

# Computer Integrated Manufacturing of Polyurethane Foams Steered by Measured and Calculated Data in Comparison

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**Abstract:** Polyurethane foams were manufactured under continuous measurements of isocyanate content, temperature, expansion and viscosity. Parallel model calculations were executed based on the driving force of 50kJ/mole heat of reaction of the energy rich isocyanate group and on thermodynamic balances of weight and heat of formation as well as on a kinetic model using a first order reaction for the isocyanate consumption and a relation for the viscosity dependent on conversion and on a viscosity constant. The agreement between continuous measured and calculated data was satisfying. The parameters isocyanate content, temperature, expansion and viscosity controlled and steered the variables of the production plant, like dosage of components, temperature and conveyer speed. The kinetic model was also valid for polyurethane foams with additives, which did not react with components of foam, like flame retardants or pigments. The thermodynamic balances of weight and heat predicted residues and consumed heats by degradation under fire, which correlated with those measured by TGA and DSC. The target was to establish computer integrated manufacturing without continuous measurements but by mere model calculation. This was possible with the knowledge of the first order velocity constant and the viscosity constant.

**Keywords:** Thermodynamic, Kinetic, foaming model, flame retardants.

## 1. INTRODUCTION

World wide 15 Mio metric tons polyurethane have been produced in 2014. Half of them are foams: rigid foams with compressive strength about 0.100MPa for insulation in buildings and soft foams with compressive strength of 0.003MPa for mattresses for furniture. Though the commercial importance is high, still improvable aspects are the safe and economic production of efficient flame retarded polyurethane foams by computer integrated manufacture [1-13].

Computer integrated manufacturing CIM is the integration of total manufacturing enterprise by using integrated systems and data communication coupled with new managerial philosophies that improve organizational and personnel efficiency. In the 1980's the CIM wheel has been invented by CASA/SME (Computer and Automated System Association of the Society of Manufacturing Engineers of the USA), which is steered by the integrated system architecture with common data and information resource management and communication. The CIM wheel is further developed to the Manufacturing Enterprise Wheel, where in the centre is no longer the integrated system architecture but the customer.

The software to manage a continuous production of flexible polyurethane foams by slabstock technology is available [14-19]. Continuous measurements are

described concerning the temperature with contactless pyrometer determining the IR radiation emitted from the foam and those of the expansion of the foam by ultra sound distance sensors in order to steer the controlled variables as conveyer speed, composition of the materials, temperature of materials, temperature of facing layers fed to the process and temperature of pouring plate. A new aspect is introduced by continuously measuring isocyanate consumption, viscosity and by using a foaming model in addition.

Therefore soft foam formulations with the flame retardants melamine [20] and aluminium trihydrate [21] and rigid foam formulations in the presence of ammonium polyphosphate [22] or polyisocyanurate foams [23-25] in combination with tris butoxyethylphosphate are investigated. During the foaming process the isocyanate concentration is recognized by IR spectroscopy, the temperature by contactless IR thermo sensors, the expansion height by ultrasound distance sensors and the viscosity by an oscillating viscometer. The produced foams are characterized by their density, tensile strength, compressive strength and burning behaviour [26]. The decomposition of the foams is followed by DSC and TGA measurements.

Furthermore balances of weight and heats of formation are established, which allow to follow the path of synthesis, which is driven by the energy rich isocyanate bond with 50kJ/mole, which is deduced from the balances of heat. 75kJ/mole is published for the reaction between methanol and methylisocyanate [27].

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For the reaction  $-N=C=O + O-H = -NH-COO-$  the N=C bond (615kJ/mole) and O-H bond (463kJ/mole) have to be broken and the bonds N-H (305kJ/mole), C-N (391kJ/mole) and C-O (358kJ/mole) will be made. By difference a reaction heat of 24kJ/mole is gained [28].

Synthesis of  $n$  moles of reactants with equivalent weight  $EW_n$  (g/equivalent) and heat of formation  $H_{fn}$  (kJ/equivalent weight) react under heat of reaction  $H$  to polyurethane:

$$n \cdot EW_n \text{ reactants} = EW \text{ polyurethane}$$

$$n \cdot H_{fn} \text{ reactants} + H = H_f \text{ polyurethane}$$

When the amounts of flame retardants are sufficient, then burning is prevented and only decomposition takes place, which also can be described by the balances of weight and heat.

Polyurethanes decompose under heat development  $H$  (kJ/mole) to gaseous or solid decomposition compounds. The residues  $R\%$  and heats of decomposition  $h$  (kJ/g) are calculated and compared with those measured by DSC and TGA experimentally:

$$EW \text{ polyurethane} = n \cdot EW_n \text{ decomposition products}$$

$$H_f \text{ polyurethane} + H = n \cdot H_{fn} \text{ decomposition products}$$

Also a kinetic foaming model is developed. The isocyanate conversion  $U$  follows a first order velocity reaction with  $c_{01}$  the isocyanate initial concentration and  $k_1$  the velocity constant:

$$U = 1 - 1 / (k_1 \cdot c_{01} \cdot t - 1) \quad \text{equ.1}$$

In the formulations the observed heat of reaction  $H$  depends on the initial concentration  $c_{01}$  of isocyanate groups with 50kJ/mole bond energy and on the conversion  $U$ :

$H = 50 \cdot c_{01} \cdot U / 100$  (kJ/equivalent weight). When  $H$  is divided by the equivalent weight of NCO = 42g/mole, then  $h = 11.9 \cdot c_{01} \cdot U$  (kJ/kg) is obtained.

$$h = 11.9 \cdot c_{01} \cdot U \quad \text{equ.2}$$

Foaming can take place by chemical blowing in the water reaction, where  $c_{02}$  is the initial water concentration of the formulation.

Foaming can take place by physical blowing with an auxiliary blowing agent as pentane with the initial concentration  $c_{03}$ .

The increase in viscosity starts with the initial viscosity  $\nu_0$  and follows equation 3:

**Table 1: Chemicals Used**

Brand name	Company	Formula	Abbreviation
Desmophen 7652Y	Bayer	$(C_{32}H_6O)_{32}$	
Diethanolamine	BASF	$C_4H_{11}NO_2$	
Dabco 33 LV	Bayer		
Dibutyltindilaurate	Bayer		
Stabilisator AC 3367	Goldschmidt		
Tolylene diisocyanate	Bayer	$C_9H_6N_2O_2$	
Caradole 520	Shell	$(C_3H_6O)_2$	
n-Pentane	Haltermann	$C_5H_{12}$	
Exolite 420	Lanxess	$(NH_4PO_3)_n$	APP
Caradate 30	Shell	$C_{16}H_{12}N_2O_2$	
Castor oil	Bayer	$C_{18}H_{34}O_3$	
Lupranol 3602	BASF	$(C_3H_6O)_{.3}$	
Glycerol	Bärlocher	$C_3H_8O_3$	
2Polycat 41	Abbott	Dimethylaminopropyl hydrotriazin	
K-formiate	BASF		
Melamine	BASF	$C_3H_6N_6$	M
Tributoxyethylphosphate	Clariant	$C_{18}H_{39}O_7P$	TBEP
Martinal OL107 LEO	Martinswerke	$Al(OH)_3$	ATH

$$v=v_0*k_2^U \quad \text{equ. 3}$$

$k_2$  is a constant parameter for each formulation.

## 2. EXPERIMENTAL

### Chemicals

All chemicals used in the formulations for polyurethane foams were collected in Table 1.

### Equipment and Materials

Combustion Modified High resilient foam CMHR, rigid foam PU and polyisocyanurate foam PIR were produced. During foaming over the first 10 minutes the isocyanate concentration was determined by Fourier transmission infrared FTIR spectroscopy by diminished reflection ATR of the foam using the ratio of intensity of the NCO band at  $2270\text{ cm}^{-1}$  and the CH band at  $3040\text{ cm}^{-1}$ . A FTIR Spectrometer Digilab 15B/D and a liquid light guide from Lumatec were used. The continuous IR measurements were controlled and gauged by titration of the NCO content in samples taken in time intervals. The temperature of the foam was measured by IR radiation measurement, which were performed with contactless IR thermo sensors OS 35 (Omega) and the viscosity was determined by an oscillating viscometer. The oscillating viscometer consisted of a torsion wire with a turning body, which dipped into the foam. A generator produced the oscillation, which was enhanced by operating amplifier. A stimulating coil induced oscillation to the permanent magnet. The increasing viscosity of the foam weakened and retarded the primary oscillation and produced a secondary oscillation. The secondary oscillation was transmitted over reception coils to the measuring coil and transmitted to the carrier frequency bridge. A frequency analyzer visualized the secondary oscillation.

The expansion was determined by the ultra sound distance sensor nano 24/CE from microsonic. The manufactured foams were characterized by the tensile strength the compressive strength measured on Autograph AG-X Series (Shimadzu).

The combustion behaviour was investigated by Cone Calorimeter Fire Testing Technology CFTT conformable to ASTM E 1354-1992 and by LOI measurements. Soft foams were tested under conditions described in the British Standard 5952 Part 2 Crib 5. The combustion behaviour of rigid foams was

tested according DIN 4102 and the Single Burning Item Test. Their weight losses were determined as described in ASTM D3014.

Furthermore thermogravimetric analysis TGA as well as differential scanning calorimetry DSC were performed on a Mettler Toledo TMA/SDTA 840 with TGA/SDTA 851 Modul. The intumescent ingredients were characterized by thermal gravimetric analysis (TGA) on a Mettler Toledo TMA/SDTA with TGA/SDTA 851 Modul. The samples were placed in aluminium oxide crucibles of 900  $\mu\text{l}$  volume (ME 511119, 960) with 12 mm diameter covered by punctured lids. The TGA measurements took place under air or nitrogen with 80 ml/min and heating rates of 5 -20K/min. The TMA measurements were performed in aluminium oxide crucibles with 7 mm diameter and 4.6 mm height covered by 6mm diameter lids in air or under nitrogen at heating rates of 5 to 20K/min.

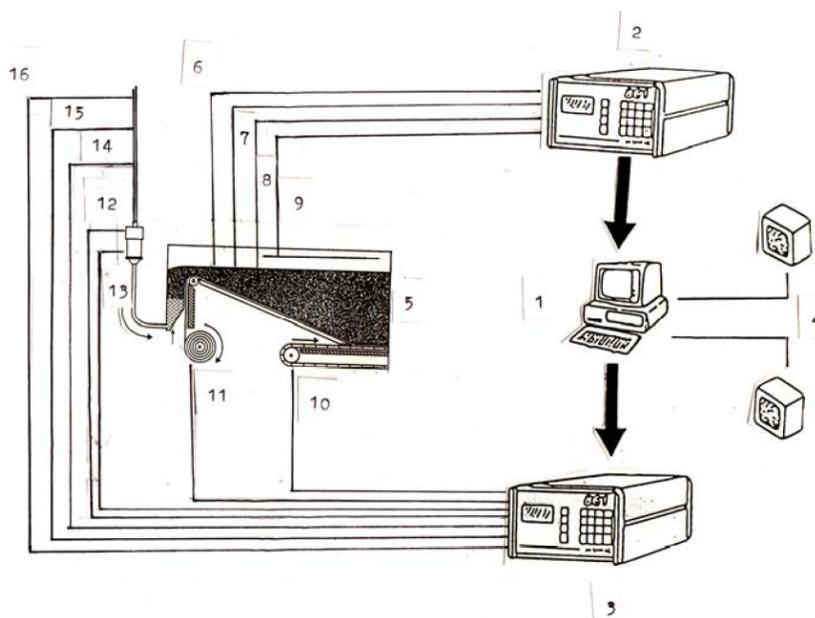
The heats of combustion  $h_{\text{comb}}$  were measured in a calorimeter according to DIN 51900 Teil 2 (1977) Heizwertbestimmung.

C(ombustion) M(odified) H(igh) R(esilient) foam was manufactured in large scale on a Maxfoam plant from Cannon shown in Figure 1 as scheme. The plant was equipped with a FTIR apparatus together with a light guide combined with FTIR applying the diminished total reflection technology for the determination of the isocyanate content 6, with IR thermo sensors OS 35 (Omega) for temperature measurements 7, with an oscillating viscometer for the continuous recognition of viscosity 8, with ultrasonic sensors Nano-24/CD (microsonic) for the continuous measurement of expansion 9.

The production plant consisted of a decentralized hardware concept. A central computer communicated with two multiplexers, one, which concentrated the data of the micro steered plant, and another, which concentrated the data for apparatus, which determined controlled variables of the plant.

The measured data were transmitted to Multiplexer for concentration of the data. A central computer was enabled to compare the measured data with the required data and to inter- or extrapolate data with the help of the foaming model. The central computer gave order to the second Multiplexer, which governed the plant.

By a master system a central computer 1 controlled the communication and integrated functions of the plant



**Figure 1:** CIM schemata for the Maxfoam plant: 1 central computer, 2 multiplexer for input data, 3 multiplexer for output data, 4 video screens, 5 foam, 6 IR sensor for NCO concentration, 7 temperature sensor, 8 viscosity sensor, 9 expansion sensor, 10 speed regulator for the conveyer, 11 temperature control of facing layers, 12 speed regulator in the mixing head, 13 pressure regulator in the mixing head, temperature regulator in the mixing head, 14 temperature control of the components, 15 control of component composition and 16 the dosage of dispersed gases.

incorporating each individual production area. The central computer communicated with the production line via area specific personal computers equipped with task oriented polyurethane specific software.

The multiplexer 2 concentrated the input data and transmitted them to the central computer 1. The central computer checked the data inter- and extrapolated the data supported by the foaming model and gave order to multiplexer 3, which concentrated the data for relay transmitters steering the plant. The whole plant was governed by microprocessors: the conveyer speed 10, the temperature of facing layers fed to the foaming process 11, the revolution in the mixing head 12, the pressure in the mixing head 13, the temperature of the components 14, the composition of the components 15 and the dosage of dispersed gases 16 were controlled and steered.

## FORMULATIONS

### Combustion Modified High Resilient Foam

In Table 2 the ingredients were summarized for the manufacture of flexible foam for mattresses. The providing companies, the parts, the formulas, the equivalent weights EW and the equivalents E were pointed out. The index I corresponded to the equivalents isocyanate divided by the sum of equivalents of isocyanate consuming components.

The measured data for the isocyanate content  $c_1$ , the conversion of isocyanate U, the viscosity  $v$ , the temperature T and the expansion b for the CMHR foam during the first 10 minutes were recorded in Table 3.

Over the period of 10 minutes the NCO content  $c_1$ , decreased from 12 to 0.9%, the conversion U reached nearly 1, the viscosity  $v$  started with 0.5 Pa\*s and reached  $1.8 \cdot 10^2$  Pa\*s, the temperature T increased from room temperature to 123°C and the expansion b ended with 36. The expression b was defined as density of the unexpanded foam  $1000\text{kg/m}^3$  divided by the density of the expanded foam minus 1.

$$b = (1000/d_f) - 1 \quad \text{equ. 4}$$

In this case the density of the foam  $d_f$  amounted  $27\text{kg/m}^3$ .

The conversion U was defined as  $(c_{01} - c_1)/c_{01}$  with  $c_{01}$  as the initial NCO concentration

As the flame retardants did not react with the ingredients, the FR's could be treated separately.

Vapour pressure measurements of melamine opened the possibility to determine the heat of sublimation of melamine  $0.97\text{kJ/g}$  using the equation of Clausius Clapeyron.

**Table 2: Formulation of High Resilient Foam HR- and CMHR-Foam**

Ingredients	Company	parts	Formula	EW	E	%
Desmophen 7652Y	Bayer	100	(C <sub>3</sub> H <sub>6</sub> O) <sub>32</sub>	1856	0.054	
Water		4		9	0.444 C <sub>02</sub>	2
Diethanolamine	BASF	2	0.33*C <sub>4</sub> H <sub>11</sub> NO <sub>2</sub>	35	0.057	
Dabco 33LV	Bayer	0.1				
Niax A-1	Bayer	0.05				
DBTDL	Bayer	0.19				
Stab. AC 3367	Goldschmidt	0.259				
TDI 80 48%NCO	Bayer	50.7	0.5*C <sub>9</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub>	87	0.583 C <sub>01</sub>	12
	Sum	157.3				
Melamine	BASF	45.1			cM	22,3
	Sum	202.4				

Index= 0.583/0.555= 1.05

Three samples were manufactured:

1. HR-foam without flame retardant.

2. CMHR-foam with 22.3% melamine.

3. CMR-foam with 43.0% aluminium trihydrate.

**Table 3: Experimental Data for CMHR-Foam with 22.3% Melamine**

time min	c <sub>1</sub> w%	U	lgv Pa*s	T °C	b
0	12	0	-0.3	25	0
1	7	0.42	1.1	68	25
2	5	0.58	1.6	85	35
3	3.5	0.71	1.8	94	36
4	3	0.75	2.0	99	36
5	2.5	0.79	2.05	104	36
6	2	0.83	2.1	109	36
7	1.5	0.88	2.15	113	36
8	1.3	0.89	2.2	117	36
9	1.1	0.91	2.23	120	36
10	0.9	0.93	2.25	123	36

The balances of weight and heat determined 1kJ/g heat of sublimation.

By sublimation melamine evolved 1 mole gas or 419ml/g gas:

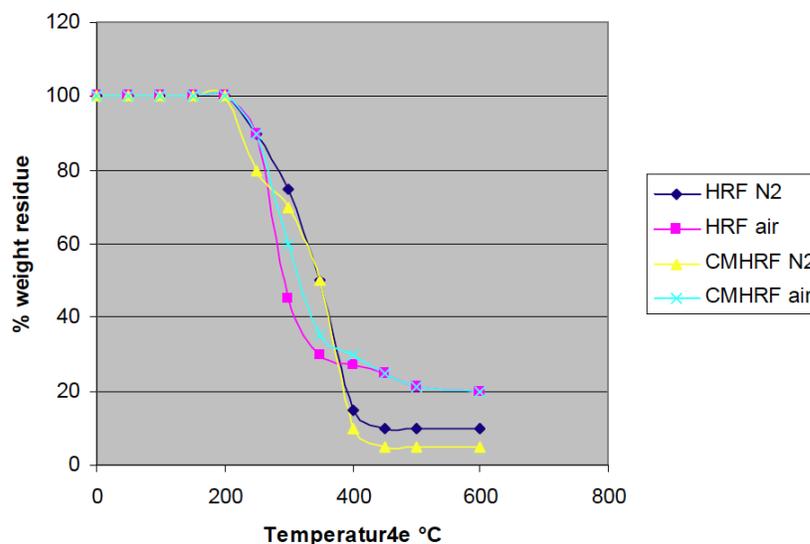
$$V_{\text{gas}} = 22400 * (1 + 370/273) / 126 = 419 \text{ ml/g} \quad \text{equ.5}$$

Melamine burned and produced 9 mole or 3768ml/g gas under -15,6kJ/g heat evolution.

$$V_{\text{gas}} = 9 * 22400 * (1 + 370/273) / 126 = 3768 \text{ ml/g} \quad \text{equ.6}$$

The TGA measurements of HR without melamine and CMHR with 22.3% melamine were performed under air and nitrogen at a heating rate of 10K/min and visualized in Figure 2. After differentiation the HR foam under nitrogen showed two peaks, one with 40% residue at 280°C and the other with 10% at 380°C. In air decomposition was enhanced but led to a higher amount of oxidized products resulting in more residues at 500°C.

The flame retardant Al (OH)<sub>3</sub> was tested as possible alternative to melamine.



**Figure 2:** TGA in air and under nitrogen: HRF-Foam and CMHR-Foam, heating rate 10K/min. After differentiation peaks of decomposition occurred at 280°C R=60% and at 380°C R=10% for HRF in nitrogen and at 250°C R=50% and 380°C R=25% in air. CMHR exerted peaks at 250°C R=80%, 300°C R=50% and 380°C R=5% under nitrogen at 250°C R=60% and 380°C R=25% in air.

At 300°C aluminium trihydrate split off 452ml/g water under 1,18kJ/g heat uptake measured by DSC.

$$V_{\text{gas}} = 1.5 * 22400 * (1 + 300/273) / 156 = 452 \text{ ml/g} \quad \text{equ. 7}$$

In the limiting oxygen test (LOI test) melamine was twice more active than Al(OH)<sub>3</sub>.

$$\text{LOI} = 19 + 0.29 * w\% \text{ melamine} \quad \text{equ. 8}$$

$$\text{LOI} = 19 + 0.15 * w\% \text{ Al(OH)}_3 \quad \text{equ. 9}$$

When 22.3w% melamine were added, a LOI value of 25.5% was reached, the same LOI value was achieved by the addition of 43% Al(OH)<sub>3</sub>.

The foams comprising 22.3% melamine and 43% ATH fulfilled the demands of the British Standard test BS 5852 Part 2 Crib 5: flame extinguished after 10 minutes, no smoke after 60 seconds and weight loss less than 6%. As a consequence of high filling the flexible foam with 43% aluminium trihydrate was no longer high resilient. The CMHR foam based on melamine was also investigated by Cone calorimeter at a heat flux of 50kW/m<sup>2</sup>. The rate of heat release RHR was as much as 1200 kW/m<sup>2</sup> for the HR foam and was reduced to 600kW/m<sup>2</sup> for the CMHR foam.

### Rigid PU Foam

Rigid PU foams applied in the building industry as insulating material were submitted various fire tests like

DIN 4102 or the Single Burning Item Test with the classifications B1 and B2 or A, B and C.

In Table 4 the formulation of the rigid foam without flame retardant was summarized.

Two types of rigid foam were manufactured one without flame retardant and one with the flame retardant ammonium polyphosphate. APP burned under -3.5kJ/g heat development.

In the DSC investigation ammonium polyphosphate exerted two heat sinks one at 350°C with 0.56kJ/g and one at 700°C with 1.9kJ/g. Over all 1.5 moles of gas were split off.

$$V_{\text{gas}} = 1.5 * 22400 * (1 + 320/273) / 97 = 752 \text{ ml/g} \quad \text{equ. 10}$$

In the run of a TGA measurement rigid foams PU without flame retardant PU and with 12.4% APP FR-PU were heated at a rate of 10K/min in air.

In the Cone calorimeter with a heat flux of 5kW/m<sup>2</sup> the rate of heat release was reduced from 120kW/m<sup>2</sup> for the PU foam to 40kW/m<sup>2</sup> for the PU-FR foam with 12.4% APP.

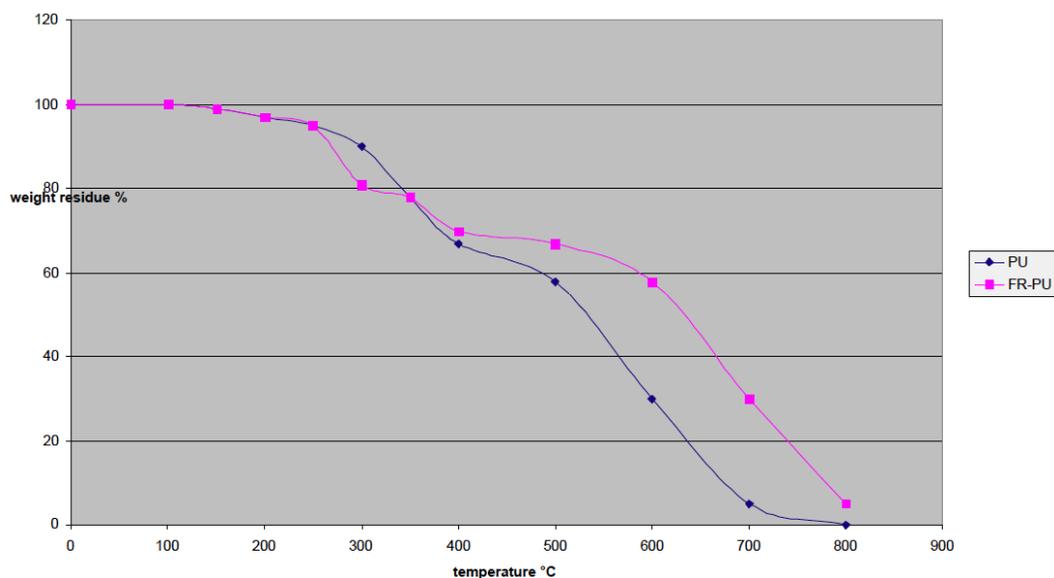
The weight loss of the PU-FR was determined according to ASTM D-3014. With 12.4% APP a weight loss of 13.3% was observed.

$$\text{Weight loss}\% = 53 - 3.8 * w\% \text{ APP} \quad \text{equ. 11}$$

Table 4: Formulation of rigid foam PU and FR-PU

Ingredients	Company	parts	Formula	EW	E	%
Caradol 520	Shell	100	$(C_3H_6O)_{1.86}$	108	0.925	
Dimethylethanolamine	BASF	3	$C_4H_{11}NO_2$	35	0.0864	
DBTDL	Bayer	0.06				
Water		2		9	0.222	$C_{O_2}$ 0,62
DC 193	Dow Corning	0.1				
Pentane	Haltermann	10.9			$C_{O_3}$	3,4
Caradate 30(NCO=31%)	Shell	166	$C_8H_6NO$	132	1.258	$C_{O_1}$ 16
	Sum	282.06				
APP	Clariant	39.90			cAPP	12.4
	Sum	321.96				

$$I = 1.258/1.233 = 1.02.$$



**Figure 3:** TGA of rigid foam PU and the rigid foam with 12,4% ammonium polyphosphate FR-PU under air at 10Kmin heating rate, after differentiation PU maxima 350°C at 65% residue and 550°C at 0% residue, FR-PU 280°C at 80% residue, 320°C at 70% residue and 650°C at 0% residue.

B2 classification was achieved according DIN 4102.

During manufacturing the NCO consumption  $c_1$ , the temperature  $T$ , the viscosity  $v$  and the expansion  $b$  were measured. The data were summarized in Table 5.

### Polyisocyanurate Foam

Polyisocyanurate foam PIR comprised the very stable and heat resistant isocyanurate ring.

In Table 6 the formulation for  $35\text{kg/m}^3$  PIR foam was given.

To the PIR formulation 4.9% liquid tributoxyethylphosphate TBEP were added as flame

retardant. TBEP decomposed at 300°C under evolution of 1240ml/g gases or 532ml/g water vapour.

$$V_{\text{gas}} = 10.5 \cdot 22400 \cdot (1 + 300/273) / 398 = 1240\text{ml/g gases}$$

$$V_{\text{gas}} = 4.5 \cdot 22400 \cdot (1 + 300/273) / 398 = 532\text{ml/g water vapour} \quad \text{equ. 12}$$

The foams with and without 4.9% TBEP were subdued a Cone calorimeter test at  $50\text{kW/m}^2$  heat flux. PIR exerted a heat release rate of  $200\text{kW/m}^2$  and FR-PIR a heat release rate of  $120\text{kW/m}^2$ .

A B1 classification was achieved and the weight loss was 5% according to ASTM D-3014.

The manufacture was performed in lab scale. The NCO content  $c_1$ , the temperature  $T$ , the viscosity  $v$  and

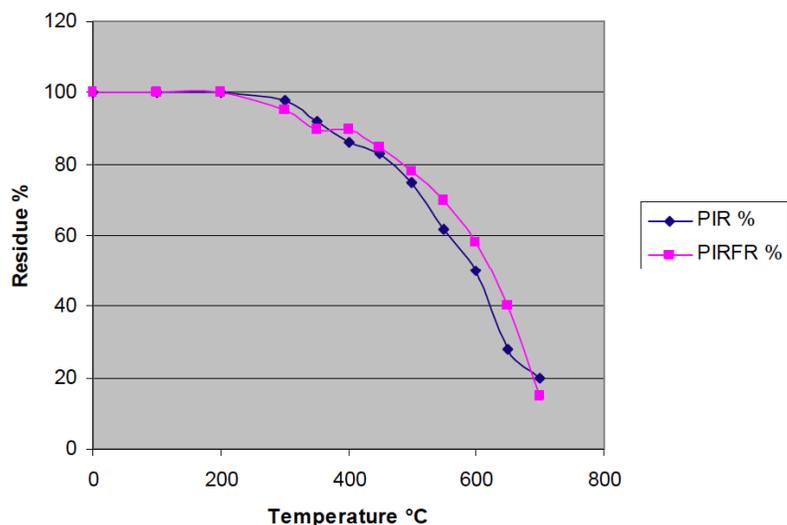
Table 5: Experimental Data of PU-FR (12.4%APP)

t min	c <sub>1</sub> w%	U	Igv Pa*s	T °C	b
0	16	0	-0.3	25	0
1	9.5	0.4	1.9	65,5	10
2	6.5	0.59	3.6	123	30
3	4.5	0.72	4	145	23
4	3.7	0,77	4.18	148	24
5	3	0.81	4.4	150	24.5
6	2.5	0.84	4.43	151	25
7	2	0.87	4,46	152	25.5
8	1.5	0.91	4,5	153	26
9	1.25	0.92	4,54	154	26
10	1	0.94	4,58	156	26

Table 6: Formulation of polyisocyanurate foam PIR and PIRFR

Ingredients	Company	parts	Formula	EW	E	%
Castor oil	Bayer	4.5	$\text{CH}_3(\text{CH}_2)_5\text{CHOHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	351	0.01	
Lupranol 3602	BASF	50.1	$(\text{C}_3\text{H}_6\text{O})_3$	148	0.34	
Glycerol		2.1	$\text{C}_3\text{H}_8\text{O}_3$	30.7	0.07	
OS 710	Bayer	5.1				
HHT	BASF	0.9				
K-formiate	BASF	1.8				
Pentane	Haltermann	26.7			$\text{C}_5\text{H}_{12}$	7
Caradate 30	Shell	267.5	$\text{C}_8\text{H}_6\text{NO}$	132	$2.027 \text{ c}_{01}$	22
	Sum	358.7				
TBEP	Clariant	18.3			cTBEP	4,9
	Sum	377				

Isocyanate index =  $2.027/0.42 = 4.83$ .



**Figure 4:** TGA of PIR foam without and with 4.9% TBEP under air at 5K/min heating rate, after differentiation PIR maxima 350°C at 80% residue, 550°C at 50% residue and 700°C at 10%; residue FR-PIR 350°C at 90% residue, 600°C at 60% residue and 700°C at 10% residue.

Table 7: Experimental Data of FR-PIR (4.9%TBEP)

t min	c <sub>1</sub> w%	U	T °C	Igv Pa*s	b
0	22	0	25	-0.3	0
1	9.7	0.54	120	2.6	28
2	7.5	0.63	150	3.9	31
3	5.2	0.72	168	4.34	32.5
4	4.6	0.78	179	4.56	33.5
5	4	0.81	186	4.66	34
6	3.3	0.84	191	4.74	34
7	2.9	0.86	195	4.81	34
8	2.5	0.87	199	4.88	34
9	2.4	0.88	201	4.95	34
10	2.2	0.9	210	4.98	34

the expansion b were continuously registered and reproduced in Table 7.

#### 4. FOAMING MODEL

In polyurethane foam production the formulations defined the streams A (components with NCO reactive groups) and B (components with isocyanate groups). The volume streams determined the isocyanate index and the initial concentration  $c_{01}$  of isocyanate as well as the initial concentration  $c_{02}$  of water.

##### Conversion U

The conversion U of isocyanate over the time t followed a first order reaction with the velocity constant  $k_1(\text{min}^{-1})$ .

$$U = 1 - 1/(k_1 * c_{01} * t - 1) \quad \text{equ. 1}$$

$$c_1 = c_{01}/(k_1 * c_{01} * t + 1) = c_{01} * (1 - U) \quad \text{equ. 13}$$

##### Heat of Reaction h(kJ/g)

The heat of reaction h depended on the NCO group with 42g/mole equivalent weight and 50 kJ/mole bond energy, the initial isocyanate concentration  $c_{01}$  and the conversion U.

$$h = 50 * c_{01} * U / (42 * 100) = 11.9 * c_{01} * U \text{ (kJ/kg)} \quad \text{equ. 2}$$

##### Temperature T(°C)

The temperature increase was calculated according to Kirchhoff.

$$\begin{aligned} T(\text{K}) &= 298 + h/C_p = 298 + 50 * c_{01} * U / (C_p * 4.2) \\ &= 298 + 9.52 * c_{01} * U \quad \text{equ. 14} \\ T(^{\circ}\text{C}) &= 25 + 9.52 * c_{01} * U \end{aligned}$$

For the specific heat of foams  $C_p = 1.25 \text{ kJ} / (\text{kg} * \text{K})$  was introduced.

##### Foam Expansion by Water Reaction $b_1$

Assuming that the water concentration  $c_{02}$  decreased at the same rate as the isocyanate reaction with conversion U equation 15 for expansion by water was obtained.

$$\begin{aligned} b_1 &= (d_0/d_f - 1) = R * T * d_0 * c_{02} * U / (100 * MW_{\text{H}_2\text{O}} * p_{\text{at}}) \\ &= 0.0456 * c_{02} * U * T(\text{K}) \quad \text{equ. 15} \\ b_1 &= 0.0456 * c_{02} * U * (298 + 9.52 * c_{01} * U) \end{aligned}$$

R the ideal gas constant  $82 \text{ cm}^3 \text{ bar} / (\text{K} * \text{mole})$  and  $MW_{\text{H}_2\text{O}}$  water molecular weight 18g/mole.

##### Foam Expansion by Physical Blowing Agent $b_3$

For the auxiliary physical blowing agent n-pentane with the concentration  $c_{03}$  the expansion  $b_3$  was calculated:

$$\begin{aligned} b_3 &= R * T * d_0 * (c_{03} - c_{L3}) / (100 * MW_3 * p_{\text{at}}) \\ &= 0.0114 * (c_{03} - c_{L3}) * T(\text{K}) \quad \text{equ. 16} \end{aligned}$$

Pentane with molecular weight  $MW_3 = 72 \text{ g/mole}$  and heat of evaporation from polyurethane  $H_v = 24 \text{ kJ/mole}$  dissolved in polyurethane with  $c_{L3}$  dissolved pentane according equation 17.

$$\lg c_{L3} = H_v / (2.3 * R) * 1000 / T = 1.312 * (1000 / T) - 3.6$$

$$c_{L3} = 20.5^{(1000/T)} / 4000 \quad \text{equ. 17}$$

After introducing the equations for  $c_{L3}$  and  $T$  in  $b_3$  equation 18 was obtained

$$b_3 = 0.0114 * (c_{03} - 20.5^{(1000/298)} / 4000) * (298 + 9.52 * c_{01} * U)$$

$$\quad \text{equ. 18}$$

By evaporation the formulation was cooled. The temperature reduction  $dT$  was small, so that this influence was neglected.

$$dT = H_v * (c_{03} - c_{L3}) / C_p = 24 * (c_{03} - c_{L3}) / (100 * 1.25) = 0.192 * (c_{03} - c_{L3})$$

$$dT(\text{rigid foam}) = 0.192 * (3.4 - 0.23) = 0.6K$$

$$dT(\text{isocyanurate foam}) = 0.192 * (7.1 - 0.01) = 1.4K$$

$$\quad \text{equ. 19}$$

### Viscosity $v$ (Pa\*s)

The viscosity  $v$  for the formulations in the liquid state and after solidification the elastic modulus  $E$  for the cured foam were determined with the equations 3 and 20.

$$v = v_0 * k_2^U \quad \text{equ. 3}$$

The initial viscosity of the formulation was  $v_0$ .  $k_2$  (Pa\*s) was a constant for each formulation.

$$E = 2 * 3.14 * f * v \quad \text{equ. 20}$$

The frequency of oscillation  $f$  and the viscosity after curing  $v$  determined the modulus of elasticity  $E$ . In the case of  $f = 0.5$  Hertz the elastic modulus  $E$  is equivalent with  $3.14 * v$ .

In Table 8 the data of CMHR for the NCO content  $c_1$ , the conversion  $U$ , the viscosity  $v$ , the temperature  $T$  and the expansion  $b$  were collected, which had been determined with the help of the foaming model.

In Table 9 the balances of weight and heats were established taking into account 50kJ/mole for the energy of the isocyanate group. The thermodynamic model correlated with TGA and DSC data.

## 5. RESULTS

The physical properties of the manufactured foams were tested and summarized in Table 10.

The burning behaviour of the rigid foams was characterized by the weight loss of the foam according to ASTM D- 3014, the combustion of the soft foams by the LOI value and BS 5852 Part 2 (allowed weight loss 6%, flame extinguished after 10 minutes, no smoke after 60 minutes). The Cone calorimeter measurements RHR indicated the positive influence of the flame retardants. The mechanical properties of the cellular plastics were characterized by the tensile strength (Tensile Str.), the compressive strength (Comp. Str.) and the elastic modulus (E-modulus) calculated from the viscosity  $v$  after 10 minutes.

The physical properties of the flame retardants were summarized in Table 11.

In Figure 5 and 6 the calculated and experimental values were compared for  $b$ ,  $T$ ,  $v$  and NCO concentration.

**Table 8: Calculated Data for CMHRF  $k_1 = 0.08 \text{ min}^{-1}$ ,  $\lg k_2 = 2.8 \text{ Pa*s}$ ,  $\text{co}_2 = 2\%$**

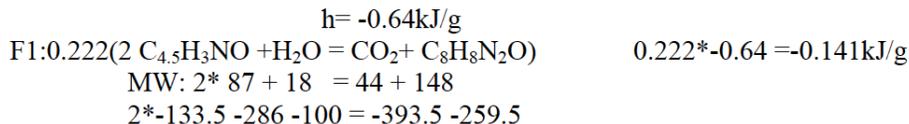
t min	$c_1$ w%	U	$\lg v$ Pa*s	T °C	$b_1$
0	12	0	-0.3	25	0
1	6.1	0.49	1.13	81	15.8
2	4.1	0.66	1.55	100.5	22.5
3	3.1	0.74	1.8	109.5	28
4	2.5	0.79	1.9	120	29.8
5	2	0.83	2	122	30.6
6	1.8	0.85	2.1	124.5	31.5
7	1.6	0.87	2.15	125.5	32
8	1.4	0.88	2.2	128	32.9
9	1.3	0.9	2.2	128	32.9
10	1.1	0.91	2.25	129	33.4

$$c_1 = 12 / (k_1 * c_{01} * t + 1); U = [1 - 1 / (k_1 * c_{01} * t + 1)]; \lg v = -0.3 + U * \lg k_2; b_1 = 0.0912 * U * (273 + T \text{ °C}).$$

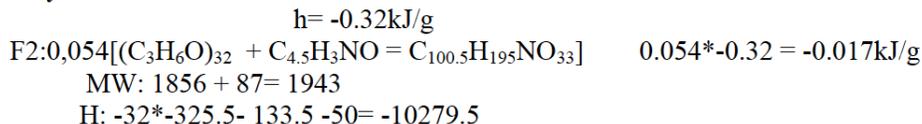
**Table 9: Balance of Weight and Heat for Synthesis, Combustion and Decomposition for HR (EW =147g/mole) and Isocyanate Reaction Heat H=50kJ/mole**

Synthesis:

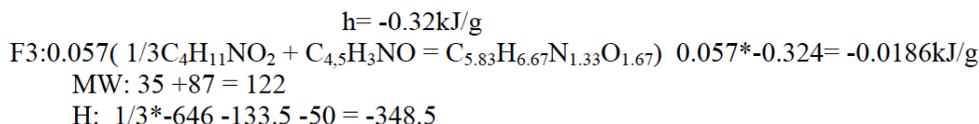
Water



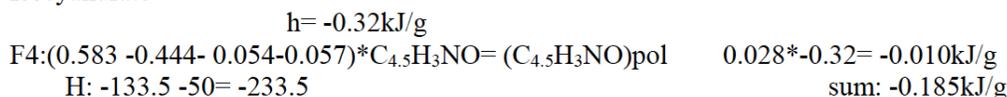
Polyole



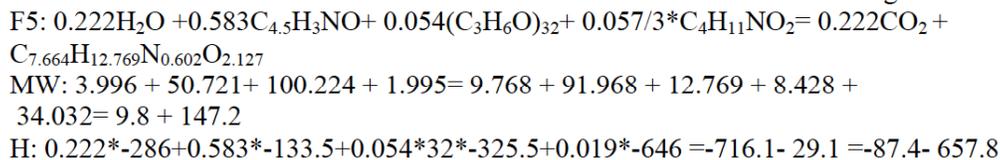
Chain extender



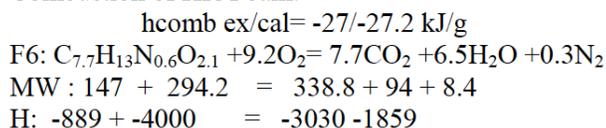
Isocyanurate



h = -0.185 kJ/g



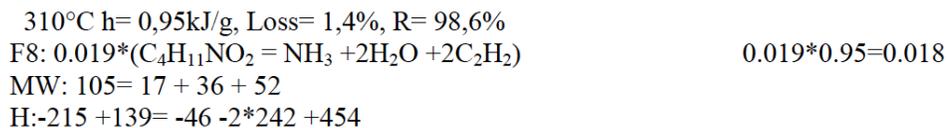
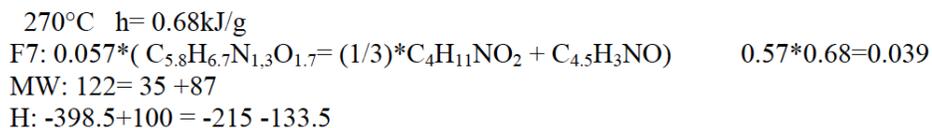
Combustion of HR-Foam:



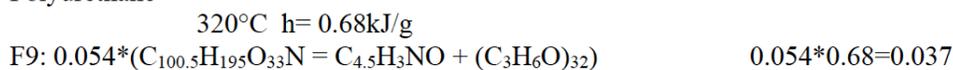
In DSC investigation under nitrogen HR- Foam decomposed and two peaks were observed: peak 1 reached from 250- 350°C with 0.3kJ/g heat consumption and peak 2 from 350 - 420°C with 0.7kJ/g heat consumption. In the following the decomposition was described by balances.

Decomposition of HR-Foam:

Chain extender



Polyurethane



MW: 1943 = 87 + 1856  
 H: -10329.5 + 100 = -133.5 -(32\*315.5=10096)  
 Polyole  
 330°C h=0.116  
 F10: 0.054\*[(C<sub>3</sub>H<sub>6</sub>O)<sub>32</sub>= 32 C<sub>3</sub>H<sub>6</sub>O] 0.054\*0.116= 0.006  
 MW: 1856 = 32\*58  
 H:-315. 5+ 17= -298.5  
 340°C h= 0.34kJ/g, Loss = 68.2%, R= 30,4%  
 F11: 0.054\*16(2C<sub>3</sub>H<sub>6</sub>O)= 16C<sub>6</sub>H<sub>12</sub>O<sub>2</sub> gas) 0.054\*32\*0.34= 0.588  
 MW: 2\*58 = 116  
 H: 2\*-298.5 +50= -547 peak1 270-340°C 0.69kJ/g, R=30.4%,  
 Polyurea  
 335°C h= 0.68kJ/g  
 F12: 0.222\*( C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>O= C<sub>3,5</sub>H<sub>5</sub>N +C<sub>4,5</sub>H<sub>3</sub>NO) 0.222\*0.68= 0.151  
 MW: 148 = 61 + 87  
 H: -359.5 +100 = -26 - 133.5  
 Amine  
 350°C h=0.20kJ/g, Loss= 9.2%, R= 21,2%  
 F13: 0.222\*( C<sub>3,5</sub>H<sub>5</sub>N = 0.5C<sub>6</sub>H<sub>6</sub> +0.5CH<sub>4</sub>+ 0.5N<sub>2</sub>) 0.222\*0.20=0.044  
 MW: 61 = 39+ 8+ 14  
 H: -26 +28.75 =41.5 - 0.5\*87.5  
 Isocyanate  
 380°C h= 0.44kJ/g, Loss= 19,9%, R=1.3%Loss, 1.5%  
 F14: (0.583-0.222)\*( C<sub>4,5</sub>H<sub>3</sub>NO = 0.5C<sub>6</sub>H<sub>6</sub>+ CO +0.5N<sub>2</sub> +0.5C) 0.361\*0.44= 0.157  
 MW: 87= 39 + 28 +14 +6  
 H: -133.5 +64=-41.5-111  
 peak2 325-400°C 0.35 kJ/g, R= 1,5%  
 sum: 1.04kJ/g  
 Summarized hdec=1.06kJ/g, R=1.6%  
 F15: C<sub>7,7</sub>H<sub>13</sub>N<sub>0,6</sub>O<sub>2,1</sub>= 0.764C<sub>6</sub>H<sub>12</sub>O<sub>2</sub>+ 0.306C<sub>6</sub>H<sub>6</sub> + 0.019NH<sub>3</sub> + 0.195C + 0.389CO+  
 0.111CH<sub>4</sub>+ 0.038C<sub>2</sub>H<sub>2</sub>+ 0.306N<sub>2</sub>+ 0.038H<sub>2</sub>O  
 MW: 147= 100.2+ 23.9 + 0.3 + 2.3 +10.9 +1.8 +1.0 +8.6 +0.7=149.6  
 H: -657.8+ 146.2= -472.6 +25.4 -0.9 -43.2 -9.7+8.6 -9.2= 501.6

Table 10: Physical Properties of Foams

Type	HRF	CMHR	CM	PU	PUFR	PIR	PIRFR
FR	0	22.3%M	43%ATH	0	12.4%APP	0	4.9TBEP
MW(g/mole)	147	147	147	266	266	324	324
Hf(kJ/mole)	-687	-687	-687	-698	-698	-702	-702
Hf(comb.)	-890	-890	-890	-700	-700	-550	-550
hsynth(kJ/g)	-0.37	-0.37	-0.37	-0.23	-0.23	-0.31	-0.31
hcomb(kJ/g)	-27	-21	-14	-30	-26	-30	-28
Tdec TGA °C	280, 380	250,300,380		300, 600	250,300,650	350,550,650	350,600,700
R% TGA	60 ,10	80,50,5		65, 5	80,70,5	85,55,10	90,60,10
R% calculated	30, 9			63,15		84,67, 7,5	
hdec(kJ/g)	0,69, 0,38			0,41, 0,38		0,12,0,68,0,57	1,34
density(kg/m <sup>3</sup> )	25	27	45	35	38	30	33
Tensile Str.(kPa)	100	80	60	400	360	450	420
E-moduluskPa(v)		31			120		345

(Table 10). Continued.

Type	HRF	CMHR	CM	PU	PUFR	PIR	PIRFR
Comp. Str. (kPa)	1.5	2		90	120	120	160
BS5952/2 Crip5		Positive	Positive				
LOI (K/%)		0.29	0.15				
ASTM D-3014 (%)				53	13	25	5
RHRkW/m2	1200/50kW/m2	500/50kW/m2		120/5kW/m2	40/5kW/m2	230/50kW/m2	120/50kW/m2

Table 11: Physical Properties of Flame Retardants FRs

	M	ATH	APP	TBEP
MW g/mole	126	156	97	398
hcomb(kJ/g)	-15.6	0	-3.5	-27.9
Hf(kJ/mole)	-72	-2564	-961	-2317.5
Tdec(°C)	350	300	350	300
hdec(kJ/g)	1.0	1.2	2.5	3.2
Vgas(ml/g)	419 Mgas	452 H <sub>2</sub> O	790 H <sub>2</sub> O, NH <sub>3</sub>	1247 H <sub>2</sub> O+KW; 255 H <sub>2</sub> O
Residue (%)	0	65Al <sub>2</sub> O <sub>3</sub>	73.2P <sub>2</sub> O <sub>5</sub>	18 P <sub>2</sub> O <sub>5</sub>

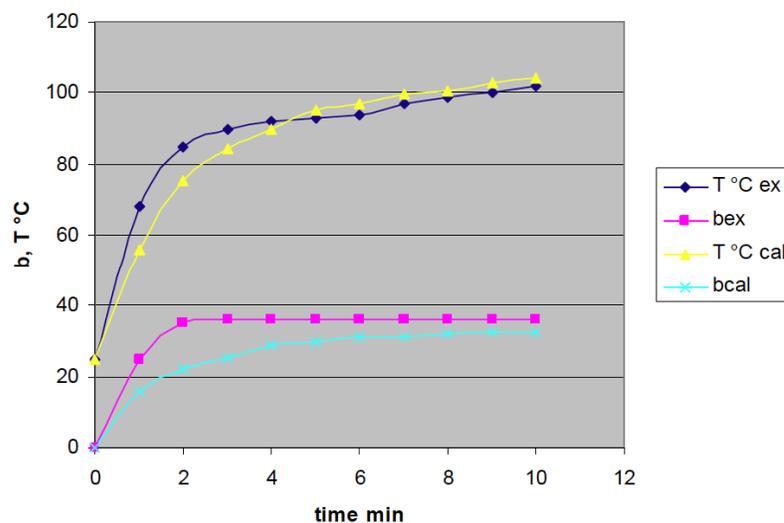


Figure 5: Comparison of experimental and calculated temperatures T and expansions b for CMHR- foam.

The highest discrepancy between calculated and experimental data was observed for the expansion  $b$  in Figure 5. The reason for this was the circumstance that only one constant  $k_1$  was used for the isocyanate consumption. No account was taken for the fact that different reactions occurred for the formation of urethane, urea, isocyanurate and carbodiimide. Also the balances of heat were accomplished with only 50kJ/mole as overall isocyanate heat of reaction. Nevertheless the agreement with experimental data was good. CIM caused a high effort of analytical and measuring equipment. But the higher expenditure was rewarded by better understanding and lead to better products at lower cost. In Table 12 the inputs for model

calculation were summarized. More sophisticated models were thinkable but would complicate the calculations.

## 6. CONCLUSION

FR-polyurethane foams were described by chemical formulas. The flame retardants were applied in such concentrations that as predominant reaction decomposition as under nitrogen the achievable optimum took place. A kinetic foaming model was established as well as balances of weight and heat of formation were set up, which described foam synthesis, combustion and decomposition giving the chemical background for CIM.

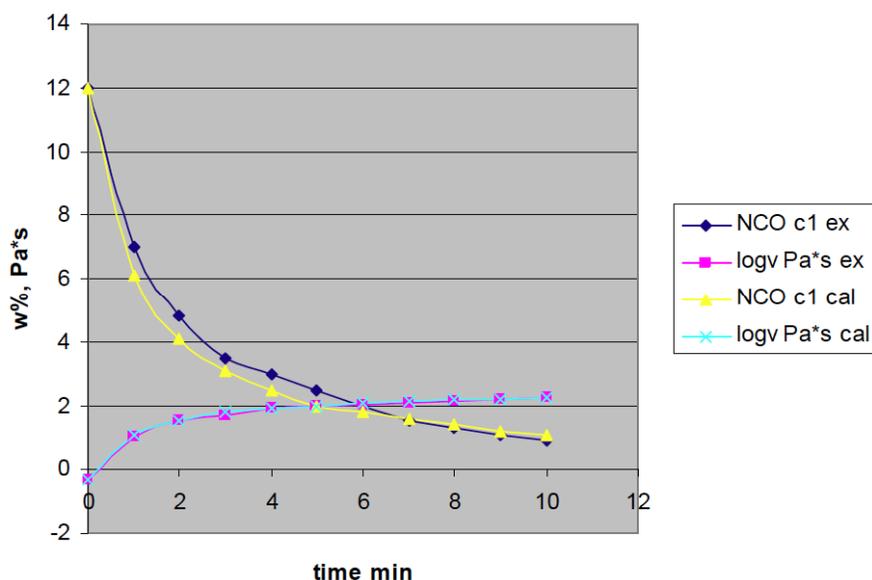


Figure 6: Comparison of experimental and calculated %NCO and viscosity  $v$  for CMHR- foam.

Table 12: Input for Model Calculations

Parameter	CMHR	PU-FR	PIR-FR
$c_{01}$ %NCO	12.0	16	22.1
$c_{02}$ % H <sub>2</sub> O	2	0.6	0
$c_{03}$ % n-Pentane	0	3,4	7
$k_1$ min <sup>-1</sup>	0.08	0.06	0.04
lgk <sub>2</sub> Pa*s	2.8	5.0	6.0
%FR	22.3M	12.4APP	4.9TBEP

In the foaming model the highest discrepancy was observed for the expansion  $b$  in Figure 5. The reason for this was to be seen in the circumstance that only one constant for the isocyanate consumption was taken into account for the polyurethane reaction as well as for the urea reaction.

The balances of masses and heats with 50kJ/mole for the isocyanate energy lead to results, which were in good agreement with experimental data.

The balance of heat and weight led to two mean peaks of decomposition from 270- 340°C and 350-400°C for CMHR foam as measured by DSC and cited by Dick [13]. The urethane scission and polyole decomposition happened first under 0.7kJ/g heat evolution followed by the urea scission and degradation of amine and isocyanate under 0.4kJ/g heat development.

The calculated heats of combustion 30kJ/g for rigid, 26kJ/g for FR-rigid foam and 30kJ/g for PIR foam were

higher than those found in literature with 21kJ/g for PUR, 12kJ/g for FR-PUR and 10kJ/g for PIR [29].

The cited heats of gasification [29]: 1.4kJ/g (DSC) for flexible foam, 1.2-5.3kJ/g (flammability apparatus) for rigid foam and 1.2- 6.4kJ/g (flammability apparatus) for polyisocyanurate foam, matched with the calculated heats of decomposition.

CIM was started successfully. The measurements conducted with high expenditure on equipment agreed with those derived from calculations.

The applied flame retardants decomposed near the decomposition temperature of the foams. They evolved non burning gases under heat uptake and enriched the char. The target was to establish computer integrated manufacturing without continuous measurements but by mere calculation. With the knowledge of the velocity constant  $k_1$  and the viscosity parameter  $k_2$  CIM without continuous measurements was possible.

## 7. APPENDIX

Table 13: Calculated Data for FR-PU (12,4% APP) NCO =16 %, co2=0,6%, k1=0,062min<sup>-1</sup>,logk2=5Pa\*s, co3=3,4%. dT=0,6°C

t min	c1 w%	U	T °C	lgv Pa*s	b1	b3	b1+ b3
0	16	0	25	-0,3	0	0	0
1	8,1	0,49	101	2,25	5	8,5	13,5
2	5,4	0,67	125	3,05	7,2	11,8	18
3	4,1	0,75	137	3,45	8,3	12,6	20,9
4	3,2	0,8	146	3,7	9,2	13,4	22,6
5	2,7	0,84	150,5	3,9	9,6	13,5	23,1
6	2,3	0,86	154	4	10,1	13,6	23,7
7	2	0,88	157	4,1	10,3	13,7	24
8	1,8	89	160	4,15	10,5	13,8	24,3
9	1,6	0,9	161	4,2	10,7	13,85	24,55
10	1,5	0,91	163	4,25	10,9	13,9	24,8

Table 14: Balance of Weight and Heat for Synthesis, Combustion and Decomposition of RF (EW=266) and Isocyanate Reaction Heat H=50kJ/mole

Synthesis:

Water reaction  $h=-0,369\text{kJ/g}$  $0,111*(2\text{C}_8\text{H}_6\text{NO} + \text{H}_2\text{O} = \text{CO}_2 + \text{C}_{15}\text{H}_{14}\text{N}_2\text{O})$  $0,111*-0,369 = -0,041\text{kJ/g}$ 

MW 264 +18 = 44 +238

H 2\*-91 -286 -100 = -393,5 -174,5

Polyol reaction  $h=-0,185\text{kJ/g}$  $0,925*(\text{C}_3\text{H}_6\text{O})_{1,86} + \text{C}_8\text{H}_6\text{NO} = \text{C}_{13,6}\text{H}_{18}\text{NO}_{2,9}$  $0,925*-0,185 = -0,171\text{kJ/g}$ 

MW 108 +132= 240

H 1,86\*-298,5 -91- 50= -696,2

Chain extender reaction  $h= -0,554\text{kJ/g}$  $0,086/3*(\text{C}_4\text{H}_{11}\text{NO}_2 + 3\text{C}_8\text{H}_6\text{NO} = \text{C}_{28}\text{H}_{29}\text{N}_4\text{O}_5)$  $0,0287*-0,554 = -0,016$ 

MW 105 + 3\*232= 501

H -646 + 3\*-91 -150 = 1069

Isocyanate contribution  $h= -0,185\text{kJ/g}$  $(1,258- 0,111-0,925- 0,086) \text{C}_8\text{H}_6\text{NO} = \text{C}_8\text{H}_6\text{NO}$  $0,025*-0,185 = -0,005$ 

MW 132=132

H = -91 -50 = -141

Sum: -0,233kJ/g

 $h= -0,233\text{kJ/g}$  $0,925(\text{C}_3\text{H}_6)_{1,86} + 0,0287\text{C}_4\text{H}_{11}\text{NO}_2 + 0,111\text{H}_2\text{O} + 1,258\text{C}_8\text{H}_6\text{NO} = 0,111\text{CO}_2 +$  $\text{C}_{15,1}\text{H}_{19,4}\text{N}_{1,3}\text{O}_{2,7}$ 

MW: 99,8 + 3 +2 +166=270,8 = 4,9 + 266

H:  $0,925*1,86*-298,5 + 0,0287*-646 + 0,111*-286 + 1,258*-91- 63 = -43,68$ 

H -513,6 -18,5-31,7-114,5=678,3- 63 = -740,7 = -43,7 -697

(Table 14). Continued.

Combustion  $h_{comb} = -30,2 \text{ kJ/g}$  $C_{15,1}H_{19,4}N_{1,3}O_{2,7} + 18,2 O_2 = 15,1CO_2 + 9,7H_2O + 0,65N_2$ MW (g/mole) :  $266 + 591,2 = 664,4 + 174,6 + 18,2$ H (kJ/mole) :  $-679$  $-8037 = 15,1 * -393,5 - 9,7 * 286$ 

Decomposition

Chain extender

 $270^\circ C \quad h = 2,707 \text{ kJ/g} \quad \text{Loss} = 1,1\%$  $0,0287 * 2,707 = 0,078$  $0,0287(C_{28}H_{29}N_4O_5 = 2C_2H_2 + 2H_2O + NH_3 + 3C_8H_6NO)$ MW  $501 = 52 + 36 + 17 + 3 * 132$ H  $-1069 + 720 = 2 * 227 + 2 * -242 - 46 + 3 * -91$ 

Polyurethane

 $280^\circ C \quad h = 0,188 \text{ kJ/g}$  $0,925 * 0,188 = 0,174$  $0,925(C_{13,6}H_{19}NO_{2,9} = 1,86C_3H_4O + C_8H_6NO)$ MW  $240 = 108 + 132$ H  $-696,2 + 50 = 1,86 * -298,5 - 91$ 

Polyole

 $300^\circ C \quad h = 0,188 \text{ kJ/g}; \quad \text{Loss} = 36,2\%$  $0,925 * 0,93(2C_3H_4O - C_6H_8O_2)$  $0,86 * 0,188 = 0,162$ MW  $2 * 56 = 112$ H  $2 * 298,5 + 50 = -547$ 

---

  
peak 1 R=62,7%;  $h = 0,414 \text{ kJ/g}$ ,  $300^\circ C$ 

Urea

 $500^\circ C \quad h = 0,724 \text{ kJ/g}; \quad \text{Loss} = 4,4\%$  $0,111 * 0,724 = 0,080$  $0,111(C_{13}H_{14}N_2O = C_8H_6NO + C_6H_6 + 0,5C_2H_4 + 0,5N_2)$ MW  $238 = 132 + 78 + 14 + 14$ H  $-174,5 + 192,5 = -91 + 83 + 0,5 * 52$ 

Isocyanate

 $600^\circ C \quad h = 0,237 \text{ kJ/g}, \quad \text{Loss} = 56,8\%$  $1,258 * 0,237 = 0,298$  $1,258(C_8H_6NO = CO + C_6H_6 + 0,5N_2 + C)$ MW  $132 = 28 + 78 + 14 + 12$ H  $-91 + 63 = -28$ peak 2 R=5,6%;  $h = 0,378 \text{ kJ/g}$ ,  $600^\circ C$ Sum:  $0,792 \text{ kJ/g}$ Summarized  $h = 0,601 \text{ kJ/g}$ , R=5,2% $C_{15,1}H_{19}N_{1,3}O_{2,7} = 0,925C_6H_8O_2 + 1,147(CO + C_6H_6 + C + 0,5N_2) + 0,111C_6H_6 + 0,055C_2H_4 + 0,055N_2 + 0,057C_2H_2 + 0,057H_2O + 0,0287NH_3$ MW  $266 = 99,8 + 151,4 + 8,6 + 1,4 + 1,5 + 1,5 + 1 + 0,5$ H  $-697 + 159,8 = -506 - 31,9 + 9,3 + 2,9 + 12,9 - 13,8 - 1,3 = -537,2$

**Table 15: Calculated Data for FRPIR (4,9%TBEP)  $k_1=0,04 \text{ min}^{-1}$ ,  $\log k_2=6 \text{ Pa}\cdot\text{s}$ ,  $\text{co}_3=7\%$ ,  $dT=1,4^\circ\text{C}$** 

t min	c1 w%	U	T °C	Lgv	cL3 w%	b3
0	22	0	30	-0,3	7	0
1	11,5	0,46	126	3,13	0,5	30,4
2	7,7	0,63	162	3,64	0,3	34,3
3	6	0,72	179	4,12	0,2	35,6
4	4,6	0,78	191	4,42	0,16	37,2
5	4	0,81	200	4,59	0,15	37,7
6	3,5	0,84	202	4,74	0,14	37,9
7	3,1	0,86	206	4,84	0,135	38,2
8	2,4	0,87	210	4,93	0,13	38,5
9	2,3	0,88	212	4,99	0,125	38,7
10	2,2	0,9	214	5,07	0,12	38,9

Their synthesis, combustion and decomposition was established by balances of weight and heat.

**Table 16: Balance of Weight and Heat for Synthesis, Combustion and Decomposition of PIR (EW= 324g/mole) and Isocyanate Reaction Heat  $H=50 \text{ kJ/mole}$** 

Synthesis:

Polyol  $h=-0,154 \text{ kJ/g}$

$0,34(\text{C}_3\text{H}_6\text{O})_{2,55} + \text{C}_8\text{H}_6\text{NO} = \text{C}_{15,65}\text{H}_{21,3}\text{NO}_{3,55}$   $0,34 \cdot -0,154 = -0,052 \text{ kJ/g}$

MW  $148 + 132 = 280$

$H \ 2,55 \cdot -286 - 91 - 50 = 870,3$

Glycerol  $h=-0,154 \text{ kJ/g}$

$0,068 \cdot 1/3 \cdot (\text{C}_3\text{H}_8\text{O}_3) + \text{C}_8\text{H}_6\text{NO} = \text{C}_9\text{H}_{8,7}\text{NO}_2$   $0,0154 \cdot -0,154 = -0,002 \text{ kJ/g}$

MW  $30,7 + 132 = 162$

$H - 298,5 - 91 - 50 = -439,5$

Ricinus  $h=-0,154 \text{ kJ/g}$

$0,015 \cdot \text{C}_{18}\text{H}_{34}\text{O}_3 + \text{C}_8\text{H}_6\text{NO} = \text{C}_{26}\text{H}_{40}\text{NO}_4$   $0,015 \cdot -0,154 = -0,002 \text{ kJ/g}$

MW  $298 + 132 = 430$

$H - 10875 - 91 - 50 = -11016$

Isocyanate  $h=-0,154 \text{ kJ/g}$

$(2,027 - 0,34 - 0,068) \cdot \text{C}_8\text{H}_6\text{NO} = \text{C}_8\text{H}_6\text{NO pol}$   $1,619 \cdot -0,154 = -0,249 \text{ kJ/g}$

MW  $132 = 132$

$H - 91 - 50 = -141$

Sum:  $-0,305 \text{ kJ/g}$

$h=-0,307 \text{ kJ/g}$

$0,867 \text{C}_3\text{H}_6\text{O} + 0,068 \cdot 1/3 \cdot \text{C}_3\text{H}_8\text{O}_3 + 0,015 \text{C}_{18}\text{H}_{34}\text{O}_3 + 2,027 \text{C}_8\text{H}_6\text{NO} = \text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_3$

MW  $50,3 + 2,1 + 4,5 + 266,8 = 323,7$  (324)

$H \ 0,867 \cdot -286 + 0,023 \cdot -298,5 + 0,015 \cdot -10875 + 2,027 \cdot -91 = -602,5 - 98,8 = -701,3$

$H - 248,0 - 6,9 - 163,1 - 184,5 - 184,5 = -787 - 99,5 = -886,5$

Combustion  $h= -30,21 \text{ kJ/g}$

$\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_3 + 22,5 \text{O}_2 = 19 \text{CO}_2 + 10 \text{H}_2\text{O} + \text{N}_2$

MW  $324 + 720 = 836 + 180 + 28$

$H - 549 - 9787,5 = -7476,5 - 2860$

(Table 16). Continued.

## Decomposition

## Glycerol

300°C h=0,562kJ/g Loss= 0,7%

 $0,068 \cdot C_9H_{8,7}NO_2 = C_8H_6NO + H_2O + 1/3C_2H_2 + 1/3C$  0,068\*0,562=0,038kJ/g

MW 163 = 132 + 18 + 8,7 + 4

H -439,5 + 182,2 = -91 -242 + 1/3\*227

## Polyole

350°C h=0,055kJ/g

0,34\*0,055=0,018kJ/g

 $0,34(C_{15,65}N_{21,3}NO_{3,55} = C_8H_6NO + 2,55C_3H_6O)$ 

MW 280 = 132 + 148

H -870 + 228 = -91 -2,55\*298,5

0,434\*0,154= 0,067kJ/g

350°C h= 0,154kJ/g Loss =15,5%

 $0,434(2C_3H_6O = C_6H_{12}O_2)$ 

MW 2\*58 = 116

H 2\*298,5 + 50 = 547

peak1 R= 83,8% h=0,123kJ/g 350°C

## Ricinus

450°C h= 35,77kJ/g Loss 1,4%

0,015\*35,77= 0,537kJ/g

 $0,015C_{26}H_{40}NO_4 - C_8H_6NO + 3H_2O + 7C_2H_2 + 0,5C_2H_4 + 3CH_4$ 

MW 430 = 132 + 54 + 182 + 14 + 48

H -11016 + 11589 = -91 -726 + 1589 + 26 -225

## Urethane isocyanate

550°C h= 0,349kJ/g, Loss=15%

0,406\*0,349=0,142kJ/g

 $0,406 \cdot C_8H_6NO_{pol} = CO + C_6H_6 + 0,5N_2 + C$ 

MW 132 = 28 + 78 + 14 + 12

H-141 + 113 = -28

peak2 R=67, 4% h=0,679kJ/g 600°C

## Isocyanurate

700°C h=0,349kJ/g, Loss=60%

 $1,621 \cdot C_8H_6NO_{pol} = CO + C_6H_6 + 0,5N_2 + C$ 

0,1621\*0,349= 0,565kJ/g

MW 132 = 28 + 78 + 14 + 12

H-141 + 113 = -28

peak3 R=7,5%; h=1,244kJ/g

700°C

Sum: 1,367kJ/g

## Summarized

h= 1,25kJ/g, R=7,6%

 $C_{19}H_{20}N_2O_3 = 0,34 \cdot 1,28C_6H_{12}O_2 + 0,113H_2O + 0,128C_2H_2 + 2,05C + 0,045CH_4 +$  $0,0075C_2H_4 + 2,027CO + 2,027C_6H_6 + 1,0135N_2$ 

MW 324 = 50,3 + 2,0 + 3,3 + 24,6 + 0,7 + 0,2 + 56,8 + 158 + 28,4 = 324,3

H -701 + 403 = 0,34\*1,28\*547 + 0,113\*242 + 0,128\*227 + 0,045\*-75 + 0,0075\*52 + 2,027-

111 + 2,027\*83

H- 701 + 405 = -238,1 - 27,3 + 29,1 -3,4 + 0,4 - 225 + 168,2 = -296,1

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