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Investigation of thermal degradation of some adhesives used in the automobile industry by thermal analysis/mass spectrometry and GC-MS

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Abstract

In order to make a direct evaluation of adhesives used in bond welding in the automobile industry we used the so-called "black box" approach. In this case we only know the trade name of the adhesive but not any further information about the raw materials. To obtain information from the thermal behavior of adhesives, we conducted thermoanalytical experiments in an inert atmosphere and coupled thermal analysis/mass spectrometry. Modelling the real situation in bond welding, we made pyrolysis experiments in the German VCI-oven in air. The volatile and semivolatile products of pyrolysis were collected on XAD-resins and after elution, qualitative and quantitative determinations were carried out by gas chromatography/mass spectrometry. According to black box theory, the results (output) were referred to adhesive type used (input). This approach is not restricted to investigating adhesives, but can be applied to all cases where high temperature must be used in the presence of organic materials. The adhesive types investigated were three epoxy resins, one component polyurethane and one butyl-chaoutchouc.

Keywords: TA; Thermal degradation; Pyrolysis; Adhesive; Epoxy resin

1. Introduction

In the automobile industry, resistance spot welding is a widely used technology. There is a lot of knowledge about the thermal and mechanical aspects of this joining technique

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[1–3]. The search for weight reduction leads to the combination of adhesive materials with resistance spot welding (bond welding). The goal of our investigation was, to determine possible pyrolysis products evolved during the thermal degradation of adhesives.

The most widely used epoxy resin-based adhesives are the reaction products of epychlorhydrin and 2,2-bis(4-hydroxyphenyl)propane (bisphenol A). The reaction products are the diglycidyl ether of bisphenol A. Both low and high molecular species can be found in the reaction mixture. Varying the ratio of bisphenol A and epychlorhydrin the average weight will be changed. In spite of this varied by-product, oligomers can be found in the end-product [4–9]. We do not intend to review the composition of epoxy resins, produced by different manufacturers, but illuminate the different thermal behavior and pyrolysis pattern of the products. It is obligatory for every trade-mark product to be controlled with regard to both thermal behavior (curing temperature) and emission of thermal degradation products in inert and oxidative atmosphere.

The terminology of segmented polyurethanes (PURs) covers a broad class of polymers produced from hard (rigid) urethane segments and soft (flexible) segments. The hard (rigid) segments can be formed from different diisocyanates; two of them are very popular MDI (diphenylmethane-4,4′-diisocyanate) and TDI (ditoluene-4,4′-diisocyanate). The soft segments mostly consist of polyethers or polyesters. The relative content of MDI or TDI (which are usually present as oligomers) and polyethers or polyesters influence not only the physical state of cured PUR but also chemical properties [10].

The thermal degradation of PURs begins as low as 150°C. At about 210°C urethane linkages cannot be detected [10–12]. At this first stage, the PURs will thermally dissociate to isocyanate and polyol (the name of polyol covers the polyethers and polyesters), and further thermodegradation proceeds via several possible ways. Rolival et al. [13] investigated the thermal decomposition of a PUR adhesive. They conducted thermal degradation experiments in air and the degradation products were drawn to impingers at 30 ml min^{-1} air flow. They only measured the acidic gases (CO_2HNC), carbonyl compounds and isocyanates at temperatures between 200 and 600°C. They found a low formation of carbonyl compounds. Nitrogen mainly evolved as different kinds of nitrogen forms, but not as hydrogen cyanide or phenylisocyanate. The majority of released gases was CO_2 and CO.

Some publications reported on thermal behavior on cured rubbers [14–16]. In one case cyclization reactions predominantly take place [16].

Approaching the subject methodically, we can find several methods dealing with thermal degradation of different polymers. The more powerful techniques used to determine the evolved gases during thermal treatment in inert gases and air are simultaneous thermogravimetry (TG)/differential thermoanalysis (DTA)/mass spectrometry (MS). See Refs. [17–21] for descriptions and applications of this coupled technique.

To improve the analytical performance of TG-DTA-MS, the effluent gases are first separated by GC (TGA-GC-MS) [17] or by TGA-MS-MS. On the one hand there are a lot of advantages of TA-MS systems, but on the other hand usage in quantitative analysis is limited [17].

The other hyphenated technique is pyrolysis mass spectrometry (PYMS) [18]. Pyrolysis can be done in front of an ion source, near the ion source or inside the ion source. However, only the atmospheric pressure ion (API) source can be used in any atmosphere.

Unfortunately, most PYMS instruments work with a pyrolysis chamber outside the ion source. Several secondary reactions may occur between the pyrolysis chamber and the ion source of the mass spectrometer. This method can be used successfully for fingerprinting of different materials.

At the so-called off-line PYMS method the reaction products are trapped at low temperature and introduced into a GC-MS system. Generally every technique for studying the thermal behavior of a material by trapping evolved gases and analyzing them by GC-MS can be attributed to this category.

All thermoanalytical techniques offer information as presented above, but modelling of the thermal behavior of synthetic polymers, used in industry, can be done by independent methods and by evaluating the results. The closer the model is to the real situation, the better the risk assessment is for evolved gases. On the one hand, in our approach we used TA-MS in an inert atmosphere and on the other hand we used the VCI-oven. With the VCI oven we are able to model real conditions and to analyze the gaseous end-products. The end-products of thermal degradation at high temperature will be different from primary degradation species because several reactions may take place. In addition to this curing polymerization, evaporation may occur at bond welding. In the gas phase reactions between evaporating substances and degradation products are possible. New compounds can be generated on surfaces by secondary reactions.

2. Material and methods

2.1. *Thermal analysis/mass spectrometry (Table 1)*

Kettrup et al. [22–27] have proved the combination of thermal analysis and mass spectrometry to be a very useful method for studying the thermal degradation processes of polymeric materials. Beside the thermal effects, as recorded from TG or DTA, the evolved degradation products can be determined and identified by the on-line coupled mass spectrometer For the investigation of epoxy resin, PUR and butyl-chaoutchouc-type adhesives a Netzsch/Balzers STA 429/QMG 420 coupling system was used. The samples (about 20–25 mg each) were examined in a synthetic air or argon atmosphere (dynamic

Table 1

Adhesives investigated in thermal degradation and pyrolysis experiments

Adhesive	Basis	Viscosity	Pre-hardening	Hardening	Produced by
WB 5103	Epoxy resin	Paste	145°C, 13 min	180°C, 30 min	Ciba-Geigy
XW 1044–2	Epoxy resin	2800–3400 mPa	160°C, 7–10 min	180°C, 20–25 min	Ciba-Geigy
EPS 110	Epoxy resin	400000 mPa	–	180°C, 15 min	DELO Kunststoff-chemie
TIVO 9551/43	Polyurethane	Thixotrop	120°C, 20 min	180°C, 30 min	Tivoli Werke
Terostat 1244	Butyl-chaoutchouc	Thixotrop	–	180°C, 30 min	Teroson

atmospheres ca. 50 ml min^{-1}). Thermal analysis experiments were carried out, starting at ambient temperature (RT) up to ca. 800°C, using a heating rate of 10°C min^{-1}. As reference we used an empty crucible (alumina). The simultaneous mass spectrometric investigations were also carried out from room temperature up to 800°C. Mass spectra were recorded every 20°C in three ranges: (1) 10–60 amu (atomic mass unit); (2) 50–150 amu; and (3) 150–300 amu.

The registration was done by SEM (1700 V) and ionization by means of a cross beam rhenium cathode, using 70 eV ionization energy.

2.2. *VCI-combustion furnace*

For simulation of the pyrolysis processes the VCI-furnace (Heraeus, Hanau, Germany) was used [28]. This type of combustion device simulates burning processes of solid and liquid high boiling substances at different preselected temperatures. The sample is placed into a quartz crucible. It vertically falls from the charging device (insertion lock, Fig. 1) into the hot zone. The heated zone can be tempered between 200°C and 1200°C. The decomposition products pass though the hot zone twice. They are sampled by the adsorption device on suitable materials such as XAD-4 resin, activated charcoal or other special adsorbents. Due to this technique, the sample is heated quickly to the preselected

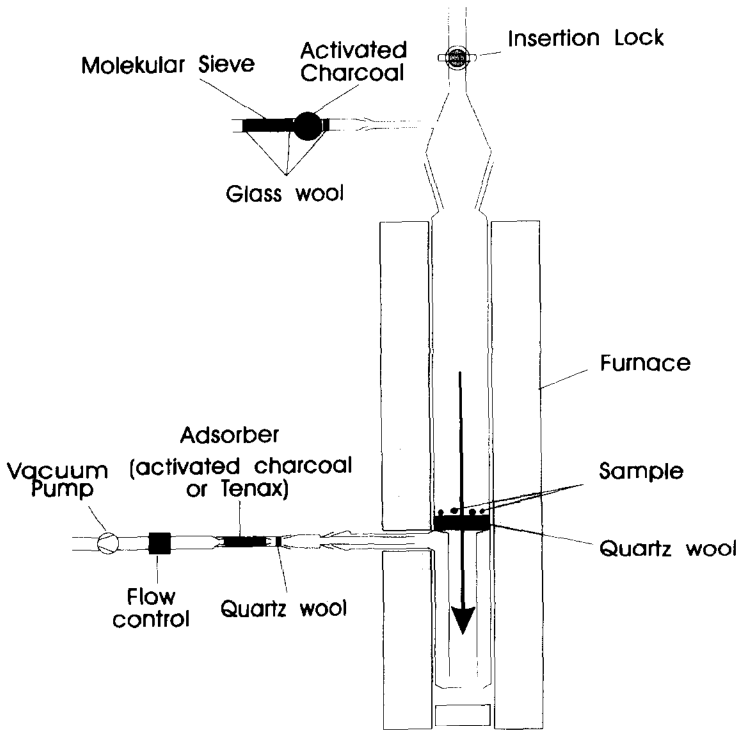

Fig. 1. VCI-combustion furnace.

temperature and distillation processes are avoided. The burning process finishes in approximately 2 min. For the quantitative collection of the degradation products about 10 min are necessary. The products are desorbed and analyzed by means of GC and GC-MS.

With this type of furnace, the combustion atmosphere and the combustion temperature can be varied and their influence on the spectra of pyrolytic products can be studied. The combustion experiments were made at different preselected temperatures from 400 to 1200°C at a constant air flow at 100 ml min^{-1}. The amount of sample investigated was 30 mg in each experiment.

2.3. *Gas chromatography/mass spectroscopy*

A GC-MS system (Varian GC 3100 – Varian Ion Trap Saturn II with MS DOS Workstation) was used. The chromatographic parameters were: analytical column, J&W DB 5, 30 m, 0.32 mm, 0.25 μm film; column head pressure (helium)m 100 kPa; injector temperature, 280°C; GC temperature program, 40°C, 2 min isothermic, with 25 min to 90°C, 1 min isothermic, with 5°C min^{-1} to 300°C, 10 min isothermic.

2.4. *Mass spectrometry parameters*

Scan rate, 1 scan per s; mass range, 45–450 amu; electron ionization energy, 70 eV.

3. Results and discussion

3.1. *TA-MS investigations*

The TA data of all adhesive samples are summarized in Table 2.

3.1.1. *Thermal analysis results*

Epoxy resin XB 5103. The degradation of the sample in an argon atmosphere occurred in a one step process to ca. 50%. No significant effect on the DTA curve is related to this degradation step. A significant DTA effect can be observed after the complete degrada-

Table 2

TA data of adhesive samples in an argon atmosphere

Adhesive	T_i	Δm/%	$\mathrm{DTG}_{\max}$/°C	$\mathrm{DTA}_{\max}$/°C
XB 5103	316°C	(1) 49.6 (RT–697°C)	380	167; 588
XW 1044-2	306°C	(1) 51.6 (RT–441°C)	412	174
ESP 110	290°C	(1) 50.6 (RT–550°C)	393	160; 646(endo)
TIVO 9551/43	165°C	(1) 22.1 (RT–379°C) (2) 15.6 (379–532°C)	300; 430	125 (exo); 345 (exo); 433 (endo)
Terostat 1244	255°C	(1) 36.7 (RT–543 °C) (2) 16.9 (543–831°C)	430; 442; 780	150

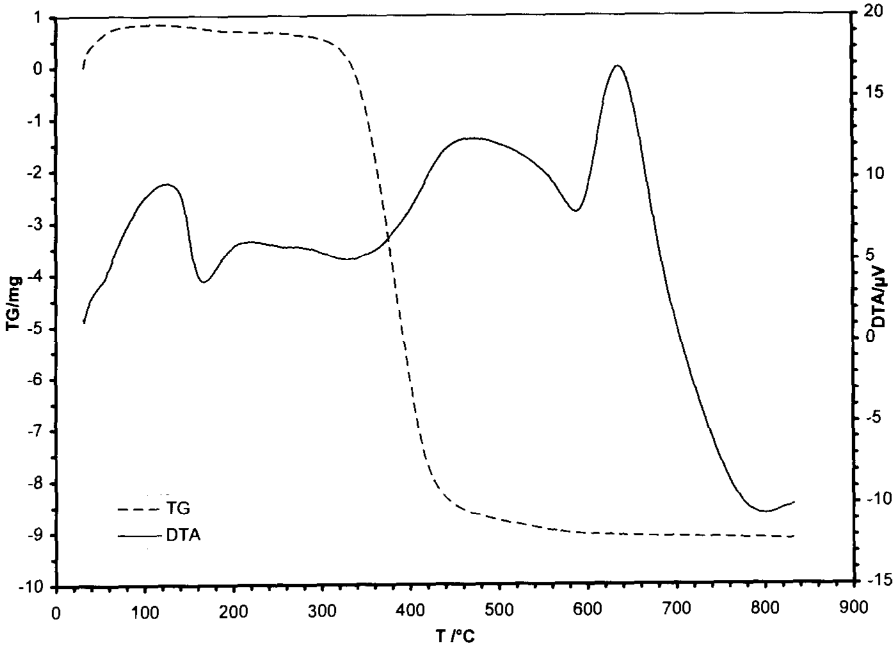

Fig. 2. TA curves from sample XB 5103.

tion of the sample (cf. Fig. 2). These two effects (first exo- then endothermic) are due to reactions of the filler materials. The first exothermic effect at a temperature below the degradation of the sample is related to the hardening process of the glue.

Epoxy resin XW 1044-2 (Fig. 3). The investigation of the sample led to a two step degradation of ca. 50% of the sample mass. No significant thermal effect is related to this process, starting at about 300°C. The DTA curve did not show any significant effect in the related temperature range. The only clear exothermic process during heating of the sample is related to the hardening process at 174°C.

Epoxy resin ESP 110. The degradation of the sample ESP 110 occurred in an argon atmosphere in one step to 50% of the sample mass. This degradation process did not show any significant thermal effect either. The two significant DTA effects occurred before and after the weight loss of the sample. The first exothermic effect is again related to the hardening process of the glue. The second endothermic effect might be due to effects (melting, reaction) from the inorganic filler materials. For details see Table 2. The spike within the DTA curve (cf. Fig. 4) is a single point measuring error.

Polyurethane TIVO 9551/43. The thermal degradation of the sample TIVO 9551/43 occurred in two steps to ca. 22% and 15% of the sample mass. The first degradation step was accompanied by a weak exothermic, and the second step by a weak endothermic effect (cf. Fig. 5). The weight loss of the sample started at 165°C.

Butyl-chaoutchouc Terostat 1244. The degradation of the sample occurred in two steps to ca. 37% and 17% of the total sample mass. During thermal treatment, only one

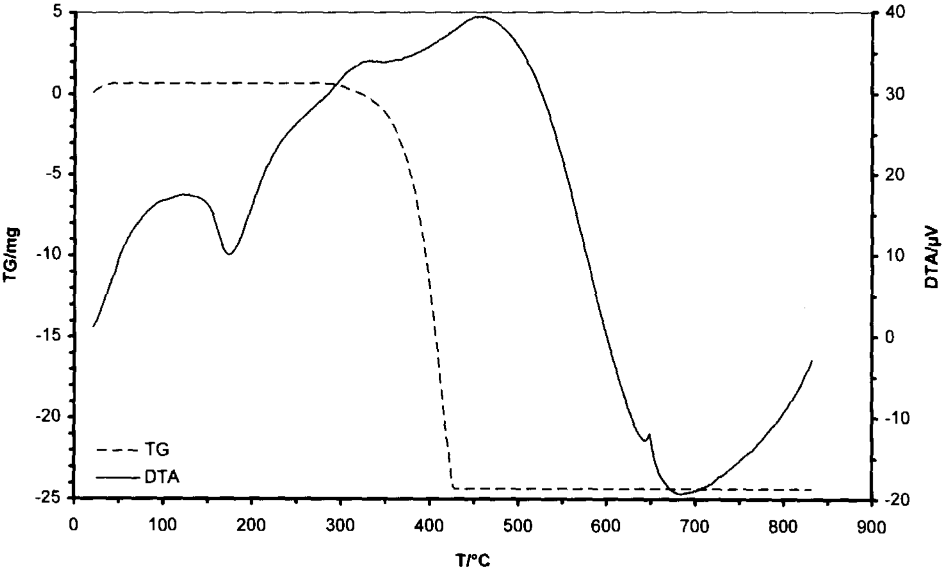

Fig. 3. TA curves from sample XW 1044-2.

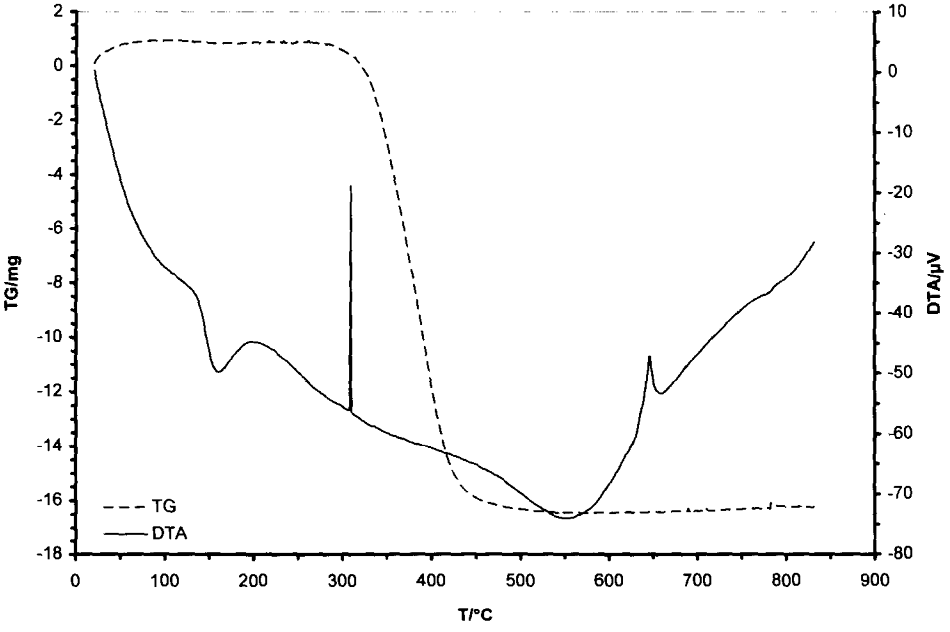

Fig. 4. TA curves from sample ESP 110.

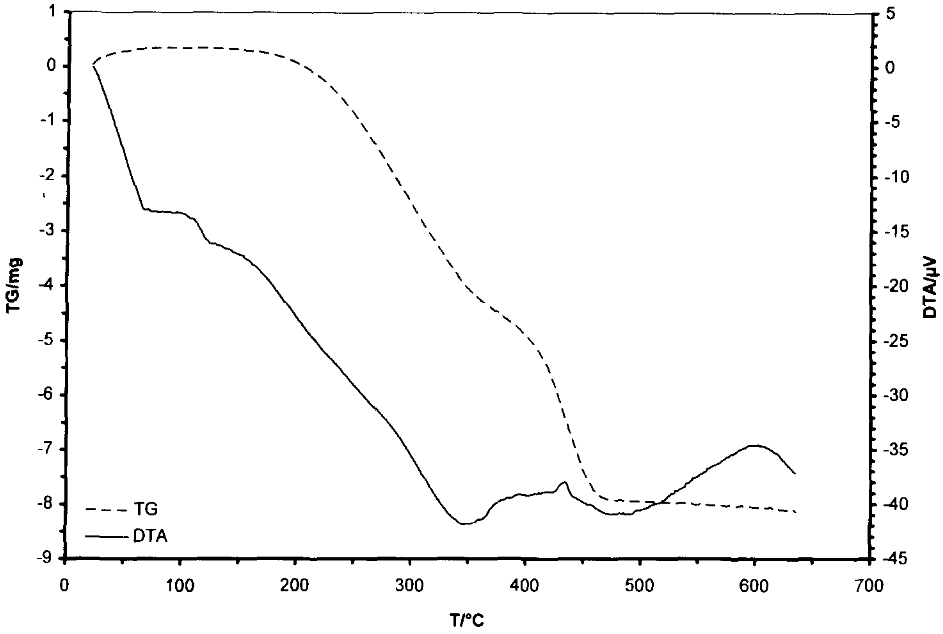

Fig. 5. TA curves from sample TIVO 955/43.

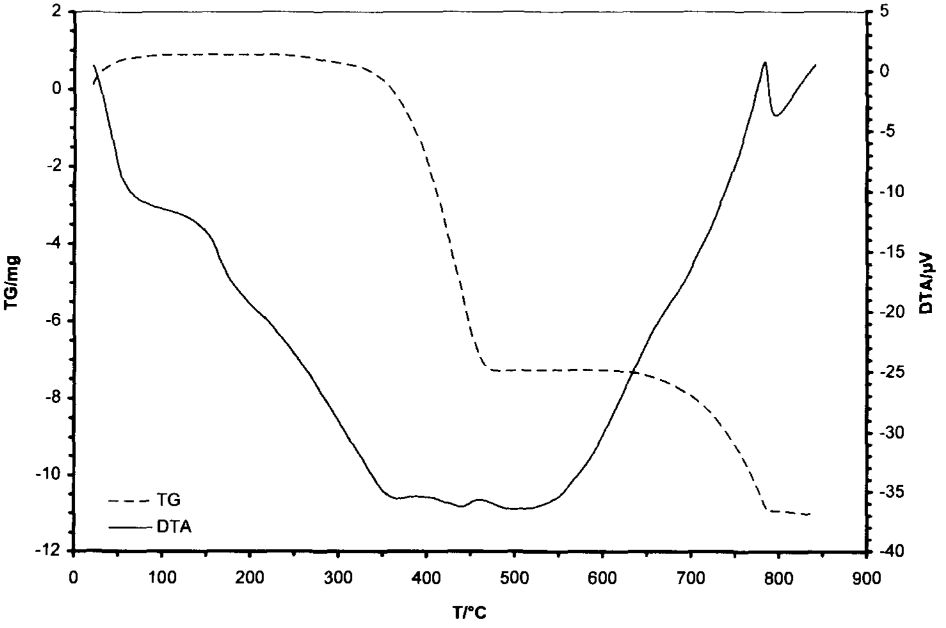

Fig. 6. TA curves from sample Terostat 1244.

Table 3

Selected possible substances and structural elements from samples XB5103, XW 1044–2 and ESP 110

m/z	Possible substances and structural elements
18	H_2O
55	$C_3{}_5N$, C_3H_3O, C_4H_7
66	C_4H_2O, C_5H_6, C_4H_4N
77	C_5H_3N, C_6H_5
91	C_6H_5N, C_7H_7 (Tropylium), C_6H_4O
94	C_6H_6O, C_7H_{10}
107	C_7H_9N, C_7H_7O, C_6H_5NO, C_8H_{11}
121	C_7H_7NO, $C_8H_{11}N$, C_8H_9O, C_9H_{13}

weak endothermic maximum at ca. 150°C and a baseline shift can be obtained (cf. Fig. 6 and Table 2).

3.1.2. MS results

Epoxy resins XB 5103, XW 1044–2 and ESP 110. The three epoxy resins showed quite similar results from the mass spectrometric investigations and are therefore discussed together.

The mass spectrometric investigation of the degradation products showed the typical pattern of aromatics, acylated aromatics, phenols and acylated phenols. As the main degradation product in all cases, phenol (*m/z* 94) could be observed in addition to H_2O, CO and CO_2. A list of possible structural elements and evolved substances related to the registered main fragments is given in Table 3.

Polyurethane TIVO 9551/43. The mass spectrometric investigation of the degradation products of TIVO 9551/43 also leads to a two step degradation of the sample. Within the first step, no phenols or acylated aromatics can be detected. Significant peaks can be found at *m/z* 149 and 167. The fragment *m/z* 149 is characteristic for the evolution of

Table 4

Fragments and their possible sum-formulas from sample TIVO 9551/43

m/z	Possible substances and structural elements
55	C_3H_5N, C_3H_3O, C_4H_7
57	C_3H_7N, C_3H_5O, C_4H_9
67	C_4H_2O, C_5H_6, C_4H_4N
70	C_4H_6O, C_5H_{10},
79	C_5H_3N, C_6H_5
81	C_5H_5O, C_6H_9
83	C_5H_7O, C_6H_{11}
91	C_6H_5N, C_7H_7 (Tropylium), C_6H_4O
104	$C_5H_{12}O_2$, C_8H_8,
149	$C_8H_5O_3$,
167	$C_9H_{11}O_3$, $C_{13}H_{11}$

phthalester (softener) from the sample. The fragment m/z 167 is less characteristic. Within the second step, acylated aromatic compounds can be detected. The fragment ions and their possible sum-formulas are listed in Table 4.

Butyl-chaoutchouc Terostat 1244. From the degradation of Terostat 1244 no phenol or phenol compounds could be detected. Beside some aromatic substances, a fragment at m/z 27 could be detected. This is due to the evolution of HCN during thermal degradation of polyurethane products.

3.2. Pyrolysis tests in the VCI-combustion device

3.2.1. Epoxy resins XB 5103, XW 1044–2 and ESP

A 30 mg epoxy resin sample was pyrolyzed in the VCI-oven under equal conditions. Tables 5–7 show the results of the GC-MS investigation.

The main degradation products were benzene and toluene. From the results we can conclude that the amount of benzene increases if the pyrolysis temperature is increased to 1000°C. For other compounds such as oxo-compounds, no characteristic pattern can be found. The aromatic compounds indicate a fragmentation of polymer or prepolymer chains followed by a cyclization and aromatization step. A similar mechanism is known for the formation of polycyclic aromatic hydrocarbons [29–31].

3.2.2. Polyurethane TIVO 9551/43

The result of the pyrolysis experiments is summarized in Table 8.

The main degradation products again are benzene and toluene. The measured amounts of benzene were less than that of epoxy resin except XB 5103. No characteristic difference could be found for other compounds. The detectable compounds again are aromatics.

Table 5

GC-MS results of the VCI-pyrolysis experiment with the XB 5103 epoxy resin adhesive (μg product of pyrolysis per g burned sample)

	T/°C				
	400	600	800	1000	1200
Benzene	10	60	234	1780	450
Toluene	127	123	149	134	30
Dimethylbenzene			17		
Phenol	68		27		
Benzofuran	126		16		
Cresol			14		
1-Ethyl-4-methoxybenzene	102				
Dibenzofuran		18	20		
Biphenylene			23	34	
Naphthalene			33	86	
2-Methylnaphthalene		17	6		
9-Methylfluorene			15	68	

Table 6

GC-MS results of the VCl-pyrolysis experiment with the Delo ESP-110 epoxy resin adhesive (μg product of pyrolysis per g burned sample)

	T/°C				
	400	600	800	1000	1200
Benzene	10	50	420	11800	650
Toluene	60	90	120	170	30
Phenol	31	26	11		
2-Methylbenzaldehyde	9				
1-Ethyl-4-methoxybenzene	8		10		
Biphenylene		20		20	
Naphthalene			31	87	
2-Methylnaphthalene	7		11		
9-Methylfluorene			6	25	

3.2.3. *Butyl-chaoutchouc Terostat 1244*

The result of pyrolysis experiment is summarized in Table 9. In this case, benzene is the main characteristic compound. The amount of toluene is in the range of other aromatics. We could not find a significant difference between the aromatics formed in this case and as described above.

Table 7

GC-MS results of the VCl-pyrolysis experiment with the XW 1044-2 epoxy resin adhesive (μg product of pyrolysis per g burned sample)

	T/°C				
	400	600	800	1000	1200
Benzene	48	93	2260	16400	235
Toluene	40	30	12	40	34
Dimethylbenzene			4		
Ethylbenzene			21		
Propinylbenzene		8	13		
Phenol		99	27		
Benzofuran			12		
Cresol			21		
2-Methylbenzaldehyde			40		
1-Ethyl-4-methoxybenzene			31		
Dibenzofuran			11		
Biphenylene			18	28	
Naphthalene			26	53	
Naphthalenol or 3-phenylfuran			6		
2-Methylnaphthalene		10	6		
Acenaphthylene			4		
9-Methylfluorene			19	80	

Table 8

GC-MS results of the VCI-pyrolysis experiment with the Tivo 9551/43 polyurethane adhesive (μg product of pyrolysis per g burned sample)

	T/°C				
	400	600	800	1000	1200
Benzene	30	480	800	1610	260
Toluene	30	40	120	100	180
Phenol	31	26	11		
2-Methylbenzaldehyde	9				
1-Ethyl-4-methoxybenzene	8		10		
Biphenylene				20	
Naphthalene		20	31	87	
2-Methylnaphthalene	7		11		
9-Methylfluorene			6	25	

4. Conclusion

We performed a series of experiments for the characterization of thermal and pyrolytic behavior of three different types of epoxy resin, one PUR and one butyl-chaoutchouc adhesive. Our working philosophy was that the composition of adhesives does not change significantly. The thermal and pyrolytic behavior of materials investigated must be the same within the range of determination error. The input parameter is the given trade-mark product and output is the degradation product in an inert atmosphere (thermoanalytical curves and degradation products) and end products of pyrolysis. This approach may be useful for the evaluation of materials used in industry because if we know the characteristics of adhesives and if we carry out the experiments we can prove the identity

Table 9

GC-MS results of the VCI-pyrolysis experiment with the Therostat 1244 butyl-chaoutchouc adhesive (μg product of pyrolysis per g burned sample)

	T/°C				
	400	600	800	1000	1200
Benzene	20	30	2260	6800	230
Toluene	20	20	30	30	30
Phenol	15	18	10		
Cresol			26		
1-Ethyl-4-methoxybenzene			10		
Biphenylene		12		16	
Naphthalene			29	76	
Fluoranthene			13		
9-Methylfluorene			11	31	

of materials offered by the manufacturer. The starting-point of this black box experiment was the trade name of the material (input). We determined the thermal and pyrolysis pattern of materials of different producers. This approach offers greater confidence than the widely used finger print techniques. First, two independent and authentic experiments have to be carried out. Second, when the results of pyrolysis are compared, the main characteristic compounds are the same. The amount of these compounds varies from sample to sample, but there is no characteristic difference between the various trade-mark products. Several reactions can be run simultaneously in solid or liquid phase or gas phase. It is difficult to predict these complex reactions, but the end-products can be measured with high accuracy.

Adhesives used in our experiments were of different trade origin, but pyrolysis at high temperature, modeling the real situation, shows similar patterns which are known for formation of aromatics and polycyclic aromatic hydrocarbons.

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References

[1] E.W. Kim and T.W. Eagar, Welding J., 69 (1989) 303s.
[2] Z. Han, J. Orozco, J.E. Indacochea and C.H. Chen, Welding J., 69 (1989) 363s.
[3] C.L. Tsai, O.A. Jammal, J.C. Papritan and D.W. Dickinson, Welding J., 72 (1992) 47s.
[4] K. Assato, K. Yokohama and H. Kakiuchi (Eds.), Epoxy Resins, Shokodo, Tokyo, 1960, pp. 58–60.
[5] H. Batzer and S.A. Zahir, J. Appl. Polym. Sci., 19 (1975) 601.
[6] H. Batzer and S.A. Zahir, J. Appl. Polym. Sci., 19 (1975) 585.
[7] J. Anderson and P.S. Melstrom, Jpn. Pat. 35-7497 (1960).
[8] J.J. Baliker, K.B. Hoffer, P.M. Schiez and L.H. Griffin, Jpn. Pat. 38-26593 (1963).
[9] W.J. Belanger and S.A. Schulte, Mod. Plastics, 37 (1959) 154.
[10] V. Gajevski, 33rd Ann. Polyurethane Tech. Marked. Conf., 1990, p. 506.
[11] H.H.G. Jelinek, Degradation and Stabilisation of Polymers, Vol. I., Elsevier, New York, 1983, p. 91.
[12] M. Chapman, D.M. Rakiewitz-Nemeth, I. Svestok and R. Benrashid, J. Polym. Sci. A: Polym. Phys., 28 (1990) 147.
[13] C. Rotival, E. Renacco, C. Arfi, A.M. Pauli and J. Pastor, J. Therm. Anal., 41 (1944) 1519.
[14] V.G. Zaikin, R.G. Mardanov, V.A. Yakovlev and N.A. Plato, J. Anal. Appl. Pyrolysis, 23 (1992) 33.
[15] T. Yamoda, T. Okumoto, H. Othani and S. Tsues, Rubber Chem. Technol., 64 (1991) 708.
[16] M.R. Rao and T.S. Radhakrishnan, J. Appl. Polym. Sci., 41 (1990) 2251.
[17] G. Székely, M. Nebuloni and L.F. Zerilli, Thermochim. Acta, 196 (1992) 511.
[18] J.J. Boon, Int. J. Mass Spectrom. Ion Process, 118/119 (1992) 755.
[19] J. Anal. Appl. Pyrolysis, 8 (1984).
[20] J. Anal. Appl. Pyrolysis, 15 (1988).
[21] J. Anal. Appl. Pyrolysis, 19,20 (1990).
[22] K.-H. Ohrbach, W. Klusmeier and A. Kettrup, J. Thermal Anal., 29 (1984) 147.
[23] K.-H. Ohrbach, W. Klusmeier and A. Kettrup, Fresenius Z. Anal. Chem., 320 (1985).

[24] K.-H. Ohrbach, G. Radhoff and A. Kettrup, Thermochim. Acta, 85 (1985) 403.

[25] K.-H. Ohrbach and A. Kettrup, J. Polym. Degradation Stab., 13 (1985) 99.

[26] K.-H. Ohrbach, G. Matuschek and A. Kettrup, Thermochim. Acta, 112 (1987) 101.

[27] K.-H. Ohrbach, G. Matuschek and A. Kettrup, Thermochim. Acta, 121 (1987) 86.

[28] W. Merz, M. Neu, M. Kuck, K. Winkler, S. Gorbach and H. Muffler, Fresenius Z. Anal. Chem., 325 (1986) 449.

[29] B.D. Crittenden and R. Long, in R.I. Freudenthal and P.W. Jones (Eds.), Carcinogenesis – A Comprehensive Survey, Vol. 1, Raven, New York, 1976, p. 209.

[30] I. Schmelz and D. Hoffmann, in R.I. Freudenthal and P.W. Jones (Eds.), Carcinogenesis – A Comprehensive Survey, Vol. 1, Raven, New York, 1976, p. 225.

[31] M.M. Krahn, G.M. Ylitalo and J. Joss, Mar. Environ. Res., 31 (1991) 175.