Thermal Analysis of Urethane and Alophanate Compounds Obtained by Chemical Reactions Between Phenylisocyanate and Mono- or Bifunctional Stabilizers

CONSTANTIN BOLCU*, FLORIN BORCAN, CORINA DUDA-SEIMAN, REMUS NUTIU
West University Timişoara, Faculty of Chemistry-Biology-Geography, Chemistry Department, 16th Pestalozzi Str., 300115, Timişoara, România

This paper contains the results of an experimental study regarding the thermal stability of the urethane and alophanate groups from model compounds obtained in chemical reactions between phenylisocyanate and mono- or bifunctional stabilizers. The results can be used to estimate the thermal stability of the polyurethanes which were thermal and photo-oxidative (additive and reactive) stabilized.

Keywords: urethane, alophanate, phenylisocyanate, antioxidant compound, photo-stabilizer compound

Otto Bayer initiated the pioneer work and published the first papers regarding polyurethanes in the I.G. Farbenindustrie – Germany – in 1937. Since then the production of these polymers had a progressive growth in time; also, the types of polyurethanes were rapidly diversified [1]. Polyurethanes have special physical, mechanical and chemical features (elasticity, thermal and electrical insulating properties, high resistance to mineral oil products action, chemical resistance to degrading agents, etc.). So, polyurethanes became unique in several fields: ship building industry, shoe industry, civil and industrial buildings, automobile industry, Jarvick artificial heart, reference points production in aeronautic industry [2]. Properties of polyurethanes depend on the nature, on the functionality and on the proportion of reactants in the obtaining process. Aromatic diisocyanates are used in polyurethanes synthesis in order to define their important properties , mainly 4,4'-diphenylmethandiisocyanat (MDI) and 2,4- and 2,6-toluylendiisocyanat (TDI)[3,4].

Unfortunately, polyurethanes obtained from aromatic diisocyanates, with superior physical and mechanical properties, are less resistant to thermal and photo-oxidation comparative to aliphatic polyurethanes. Over 80% of the world production of polyurethanes uses aromatic diisocyanates making necessary their thermal and photo-oxidative stabilization.

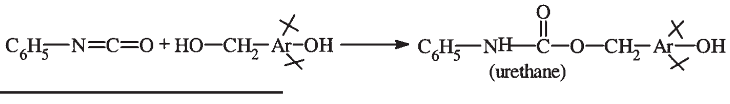
Polyurethanes stabilization comprises adding of usual antioxidants and photo-stabilizers presenting the already known disadvantages of polymer additive stabilization. Stabilizers are low molecular weight compounds, incompatible with polymers, which migrate from the polymer's matrix when it is long time utilized. Some stabilizers are volatile ore they are easily extracted by fluids in contact with the polyurethane during utilization; thus, the amount of stabilizers inside the polymer decreases in time, reducing the efficiency of the stabilizing process [5].

By these means, increased interest is shown by the idea of reactive stabilization with stabilizers chemically bound with the polyurethane's chains during its synthesis through the reaction of some functional groups of stabilizers (–OH; $-NH_2$; –NH–) with the –NCO group from the isocyanate part of the polyurethane. The obtained chemical bonds between the stabilizer and the polyurethane (urethane and alophanate) determine the disappearance of the possibility of losing through physical processes of stabilizers from the polymer's matrix [6].

The –NCO group from phenylisocyanate has an increased reactivity and the majority of commercial stabilizers contain –OH, $-NH_2$ and –NH- groups; thus, reactions between stabilizers and isocyanates can be anticipated during polyurethane's synthesis [7,8]. In our experiments, we have studied the reactions of some usual stabilizers containing only one type of functional group, with phenylisocyanate. Such stabilizers are anti-oxidants with structure of steric hindered phenol with one (AO-1 and AO-3) ore more identical –OH groups (AO-4), as well as the 2-hydroxi-4-alcoxibenzophenone UV absorber (UVA-1). Comparatively, we studied also the reactions of phenylisocyanate with reactive stabilizers (compounds with similar structures with usual stabilizers) that contain an additional reactive group beyond the stabilizing group. Reactive stabilizers are the AO-2 anti-oxidant and the UVA-2 absorber, HALS-2, respectively.

To elucidate the nature of stabilizers binding in the polyurethane's macromolecule model compounds were taken in consideration to study the possible reactions given by phenylisocyanate with usual and reactive anti-oxidants and photo-stabilizers. The experimental study tried to show that the stabilizer is in a higher proportion bound to isocyanate by –OH and –NH- steric hindered groups. These groups (others than the –OH implied in the stabilization process) represent the way the stabilizer will be bound in the polyurethane's matrix during reactive stabilization. In the next scheme we show the main mechanisms of reactions with reactive stabilizers containing the reactive –OH group with phenylisocyanate; the evolution of the processes depend on reactants proportion and on the conditions of the reaction:

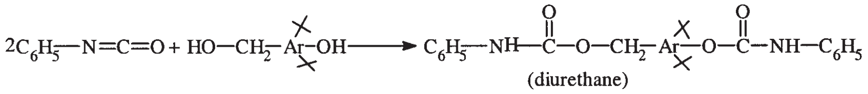
a) phenylisocyanate / stabilizer molar ratio = 1 / 1 and temperature lower than 60 - 70°C:



$$C_6H_5{-}N{=}C{=}O + HO{-}CH_2{-}Ar{-}OH \longrightarrow C_6H_5{-}NH{-}\underset{\text{(urethane)}}{\overset{\overset{O}{\|}}{C}}{-}O{-}CH_2{-}Ar{-}OH$$

Tel.: (+40) 0256 201458, 0256 492258, 0256592624

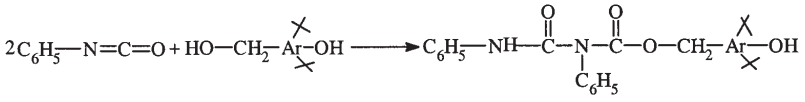
b) phenylisocyanate / stabilizer molar ratio = 1 / 1 and temperature lower than 60 - 70°C:



$$2C_6H_5-N=C=O + HO-CH_2-Ar-OH \longrightarrow C_6H_5-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-Ar-O-\overset{O}{\overset{\|}{C}}-NH-C_6H_5$$

(diurethane)

c) phenylisocyanate / stabilizer molar ratio = 1 / 1 and temperature lower than 60 - 70°C:



$$2C_6H_5-N=C=O + HO-CH_2-Ar-OH \longrightarrow C_6H_5-NH-\overset{O}{\overset{\|}{C}}-\underset{C_6H_5}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-CH_2-Ar-OH$$

(alophanate)

In order to take place the process of polyurethanes reactive stabilization it is necessary to ensure those conditions that favor (a) and (c) reactions because, in these cases, the steric hindered –OH group (participating to the stabilizing process) is not affected and it can act as stabilizer in the structure bound to the polyurethane's chain. If the stabilizer reacts as in (b) reaction, the steric hindered –OH group can not act as a stabilizer, now being a chain extender .

We performed the thermal analysis of the urethane and alophanate compounds of phenylisocyanate with mono- and bifunctional stabilizers in order to investigate the issues concerning the efficiency of polyurethanes reactive stabilizing process in certain applications. So, thermal lability of urethane and alophanate groups that bind the stabilizer to the polyurethane's chains intervenes in those applications where the reaction or the use temperature is beyond the temperature when bonds split up [9,10]. For instance, in the process of producing flexible polyurethane foam blocks, the difficult elimination of the reaction heat leads to temperature increase inside the block and to polymer degradation. Anti-oxidants should diminish these consequences.

In experiment it has also been shown that thermal analysis (besides IR spectroscopy, UV and high performance liquid chromatography in reverse phase – RP-HPLC) can be used to study mixtures of urethane and alophanate compounds resulting from phenylisocyanate reacting with mono- and bifunctional stabilizers.

Experimental part

Urethane and alophanate compounds of phenylisocyanate were synthesized with mono- and bifunctional stabilizers, using raw materials presented in table 1.

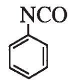
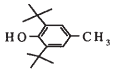
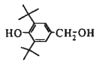
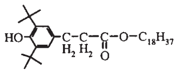
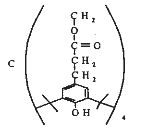
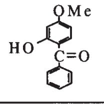
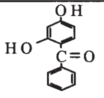
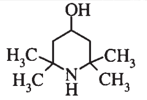
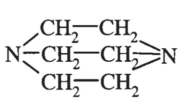
Chemical, commercial name	Structural formula	Features	Firm
a) **Isocyanate**			
Phenylisocyanate (PhI)		transparent liquid M = 119 g/mol ρ = 1.093 g/cm^3 b.p. = 62-64 °C	Fluka (Swiss)
b) **Anti-oxidants**			
2,6-Ditertbuthyl-4-methylphenol (AO-1), MPJ		white-yellow crystals M = 220 g/mol m.p. = 68-70.5 °C	Metafin (Austria)
4-Hydroxymethyl-2,6-ditertbuthylphenol (AO-2), Ethanox 754		white powder M = 236 g/mol m.p. = 140-143 °C	Ethyl Corporation (U.S.A.)
Octadecyl-3-(3,5-ditertbuthyl-4-hydroxyphenyl)propionate (AO-3), Irganox 1076		white powder M = 531 g/mol ρ = 1.02 g/cm^3 m.p. = 50-55 °C	Ciba-Geigy (Swiss)
Pentaeritritil tetrachis-[3-(3,5-ditertbuthyl-4-hydroxyphenyl)propionate] (AO-4), Irganox 1010		white powder M = 1178 g/mol ρ = 1.15 g/cm^3 m.p. = 110-125 °C	Ciba-Geigy (Swiss)
c) **Photo-stabilizers**			
2-Hydroxy-4-metoxy-benzophenone (UVA-1), UVASORB MET		yellow powder M = 228 g/mol ρ = 0.70 g/cm^3 m.p. = 63-64.5 °C	Sigma Prodotti Chimici (Italy)
2,4-Dihydroxy-benzophenone (UVA-2), UVASORB 2 OH		yellow powder M = 214 g/mol ρ = 1.30 g/cm^3 m.p. = 144-146 °C	Sigma Prodotti Chimici (Italy)
2,2,6,6-Tetramethyl-4-piperidinol (HALS-1)		yellow-pink powder M = 152 g/mol ρ = 0.85 g/cm^3 m.p. = 128-130 °C	Sigma Prodotti Chimici (Italy)
d) **Catalysts**			
Dibuthyl-staniu-dilaurate (DBSnDL)	$[CH_3(CH_2)_3]_2Sn[OOC(CH_2)_{10}CH_3]_2$	yellow liquid M = 598.7 g/mol ρ = 1.078 g/cm^3 b.p. = 187 °C	Air Products and Chemicals (U.S.A.)
Trietylen-diamine (DABCO), Dabco crystalline		white hygroscopic crystals M = 112 g/mol ρ = 0.14 g/cm^3 m.p. = 159.8 °C b.p. = 174 °C	Air Products and Chemicals (U.S.A.)

Table 1
FEATURES OF USED RAW MATERIALS

Table 2
PREPARATIVE CASES

Reactants and synthesis conditions	M.U.	Molar ratio of reactants													
		1a	1b	1c	2a	2b	2c	2d	3	4	5	6a	6b	7a	7b
PhI/AO-1	mol/mol	1/1	1/1	1/1											
PhI/AO-2	mol/mol				1/1	2/1	2/1	2/1							
PhI/AO-3	mol/mol								1/1						
PhI/AO-4	mol/mol									4/1					
PhI/UVA-1	mol/mol										1/1				
PhI/UVA-2	mol/mol											2/1	2/1		
PhI/HALS-1	mol/mol													1/1	1/1
DBSnDL	10^{-3}mol	3	3		3	3	3		3	3		3		3	
DABCO	10^{-3}mol			3				3			3		3		3
Hexane	ml		100	100		100		100	100	100	100	100	100	100	100
CCl_4	ml	100			100		100								
Temperature	°C	20	69	69	20	69	20	69	69	69	69	69	69	69	69
Reaction time	h	24	4	4	24	4	24	4	4	4	4	4	4	4	4

The recipes and the reaction conditions of phenylisocyanate with the four anti-oxidants and the three photo-stabilizers are shown in table 2.

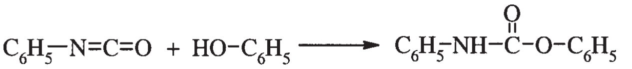
In most cases, the reactions of phenylisocyanate with stabilizers lead to a mixture consisting of different chemical compounds (urethane and alophanate types), identified with no doubt by high performance liquid chromatography in reverse phase (RP-HPLC). The structures of these compounds are shown in table 3.

To investigate the thermal stability of the synthesized compounds we used following methods: thermo-gravimetry and derived thermogravimetry with the -1500 T, MON thermal balance derivatograph (Hungary) and following experimental conditions:

- weight of probe: 100 mg (reference compound Al_2O_3);
- constant heating velocity: 10°C / min.;
- atmosphere: static air.

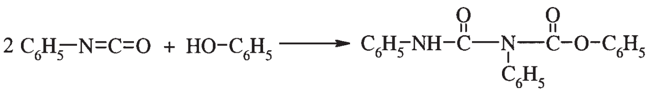
To point out the differences in thermal behavior of urethane and alophanate groups, model compounds were synthesized with reaction conditions to favor predominant formation of certain structures. Thus, phenol reacting with phenylisocyanate led to:

- diphenylurethane (hexane 20°C, 24 h, PhI / ArOH molar ratio = 1 / 1



$$C_6H_5{-}N{=}C{=}O + HO{-}C_6H_5 \longrightarrow C_6H_5{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}C_6H_5$$

- triphenylalophanate (hexane, reflux, 4 h, PhI / ArOH molar ratio = 2 / 1



$$2\,C_6H_5{-}N{=}C{=}O + HO{-}C_6H_5 \longrightarrow C_6H_5{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle C_6H_5}{|}}{N}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}C_6H_5$$

Thermal stability of urethane and alophanate structures in the obtained model compounds from the reaction between phenylisocyanate and phenol and with AO-1 anti-oxidant respectively was investigated by TG. The above mentioned reaction was performed under controlled conditions to obtain only one structure without any significant differences (fig. 1).

The investigated products decompose at relatively low temperatures (initial decomposing temperature, T_i = 100 – 120°C) by splitting up of carboxyl bonds in urethane and alophanate groups. The TG curve shows a rapid decrease of the probes weight up to 220 – 270 °C (final decomposing temperature, T_f), when the process ends by complete volatilization of the decomposing compounds. Anyway, there is a slight difference between urethane and alophanate structures, especially in the case of the products derived from the reaction between phenylisocyanate and the AO-1 anti-oxidant. The alophanate structure decomposition starts a little bit later than that of the urethane structure (T_i = 120°C vs. 100°C) and it evolves in two steps, probably due to successive division of ester and urea substituted bonds in the alophanate group.

Results and discussions

The experimental study comprised a thermogravimetric analysis both of reactants and obtained products in every preparative variant. To present the obtained thermograms, results were shown in tables: weight losses at different temperatures, both in raw materials (table 4) and in obtained products (table 5).

Regarding stabilizers, obtained data show the dependence of thermal stability on the compounds chemical structures (table 4). Thus, in the AO-1, AO-2, AO-3, AO-4 anti-oxidants series, the initial temperature T_i increases and the weight losses decrease with the molecular weight increase. At the edges of this series we find the AO-1 volatile anti-oxidant (15% weight loss at 200°C) and the AO-4 anti-oxidant (first weight losses appear no sooner than 300°C).

Discussing about UV absorbers (derivatives of 2,4-dihydroxibenzophenone – their thermal stability depends on the nature of the substitute of the hydrogen of the 4-hydroxi group), the initial temperature T_i increases and weight losses decrease in UVA-2 in contrast to UVA-1.

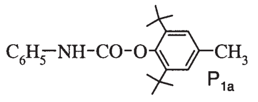
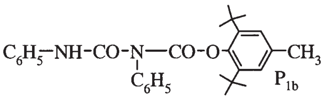
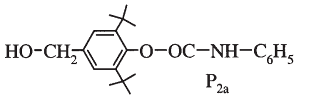
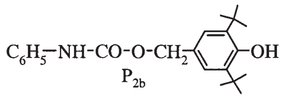
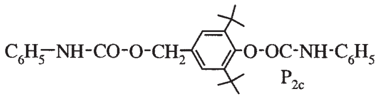
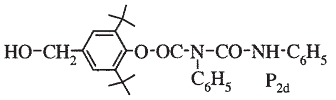
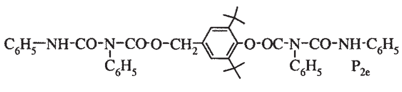
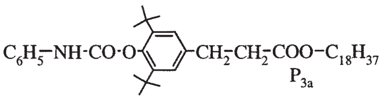
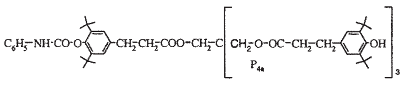
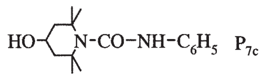
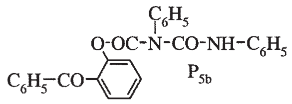
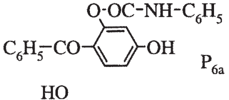
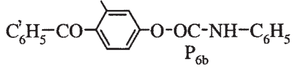
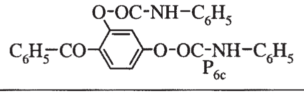
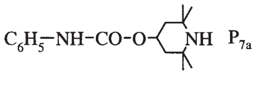
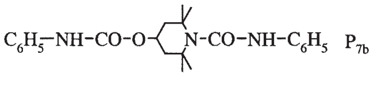
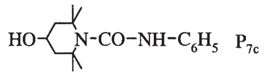
HALS-1 photo-stabilizer (low molecular weight compound), like the AO-1 anti-oxidant, is volatile and the first weight losses appear already at 125°C (table 4).

Phenylisocyanate (b.p. = 62 – 64°C) is a liquid compound with a quite low boiling point making no sense to perform the TG analysis. The DABCO catalyst, although in solid state (m.p. = 159.8°C), is a volatile product (b.p. = 174°C) as it results from the shape of the TG curve table 4). The DBSnDL catalyst is a liquid with a relative low boiling point (table 1) making not necessary the TG analysis.

Depending on the nature of the reactants and on synthesis conditions, significant variations of thermal stability of the investigated compounds were observed (initial decomposing temperature, T_i, temperature for maximal decomposing velocity, T_m, and weight losses). Usually, the decomposing process takes place in two phases: the first one comprises the scission of urethane and alophanate bonds and the second one the volatilization / decomposition process of the regenerated stabilizer by the above mentioned bonds scission.

The results of the performed study demonstrate the thermal lability of urethane and alophanate groups in the synthesized products.

Table 3
URETHANE AND ALOPHANATE TYPE COMPOUNDS STRUCTURES ALONG PREPARATIVE CASES

Preparative case	Reactants	Composition of products mixture obtained by RP-HPLC	Reaction products structures
1a	PhI/ AO-1	97,9 % P_{1a}	 P_{1a}  P_{1b}
1b		59.0 % P_{1a} 40.9 % P_{1b}	
1c		32.6 % P_{1a} 64.5 % P_{1b}	
2a	PhI/ AO-2	49.6 % P_{2b} 33.1 % P_{2a} 17.2 % P_{2c}	 P_{2a} ,  P_{2b}
2b		34.2 % P_{2b} 8.3 % P_{2a} 14.6 % P_{2c}	
2c		47,2 % P_{2b} 31.3 % P_{2a} 3.8 % P_{2d} 16.3 % P_{2c}	 P_{2c}
2d		10.8 % P_{2b} sau P_{2a} 86.4 % P_{2e}	 P_{2d}  P_{2e}
3	PhI/ AO-3	98.8 % P_{3a}	 P_{3a}
4	PhI/ AO-4	99.8 % P_{4a}	 P_{4a}
5	PhI/ UVA-1	56.0 % P_{5a} 41.5 % P_{5b}	 P_{7c}  P_{5b}
6a	PhI/ UVA-2	45.4 % P_{6a} 52.0 % P_{6b}	 P_{6a}  P_{6b}
6b		63.6 % P_{6a} 3.4 % P_{6b} 27.1 % P_{6c}	 P_{6c}
7a	PhI/ HALS -1	12.2 % P_{7a} 72.7 % P_{7b} 15.0 % P_{7c}	 P_{7a}  P_{7b}
7b		99.1 % P_{7a}	 P_{7c}

Depending on synthesis conditions, the products of the reaction of PhI and AO-1 are whether the P_{1a} urethane compound, or a mixture of it with the P_{1b} alophanate compound. The alophanate compound in the mixture (30 – 60 % P_{1b}) is pointed out by the TG curves: decomposition in two steps starts at a little higher temperature than the one-step composition of the P_{1a} urethane compound (fig. 1 – c and d thermograms and fig. 2).

The decrease of the P_{1a} urethane compound removes to more higher temperatures the products of advanced decomposition.

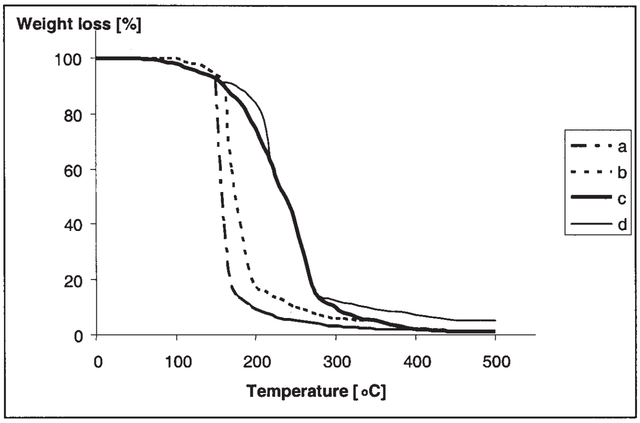


Fig. 1. Thermograms of model compounds with urethane and alophanate structure (100 mg, 10 °C / min, static air) for: a- diphenylurethane (PhI/ArOH=1/1); b- triphenylalophanate (PhI/ArOH=2/1); c- monourethane P_{1a} (PhI/AO-1=1/1); d- monoalophanate P_{1b} (PhI/AO-1=3/1)

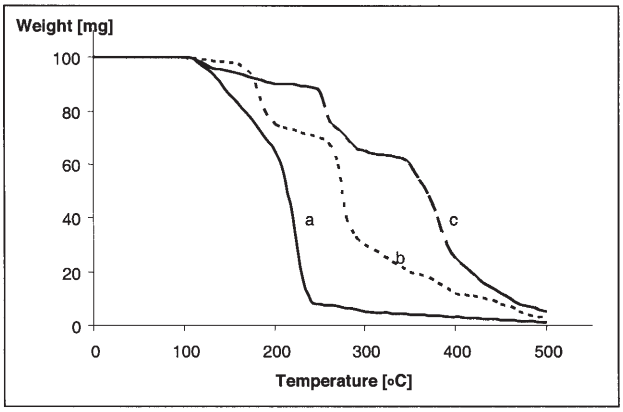


Fig. 2. Thermograms of reaction products PhI / AO-1 = 1 / 1: (a) case 1a (98,0 % P_{1a}); (b) case 1b (59,1 % P_{1a} and 40,9 % P_{1b}); (c) case 1c (32,6 % P_{1a} and 64,5 % P_{1b})

Table 4

THERMAL ANALYSIS OF RAW MATERIALS

Raw material		AO-1	AO-2	AO-3	AO-4	UVA-1	UVA-2	HALS-1	DABCO
Molecular weight		220	236	531	1178	228	214	152	112
Weight loss [%] at [°C] temperature	100	0	0	0	0	0	0	0	12
	125	0.3	0	0	0	0	0	0.9	36
	150	1.6	0.5	0	0	0,5	0	4	71
	175	5.5	1.3	0	0	1	0.3	13	97.3
	200	15	3.5	0	0	1.3	0.5	38	97.5
	250	80	23	0	0	5	3	97.8	98.3
	300	99,.	37	2	0.5	25	13	98	98.8
	350	100	66.5	10.5	4.5	95	54	98	99.1
	400	100	81	70	47	95.8	93	98	99.3
	450	100	84.5	96	75	96	93.5	98	99.6
	500	100	88	98	84.3	96	94.5	98	99.6

Table 5

THERMAL ANALYSIS OF REACTION PRODUCTS

Preparative case		1a	1b	1c	2a	2b	2c	2d	3	4	5	6a	6b	7a	7b
Molar ratio reactants		PhI/ AO-1= 1/1	PhI/ AO-1= 1/1	PhI/ AO-1= 1/1	PhI/ AO-2= 1/1	PhI/ AO-2= 2/1	PhI/ AO-2= 2/1	PhI/ AO-2= 2/1	PhI/ AO-3= 1/1	PhI/ AO-4= 4/1	PhI/ AO-2= 2/1	PhI/ UVA-2= 2/1	PhI/ UVA-2= 2/1	PhI/ HALS-1= 1/1	PhI/ HALS-1= 1/1
Weight loss [%] at [°C] temperature	100	0	0	0	0	0	0.3	0	1.9	0	1	0	0.6	0	0.2
	125	2	0	0	0	0.5	4	0.8	2,6	0.2	1,5	0	1.8	0	0.8
	150	5	0.5	0.6	0	7	13.3	1.8	3	0.3	2	1,5	5.5	0	1
	175	11	6.5	7	0,5	18	18	7	5.5	0.9	4	4,9	11	0,1	1.5
	200	20.5	11	12	3	21.5	21	12.5	6.4	1.5	7.5	10.5	20.5	1	3
	250	60	45	26.5	39,5	34	31.5	25	18.5	8.5	27.5	34	39.5	15	18
	300	97.3	99.2	42.6	48.5	52	47,5	40	40.5	20	54	47	51.5	99	98.3
	350	97.8	99.8	49	71	77.5	75	69	54	36.5	89.5	73	73	99.7	98.8
	400	98	99.9	65	82.3	89.5	88.3	81.3	80.5	60.5	92.3	92	82	99.9	99
	450	98	99.9	99.3	84.5	91.3	90	83	86	67	92.8	93	83.5	100	99
	500	98.4	100	100	87.3	93	92.5	87.5	89	82	93.6	94.3	85	100	99.5

In the reaction PhI with the AO-2 bifunctional antioxidant more reaction products are obtained (monourethane, diurethane, monoalophanate, dialophanate, etc.); each compound's predominance in the mixture leads to changes in the thermograms shape. Analyzing cases 2a – 2d, the thermograms of the reaction products indicate an increased thermal stability in products of 2a case when compared with the other three cases (Table 5). In this case the weight loss starts significantly at 200 °C (3 %), and in the other cases it starts at 150 – 175 °C.

The monourethane P_{2b} product (-NCO group addition to the alcoholic –OH) is in the greatest proportion among the products in case 2a. It leads to an increase of the initial decomposing temperature due to the higher thermal stability of the urethane group containing a rest of alkyl radical. This compound is accompanied by the P_{2a} monourethane product (-NCO addition to the phenol –OH) and by the P_{2c} diurethane product.

The P_{2b} product has a lower proportion in cases 2b and 2c (34.2% and 47.2%, respectively), concomitant with the appearance of the P_{2d} monoalophanate product (in case 2c). This situation led to the decrease of the initial decomposing temperature.

In case 2d the initial decomposing temperature increases slightly, compared to cases 2b and 2c, indicating that there is a dialophanate type compound (P_{2e}) with a better thermal stability than that of the monoalophanate (P_{2d}). There is also one of the following monourethane compounds, P_{2a} or P_{2b}. We could not affirm after performing RP-HPLC which of the two products is in the reaction mixture; though, after the TG analysis the presence of the P_{2b} monourethane product is very probable and it is more thermal stable than P_{2a}. The presence of the P_{2e} dialophanate compound less thermal stable besides P_{2b} determines that the initial temperature of the product mixture in case 2d to be lower than that in case 2a (130°C, versus 90°C).

Data obtained by RP-HPLC show that a single monourethane product (P_{3a}) is obtained in the reaction between PhI and AO-3. This compound decomposes in two steps, the first one meaning urethane bond scission at lower temperatures than those when weight losses of the monofunctional anti-oxidant AO-3 appear (T_i = 90 °C, versus 275 °C and 40,5% weight loss at 300°C, versus 2%).

A similar behaviour is observed in the products of the reaction between PhI with the trifunctional AO-4 anti-oxidant: T_i = 180 °C, versus 310°C and 20% weight loss at 300 °C, versus 0.5%.

The same behaviour is shown in the reaction products derived from the reaction between PhI and mono- and bifunctional absorbers. The first step of decomposing the reaction products of the reaction between PhI and the UVA-1 monofunctional absorber (T_i = 100 °C, versus 175°C) can be attributed to urethane and alophanate bonds scission in the corresponding compounds (P_{5a} and P_{5b}).

Although the reaction products of the reaction between PhI and the UVA-2 bifunctional absorber have a similar behavior with those in the previous case (lower thermal stability than in UVA-2 which has T_i = 210°C), there are some small differences yet: T_i = 135°C – the P_{6a} and P_{6b} monourethane compounds mixture and T_i = 112 °C – when the diurethane P_{6c} compound appears additionally. The T_i decrease in the case of the diurethane compound is due to the lighter thermal scission of one from the two urethane groups. This happens because in the structure of the product there is a second urethane group with favorable electronic effects to this process.

A different behavior is observed in the case of the products of the reaction between PhI with the bifunctional HALS-1 photo-stabilizer. HALS-1 is an easy volatile compound (T_i = 129°C) and it shows an inferior thermal stability than reaction products. Thermal decomposition of the P_{7a}, P_{7b} and P_{7c} products mixture takes place in two phases: during the first the urethane group from P_{7a} and P_{7b} splits up; during the second one the urea group from P_{7b} and P_{7c} splits up. The urea group has T_i = 180 – 260°C, compared to the urethane group with T_i = 150 – 250°C [4]. Because of the P_{7c} urea compound (12.2%) and of the P_{7b} urea-urethane compound (15%) besides the P_{7a} urethane compound (72.7) in the products mixture in case 7a, T_i removes up to higher values (200°C). These groups scissions take place at much lower temperatures than weight losses appear in the case of the bifunctional HALS-1 photo-stabilizer (18% at 250°C, versus 97.8%).

Conclusions

Performing thermal analysis upon urethane and alophanate compounds of phenylisocyanate with mono- and bifunctional stabilizers, following conclusions can be stated:

- urethane and alophanate groups have a lower thermal stability than functional groups existent in the structure of reactants;
- thermal scission of urethane and alophanate bonds takes place with great probability as an inverse reaction with the stabilizer's regeneration:
  - if the compound contains two urethane or alophanate groups, their scission takes place successively;
- thermal analysis (besides IR and UV spectroscopy and high performance liquid chromatography in reverse phase – RP-HPLC) can be successfully used to investigate mixtures of urethane and alophanate compounds resulting from reactions of isocyanates with mono- and bifunctional stabilizers.

The above mentioned conclusions are useful in chemical binding of stabilizers in polyurethanes macromolecules, extremely important issue in polyurethanes thermal and photo-oxidative stabilizing process (additive and reactive).

References

1.VIEWEG, R., HOCHTLEN, A., Kunststoff-Handbuch. Polyurethane, vol VII, Carl Hanser Verlag, Munchen, 1966, p. 76

2.BOLCU, C., SEIMAN, I., DUDA-SEIMAN, C., Chimia poliuretanilor la începutul mileniului 3, Ed. Eurostampa, Timişoara, 2003, p. 1

3.OPREA, S., STELIAN, V., STOICESCU, G., CASARIU, M., Mat. Plast., **44**, nr. 3, 2007, p.226

4.BOLCU, C., DUDA-SEIMAN, C., Mat. Plast., **58**, nr. 9, 2007, p.246

5.MUNTEANU, D., BOLCU, C., OSTAFE, V., Polymers & Polymer Composites, **8**, nr. 2, 2000, p. 87

6. VLAD, S., Mat. Plast., **45**, nr. 4, 2008, p.394

7.OPREA, S., OPREA, V., Mat. Plast., **45**, nr. 4, 2008, p.345

8. MARIES, Gh.R.E., Mat. Plast. **46**, nr. 2, 2009, p. 169

9.HALLER, A.K., FARKAS, F., Thermochimica Acta, **92**, 1985, p.297

10.VLASE, T., VLASE G., DOCA, N., BOLCU, C., J. Therm. Anal. Cal., **80,** 2005, p.59

Manuscript received: 9.10.2008