Journal of Thermal Analysis, Vol. 34 (1988) 783–791

THERMOCHEMICAL TRANSFORMATIONS OF EPOXY OLIGOMERS IN THE PRESENCE OF LEAD-CONTAINING CARBON FIBERS

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(Received January 31, 1987; in revised form October 28, 1987)

The aim of the paper is to consider the possibilities of use of differential thermal analysis in studying the interaction between active metal-carbon (lead containing in particular) fibers with epoxide oligomers. The authors examined epoxides of various chemical structure: aliphatic, aromatic, alicyclic, alicyclic-aliphatic. It was ascertained, that lead-containing carbon fibers activate the catalytic decomposition of epoxides and, at the same time, essentially influence their structurization.

Epoxy binders are widely used in polymeric composite materials, reinforced by carbon fibers. Introduction of active fibers (for example, metal-containing) may essentially influence the process of composition forming at its thermal treatment [1].

The aim of the present paper is to investigate thermochemical transformations of epoxides of various chemical nature at the introduction of modified carbon fibers (CF).

Experimental

Leaded carbon fibers (Pb–CF) with 18.2% of metal content by mass were chosen for the investigation. Epoxides were represented by alicyclic diepoxides of acetal and ester type (UP–612 and UP–632 correspondingly), UP–650D epoxide with two homogeneous glycide groups and UP–650T alicyclic-aliphatic triepoxide. These epoxy compounds are comparatively new, so their compositions with element-containing carbon fibers have not been studied systematically. They also used epoxides of aromatic (ED–20) and aliphatic (DEG–1) series.

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It is known that liquid-solid transition of epoxy oligomers is accompanied by intensive heat release [2–5]. That is why differential thermal analysis was used in estimation of the effect of leaded carbon fibers on the structural transformations of epoxy compounds.

The investigation was carried out on a Paulik–Paulik–Erdey derivatograph (Hungary, MOM) within the 293–773 K temperature range, in air stream (10 ml/min), and in the furnace atmosphere, i.e. under the condition of reduced oxygen supply. The latter is similar to conditions of composition material forming in closed volume of moulds. Heating rate was 5 deg/min. Aluminium oxide was the reference material.

The hardening degree was determined according to the content of insoluble polymer fraction on extracting mixtures of oligomer with Pb–CF, thermally treated with boiling acetone in the Soxhlet apparatus for 24 hours. The infrared spectra of absorption in the range of 4000–400 cm^{-1} were recorded on a UR–20 spectrophotometer with the use of heated cell and KBr plate. The analyzed mixture was deposited on the KBr plate to form a thin layer of 10–15 μm. It had been ascertained previously that the components of mixture were indifferent to the plate under the experimental conditions. The base-line method was used for the quantitative analysis of the infrared spectra. The absorption band at 1610 cm^{-1} (oscillations of aromatic ring) was the inner standard in the range of 2000–400 cm^{-1}, the absorption band at 2930 cm^{-1} (valent oscillations of methyl group) was the inner standard in the range of 4000–2000 cm^{-1}.

Results and discussion

DTA, DTG and TG curves of the epoxides and their mixtures with CF and Pb–CF are represented on Fig. 1. The shape of the curves reflects complexity of processes for both non-filled epoxides and those reinforced by CF. Thermal instability at temperature higher than 573 K, displayed by intense decomposition of oligoepoxide, is common for all systems. Temperature range alterations within 293–473 K are insignificant (Pb–CF composition with DEG–1 excluded). Low-intensity endothermic processes at temperature below 423 K, accompained by some mass loss of the sample, are caused by vaporization of residues of low-molecular mass initial components present in the oligomers.

According to the thermal analysis data the range of temperatures, preceding intensive thermodecomposition of oligoepoxides (473–573 K), is the most remarkable in the case of epoxides filled with Pb–CF. Within this temperature range epoxides already display a tendency to destruction. The authors of paper [6] observed, within the mentioned temperature range, the breaking off of finite clusters from macromolecules of dianepoxy resins with the help of pyrolytic mass spectrometry method. Introduction of filler into epoxy oligomer results in the formation of multiple interfaces, which influences the thermal destruction of the oligomer [7]. This influence in some cases is not single-valued, because it is possible to observe both the activation of thermal decomposition process in the presence of the same filler and inhibition of the process depending upon the character of interaction between the filler and the oligomer.

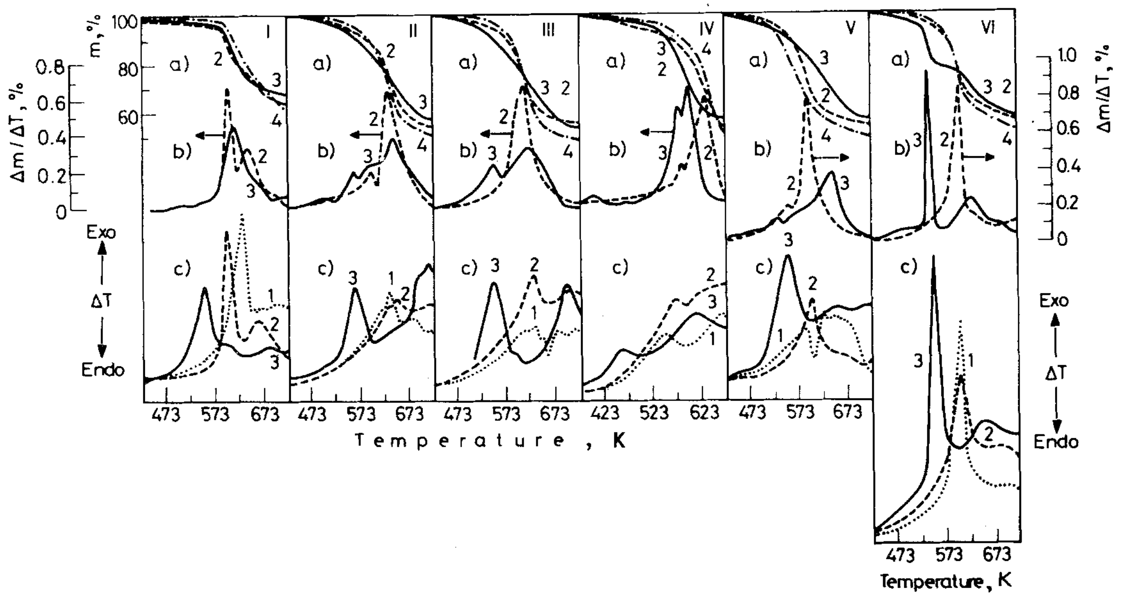

Fig. 1 TG- (a), DTG- (b) and DTA- (c) curves for epoxide (1), its mixture with non-modified CF (2) and with Pb–CF (3); 4 – calculated additive curve of the Pb–CF composition with epoxide. I – ED–20; II – UP–612; III – UP–632; IV – DEG–1; V – UP–650D; VI – UP–650T

As it follows from TG data, Pb–CF catalyze the decomposition of epoxides at early stages of heating: TG curves for Pb–CF mixtures with epoxides are lower than additive curves, which were calculated using TG data for initial components (see Fig. 1a, curves 3, 4). This effect is most distinctly displayed with alicyclic epoxides. There appear new low-intense peaks at 538–563 K on the DTG curves of compositions of these epoxides with Pb–CF (see Fig. 1/II, III b, curves 3). Mass loss for maxima of new peaks of DTG-curves for Pb–CF compositions with UP–612 (563 K) and UP–632 (548 K) diepoxides constitutes 8.8% and 10.6% by mass (calculated values of additive sum according to initial components data are 5.7% and 4.3% by mass correspondingly).

The Pb–CF composition with UP–650T triepoxide is very significant, UP–650T epoxide differing from UP–650D only by additional epoxy group at alicyclic fragment of chain. Introduction of that additional group changes the thermal behaviour of the epoxide in the presence of Pb–CF. Heating at temperatures higher than 533 K leads to intensive thermal decomposition of UP–650T epoxide with high speed and within a short temperature range (see Fig. 1a, b, VI, curves 3). This process is neither characteristic of Pb–CF composition with UP–650D, nor observed in the mixture of initial triepoxide with non-modified CF (curves 1, 2). Investigations proved that in the presence of Pb–CF thermal stability of studied epoxy compounds decreases in the order ED–20 > UP–612 > UP–650D > > DEG–1 > UP–632 > UP–650T.

Activating the catalytic decomposition of epoxides, Pb–CF at the same time sufficiently influence their structurization. There appears a new significant exothermic peak in the temperature range of 523–573 K, with maxima at 548–563 K, on DTA curves of Pb–CF composition with epoxy oligomers (for DEG–1 this effect is observed within 373–473 K with maximum at 458–463 K). This effect is not characteristic of non-filled epoxides and their mixtures with non-modified CF. The new exothermic effect, revealed for all Pb–CF epoxide compounds, neither can be regarded as heat release of separate components of mixture nor as their sum. Reduction of the number of epoxy groups with simultaneous increase the number of hydroxy groups and emergence of a new absorption band at 1720 cm^{-1} at heating of Pb–CF mixture with epoxy oligomer (Fig. 2) prove that this new exothermic effect is due to complex chemical transformation of epoxy compounds under the influence of metal-containing CF.

It should be mentioned that there are two sections at the ascending part of the exothermic peak. Monotonous ascent with gradually increasing heat release is observed at the first section, beginning from 423–433 K. The first section is followed by steep curve with maximum exothermic effect. That is, an induction period is observed, which is most sharply observed for alicyclic dioxides, and which is followed by a pronounced exothermic peak. The analysis of Pb–CF mixtures with oligoepoxides indicates the formation of three-dimensional product after heat treatment of compositions within the temperature range of the second section of exothermic effect (see Table). At the same time momentary heating of the compositions at lower temperatures, corresponding to the first section of exothermic curve, does not result in the formation of significant quantities of insoluble fraction, though some changes in epoxy groups number are registered. Spatial-net structure of polymer for this temperature range is formed only after long heating, its period being reduced with an increase of the temperature of thermal treatment.

In this respect it is worth considering the transformations of Pb–CF composition with UP–650T triepoxide. A 30 minutes thermal treatment of the composition at 513, 533 and 553 K, i.e. at the temperatures, corresponding (see Fig. 1(VI)) to gradual increase of heat release, the onset temperature of exothermic effect, and peak temperature of the exothermic reaction, results in the following. The content of insoluble polymer is 9.04% of mass at heating of the composition at 513 K, when the exothermic effect is of low-intensity. The beginning of intensive heat release is accompained by accelerated increase of gel-fraction quantity (87.32% of mass at 533 K). The insoluble component constitutes only 48% by mass at 553 K, which corresponds to maximum of heat release.

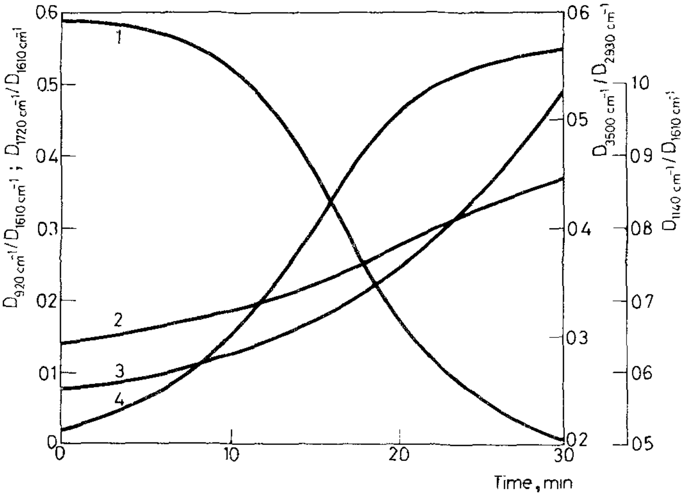

Fig. 2 Change of content of epoxy (1), carboxylic (2), hydroxyl (3) and ester (4) groups at thermal treatment of ED–20 in the presence of Pb–CF

According to [8] during heating at high temperatures the start of the destruction of epoxy compounds is accompanied by the thermal isomerization of initially separated finite epoxide groups, isomerization accompanied by heat release. This reaction probably concurs with the reaction of epoxide curing under the influence of Pb–CF at heating of their compositions with UP–650T at 553 K, when an intensive decomposition of the triepoxide is detected (see Fig. 1, a, b (VI), curve 3). The observed exothermic effect (Fig. 1, c (VI), curve 3) may be regarded as superposition of simultaneous processes: epoxide groups isomerization and formation of three-dimensional product. However, the decomposition of oligomer molecules prevails in this case, which results in a considerable reduction of insoluble fraction content. At heating of Pb–CF composition with UP–650T at 533 K (when there is no intense decomposition of the triepoxide, but only a tendency) exothermic effect is mostly due to quick-proceeding processes of chemical transformations of the epoxide with opening of the epoxide ring and formation of crosslinked polymer, indicated by formation of considerable quantity of insoluble gel-fraction.

Latter also relates to Pb–CF composition with ED–20 dianepoxide resin. According to TG analysis data, the mass loss is 1.1–2.6% within the temperature range of pronounced exothermic effect with maximum at 553 K (see Fig. 1, a, (I), curve 3). With the same mass loss and within the same temperature range exothermic peak neither is revealed for the resin itself nor for its mixture with non-modified CF due to supposed isomerization of epoxide groups (curve 1 and 2). At the same time, chemical analysis of thermally treated mixture of Pb–CF with ED–20 indicates intense decrease in the number of epoxide groups and formation of insoluble fraction (see Table). Consequently, the observed considerable heat release for Pb–CF with ED–20 composition within 473–553 K temperature range may be considered due to oligoepoxide curing (curing degree for the composition at its 30 minute heating at 533 K is 95.94% by mass).

The same relates to Pb–CF composition with DEG–1. Slight mass loss at heating within 423–473 K along with formation of insoluble product make it possible to attribute the observed new exothermic effect (with its absence for initial DEG–1 and its composition with non-modified CF) with maximum at 458 K (see Fig. 1, c, (IV), curve 3) to chemical transformations of DEG–1 under the influence of Pb–CF.

As for Pb–CF compositions with UP–612, UP–632, UP–650D alicyclic epoxides, thermal stability of which is decreased in the presence of metal-containing fibers, as mentioned above, superimposition of thermal releases on new exothermic effect, observed at 473–563 K, is possible due to epoxy compound decomposition and supposed isomerization. However, comparison of characters of DTA-curves of the above mentioned epoxides and their mixtures with Pb–CF shows the following. If we suppose that the first exothermic peak for unfilled epoxide, observed at temperatures higher than 573 K, relates to isomerization of the broken off epoxy groups [9], it should be stated that exothermic effect of this process is clearly displayed at rather deep destruction of epoxide compound: maximum of exothermic effect falls on mass loss more than 50–60% by mass. Besides, intensity of this effect is lower than that for the new one in compositions with Pb–CF at 473–563 K. If we take into account, that though the mass loss of Pb–CF compositions with alicyclic compounds in the mentioned temperature range exceeds that for Pb–CF mixture with ED–20, but is not so significantly expressed as with the first exothermic effect of non-filled epoxides, it may well be considered that the main contribution to thermal releases in Pb–CF compositions with UP–612, UP–632, UP–650D diepoxides is also made by chemical reactions of epoxide systems curing. However, decreased thermal stability of these diepoxides in the

Table 1 Quantity of cured epoxy oligomer after its thermal treatment in the presence of PbCF (components relation is 1 : 1)

Epoxy oligomer	Insoluble gel fraction, mass% with					
	PB–CF		non-modified CF		non-fibrous	
	temperature of thermal treatment*, K					
	513	533	513	533	513	533
ED–20 (488 K)•	94.28	95.94	0.40	1.14	0.49	1.0
UP–612 (533 K)	13.82	77.32	3.55	19.37	4.65	22.18
UP–632 (503 K)	54.01	59.74	1.08	2.77	0.60	9.9
UP–650D (503 K)	66.75	68.94	2.40	27.81	3.31	6.1
UP–650 T (533 K)	9.04	87.32	3.38	17.60	1.99	11.84

* The time of thermal treatment = 0.5 h.

• Onset temperatures of the first exothermic peak.

presence of Pb–CF still results in reduced quantity of the formed gel fraction (see Table 1).

Thus investigations showed that between 473 and 563 K the new exothermic effect for Pb–CF compositions with the examined epoxides is conditioned by complex processes of chemical and structural transformations of the epoxides under the influence of active fibers, leading to the system curing. It is possible to say that the beginning destructive processes as well as their further developments for oligoepoxides in the presence of Pb–CF proceed in a different way unlike those in the initial epoxide. This conclusion is supported by the fact that a tendency to thermal decomposition is revealed both for epoxide compounds and their mixtures with non-modified CF within the indicated temperature range, but exothermic effect and intense formation of three-dimensional polymer are not observed.

We have demonstrated [1] the presence of metal or its oxide in Pb–CF. Metallic skin inclusions, being homogeneously distributed on fiber skin, and probably, involving its carbon structure, initiating decomposition of epoxide compound, can be active acceptors of nonstable radicals at the same time, the latter emerging at thermal destruction of epoxide. It is sufficient to mention the known reactions of metallo-organic compounds formation as a result of interaction of lead, zinc, etc. with alkyl radicals [10]. In its turn, it can suppress catalytic influence of CF skin on the process of thermal decomposition of epoxide compound and change the direction and rate of reactions of oligoepoxide transformations in the system to the prevailing process of cross-linkage forming, not to further decomposition. The above said has been observed for the investigated compositions.

The process of three-dimensional structure formation of epoxide polymer in the presence of Pb–CF at 473–563 K is also indicated by the changed behaviour of thermal transformation of composition at preceeding heating, because it is known [11], that thermal destruction of cured epoxy oligomers differs from that of uncured oligomers. Exothermic effects on DTA-curves within the 593–653 K temperature range, characteristic of nonfilled epoxide compounds and observed for their mixtures with non-modified CF, attributed to the isomerization of free epoxy groups and their further homopolymerization [9], are slight or absent at all in compositions of the studied epoxides with Pb–CF (see Fig. 1, c). The rate of the mass loss also decreases within this temperature range (see Fig. 1, b), coke residues content increases in comparison with compositions of epoxide compounds with non-modified CF, and with the calculated mass loss data for separate components. TG curves within this temperature range lie much higher than the additive calculated ones (see Fig. 1, a, curves 4). The latter is probably caused by further structurization of the system at thermal oxidation and decomposition of the polymer in the presence of Pb–CF.

In conclusion, it should be mentioned that thermal analysis not only allows revealing the chemical transformations of oligoepoxide under catalytic effect of active lead-containing CF, but also determining the optimum temperature range of epoxide curing for each compound, filled with Pb–CF, where their maximum participation is in curing. This is the onset temperature of intense heat release on DTA curves for Pb–CF compositions with oligoepoxides.

Conclusion

Process of thermochemical transformations of epoxide oligomers of various chemical structures in the presence of lead-containing carbon fibres (Pb–CF) has been studied. A conclusion about concurring reactions of thermal decomposition of epoxide oligomer and formation of dimensional polymer has been made on the basis of thermal and chemical analysis and infrared spectroscopy data. Metal-containing inclusions of carbon fibers play the leading role in these processes.

Catalytic effect of Pb–CF on decomposition of epoxide oligomers has been revealed, the effect being stronger for alicyclic epoxide compounds. The onset temperature of oligomer decomposition considerably decreases in the presence of Pb–CF, and the decomposition proceeds with higher rate. The Pb–CF, activating the process of oligomers thermal decomposition, promote the formation of three-dimensional structure at the same time. A new exothermic effect is revealed in the temperature range from 423 to 573 K, intensive formation of insoluble gel-fraction is observed, which is not characteristic of individual epoxide compounds and mixtures of them with non-modified CF.

The data obtained allow choosing optimum temperature range for the process of hardening with the use of Pb–CF as fibrous hardener, for each particular oligomer.

References

1 V. I. Dubkova, I. N. Yermolenko and I. P. Lyubliner, High-molecular compounds, 26A (1984) 1139 (in Russian).

2 B. Ki, New Method of Polymer Studying, Mir, Moscow, 1966 (in Russian).

3 I. Vancsóné-Szmercsányi and I. Regős, Műanyag és gumi, 17 (6) (1980) 170.

4 A. Mandel, Thermochim. Acta, 13(2), (1975) 171.

5 I. V. Kolosnitsyna, S. V. Yakubovitch, G. S. Bogdanova and I. P. Antonova-Antipova, Colour Varnish Materials and their Use, 4 (1974) 68 (in Russian).

6 G. A. Kamenkevitch, I. M. Lukashenko, R. A. Khmelnytskii and others, Plastic Masses, 8 (1977) 16 (in Russian).

7 G. P. Gladyshev, U. A. Yershov and O. A. Shustova, Stabilization of Thermally Stable Polymers, Chemistry, Moscow, 1979 (in Russian).

8 M. B. Neyman, Ageing and Stabilization of Polymers, Nauka, Moscow, 1964 (in Russian).

9 H. C. Anderson, Anal. Chem., 32(12) (1960) 1592.

10 Ch. Walling, Free Radicals in Solution, Inostrannaya Literature, Moscow, 1960 (in Russian).

11 G. Antal and L. Csillag, 4th International Conference on Thermal Analysis, Proceeding, 3 (1974) 347.

Zusammenfassung — Ziel der vorliegenden Arbeit war, die Anwendungsmöglichkeiten der Differentialthermoanalyse bei der Untersuchung der Wechselwirkungen zwischen (insbesondere bleihaltigen) Aktiv-Metall-Graphitfasern und Epoxidoligomeren zu ergründen. Oligomere verschiedener chemischer Struktur wurden untersucht: aliphatische, aromatische, alicyclische, alicyclisch-aliphatische. Es wurde festgestellt, daß bleihaltige Graphitfasern eine katalytische Zersetzung der Epoxide aktivieren und gleichzeitig deren Strukturiertheit erheblich beeinflussen.

Резюме — Изучены возможности использования метода ДТА для исследования взаимодействия между активными металл-углеродистыми (в основном, свинец-содержащими) волокнами и эпоксидными олигомерами. Исследованы алифатические, ароматические, алициклические и алициклоалифатические эпоксиды с различной химической структурой. Установлено, что свинец-содержащие углеродистые волокна активируют каталитическое разложение эпоксидов, особенно затрагивая при этом их структурирование.