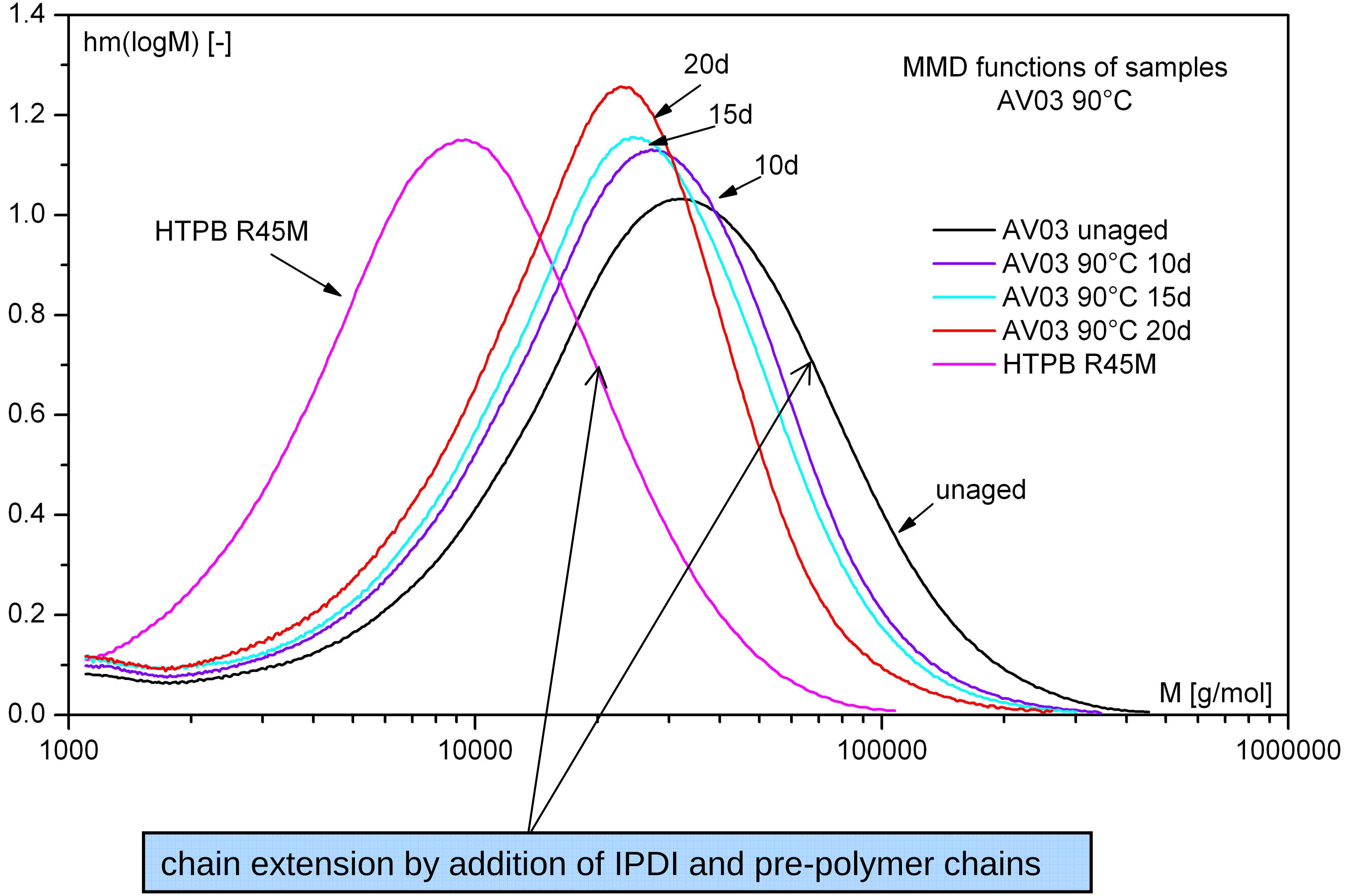
GPC analysis of extracted binder parts in terms of molar mass distribution (MMD)



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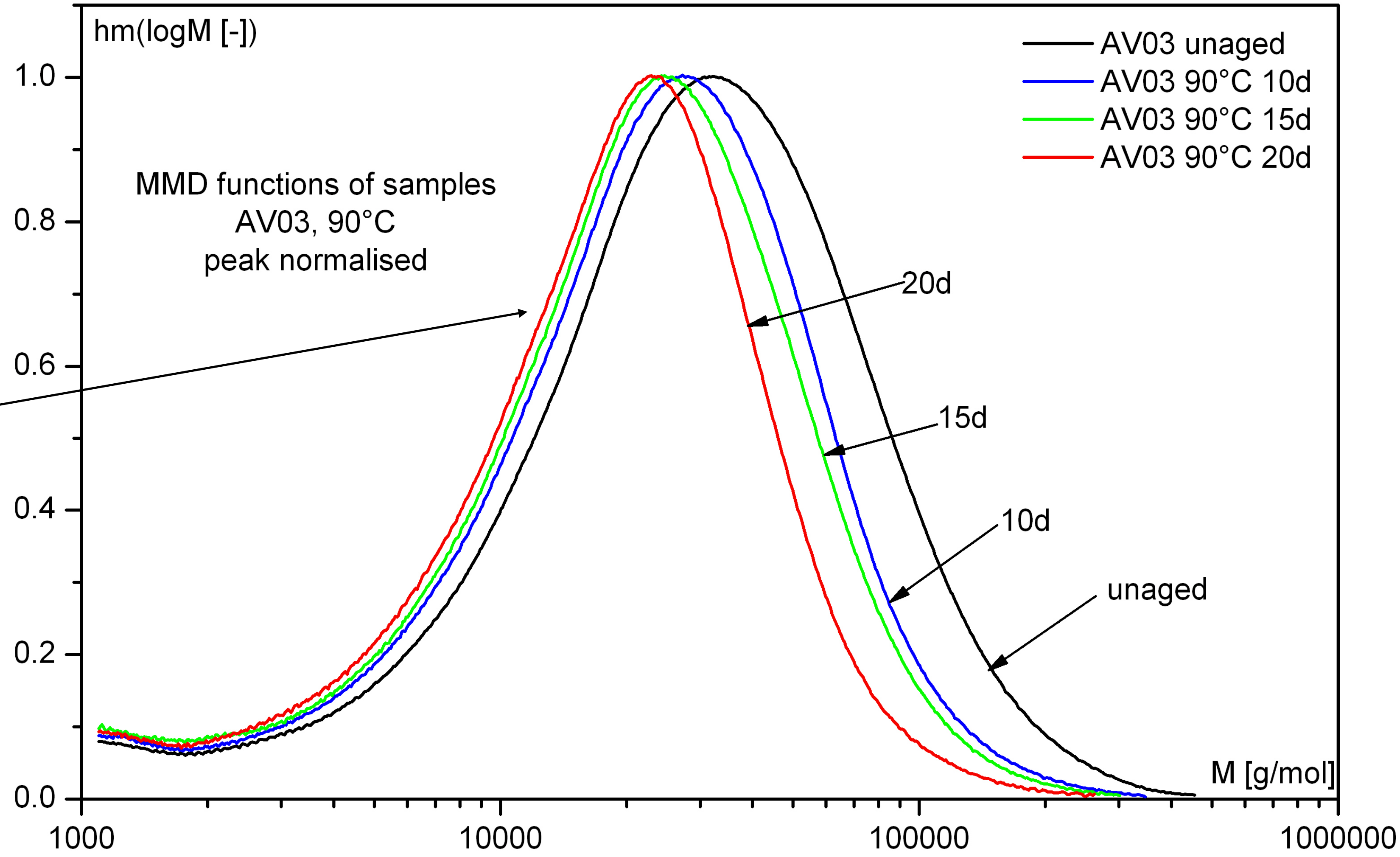
GPC analysis of extracted polymeric parts in terms of MMD

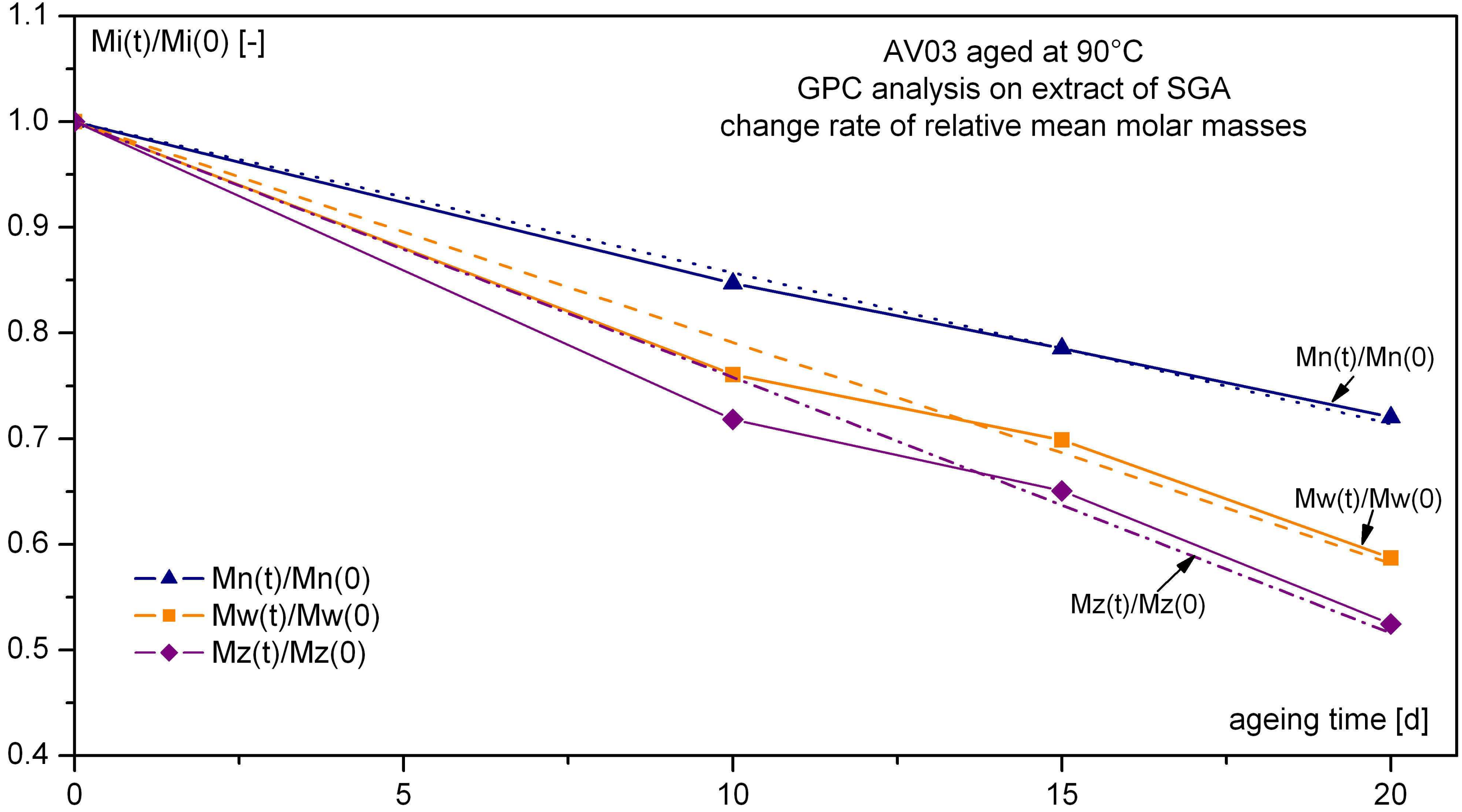
Indication of chain scission, because new short chain material appears after ageing



GPC data evaluation of extracted polymeric parts – mean molar masses

The three main types of mean molar masses, Mn, Mw, Mz change with different rates

Mz changes fastest, Mn is slowest



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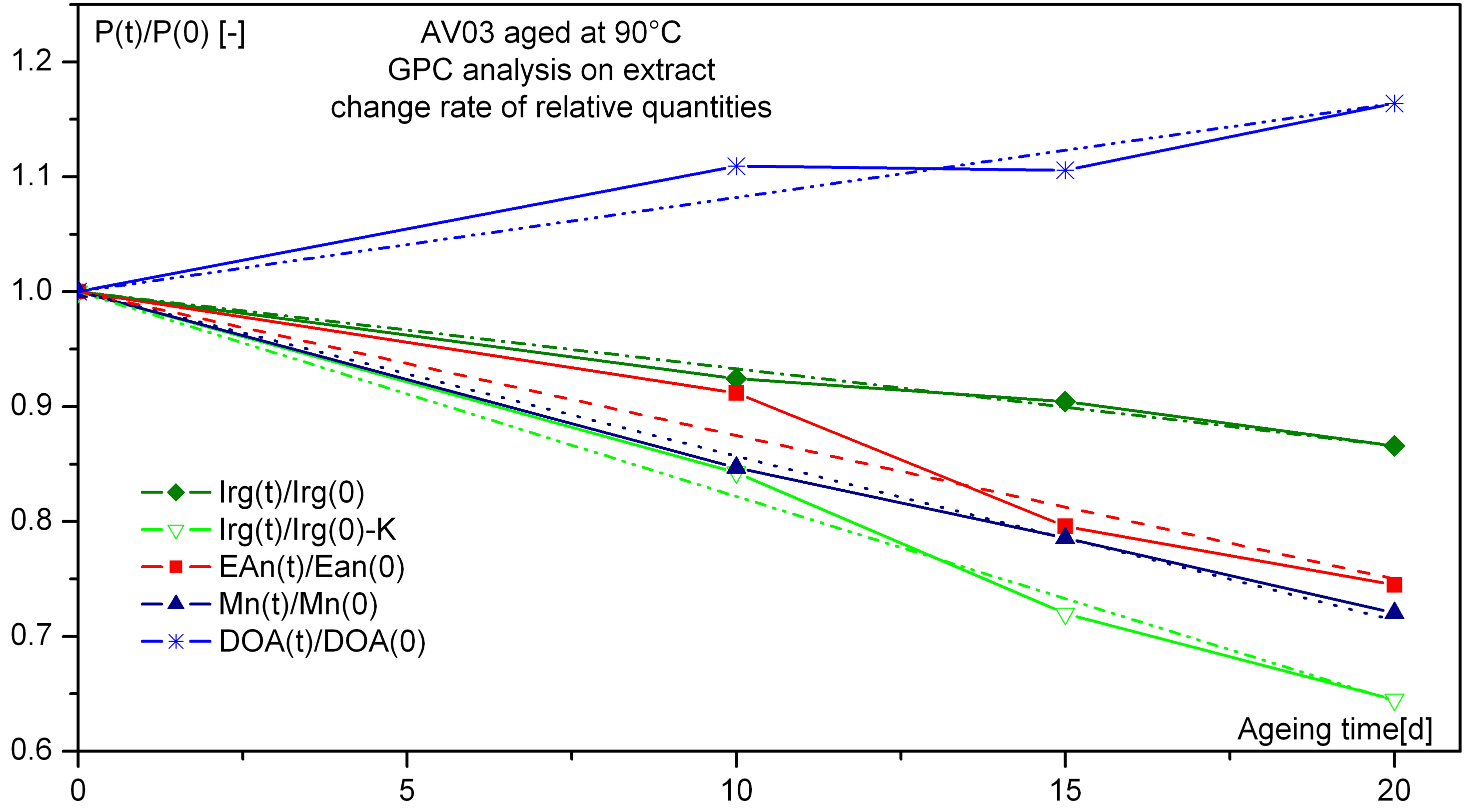
GPC data evaluation of extracted polymeric parts and of DOA and Irganox



Trends with ageing

- Increase of low M side: chain scission
- Decrease of EAn: cross-linking
- Decrease of Irg_{rel}: AO consumption

	Mn_{rel}	EAn_{rel}	Irg_{rel}	$IrgK_{rel}$	DOA_{rel}
E_a [kJ/mol]	89.0	88.4	77.0	85.9	79.5
Log(Z [℃/d])	10.958	10.787	8.870	10.585	9.376
R^2	0.9988	0.9428	0.9156	0.9476	0.9568

$$\left(\frac{dP_{rel}(t,T)}{dt}\right)\Bigg|_T = S \cdot k_P(T) = S \cdot Z_p \cdot \exp\left(-\frac{Ea_P}{RT}\right)$$

$$P_{rel}(t,T) = P_{rel}(0) + S \cdot k_P(T) \cdot t$$

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Conclusions

- Importance of using several techniques to follow the ageing of propellant formulations
- No significant variations in glass transition values $T_g^{unrestricted}$ (pure binder) with ageing
- Clear changes with ageing in the second transition range
- Decrease of the soluble content (S_{poly}) with ageing
- Simultaneous occurrence of chain scission and cross-linking, indicated by GPC results
- Modelling of the loss factor with EMG functions has evidenced the presence of three main glass transition ranges = molecular mobility transition ranges
- Time and temperature dependence (Arrhenius parameterisation and E_a evaluation) of the areas of the second and third mobility transitions (A_2, A_3), sol contents (S_{poly}), mean molar masses (Mn), normalised eluate area (EAn_{rel}), Irganox and DOA content (Irg_{rel}, DOA_{rel})
- Change of cross-linking density in binder shells around the fillers means change in strain capability in these matrix ranges – in second range a decrease is indicated