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ANALYSES OF THE QUALITATIVE COMPOSITION OF THE GASEOUS PHASE OBTAINED FROM FIRE RESISTANT NON-MODIFIED AND MODIFIED EPOXY MATERIALS USING THE FTIR TECHNIQUE

ANALÝZY KVALITATIVNÍHO SLOŽENÍ PLYNNÉ FÁZE ZÍSKANÉ Z OHNIVZDORNÝCH NEMODIFIKOVANÝCH A MODIFIKOVANÝCH EPOXIDOVÝCH MATERIÁLŮ POMOCÍ METODY FTIR

Introduction

Thanks to their characteristic properties epoxy materials are widely used in numerous industries, and first of all in electronics and electrical engineering. Furthermore, presently some technical domains, such as furniture production, aviation or the machine industry could not function any more without those materials. According to the fact that epoxy materials can be modified, their application is acquiring an increasingly growing importance [1-5].

The application of new epoxy mixtures and compositions allows obtaining products with preselected parameters, including also those related to the degree of flammability. Conduction of tests for modern epoxy materials in conditions simulating a fire is one of the elements aimed at enhancing the fire safety degree.

On the basis of available knowledge related to fire behaviour of materials, diverse research centres are working to effectively enhance fire security. There are a lot of methods that analyse the degree of combustibility, toxicity and smoke generation of materials. One of them is the thermogravimetric analysis, which allows studying changes in the structure of the product, phase transitions and mechanisms of reactions that occur between particular materials during thermal decomposition. The combination of thermogravimetric analysis (TG) with spectrophotometry in infrared by interpretation of spectra of the gaseous phase obtained from polymer materials makes possible the determination of the qualitative composition and quantities of thermal decomposition products of epoxy materials [6-11].

The objective of our research were thermogravimetric and spectrophotometric analyses in IR of epoxy materials produced of Epidian 5. With this in mind thermogravimetric tests were carried out along with an analysis of spectra of the gaseous phase in IR.

Experiment

Materials

For needs of the tests we have used the Epidian 5 (Ep5) non-modified epoxy material, produced by Zakłady Chemiczne Organika – Sarzyna [*the "Organika-Sarzyna" Chemical Plant*] in Nowa Sarzyna. Modification of flammability was achieved by adding anti-flammability agents Exolit RP 6580 and Nanomer I. 28 E to liquid Ep 5. Liquid resins were then hardened

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through application of two methods: mechanically and with the use of ultrasound, with Curing Agent Z-1 (TECZA, triethylenetetraamine).

Nanomer I. 28 E (nanoclay) is an onion ion surface modified montmorillonite mineral. It is designed to be easily dispersed into amine -cured epoxy resins to form nanocomposites.

Exolit RP 6580 is brown-red blend of TCPP (as a carrier) with stabilized, micro encapsulated red phosphorus. The paste form allows a safe and simple handling of the red phosphorus in a liquid form, and avoids the hazards associated when working with red phosphorus powders.The thixotropic nature of this concentrate hinders the sedimentation process and simplifies the re-homogenisation of the paste after long storage periods.

The basic epoxy resin was Epidian 5 (Ep 5). The thermogravimetric analysis was conducted on the following epoxy materials:

- hardened non-modified Epidian 5 (Ep 5);
- hardened Epidian 5 with a 6 % (by weight) of Exolit (Ep 5 + 6 % Exolit);
- hardened Epidian 5 with a 5 % (by weight) of Nanomer (Ep 5 + 5 % Nanomer);
- hardened Epidian 5 with a 3 % (by weight) of Nanomer and a 6 % (by weight) of Exolit (Ep 5 + 3 % Nanomer + 6 % Exolit).

Used methods

The thermogravimetric and spectrophotometric analyses of selected samples have been executed according to rules and guidelines contained in the standard PN-EN ISO 11358: 2004 Tworzywa sztuczne. Termograwimetria (TG) polimerów. Zasady ogólne. [*Plastic materials. Thermogravimetry (TG) of polymers. General Rules*]. The tests were executed on a TA Instruments Q500 device in conjunction with the Nikolet FT-IR 380 spectrometer on based on the OMNIC programme.

In the research use was made of dynamic thermogravimetric measurements in conjunction with the spectrophotometry technique for the composition of thermal decomposition and combustion products. This technique is based on a change in mass of the tested sample in the temperature function, which changes at a programmed speed, and concurrent generation of IR spectra of the gaseous phase. The tests have been carried out for four samples of epoxy materials, each of which was burnt at a constant heating speed equal to 10 °C/min to the maximum temperature of 850 °C. All the tests were executed at the same oxidising atmosphere in the air. Parameters of spectrophotometric measurements applied in testing of epoxy materials:

- resolution: 4 cm^{-1}
- maximum of the range: 4000 cm^{-1}
- minimum of the range: 400 cm^{-1}
- type of detector: temperature controlled DTGS-KBr
- duration of the experiment: 75 - 85 min.
- rate at which the samples were heated up: 10 °C/min

The qualitative analysis of generated products of thermal decomposition was based on the following libraries containing model spectra:

- HR Nicolet TGA Vapor Phase
- Aldrich Vapor Phase Sample Library

Results of tests

The conducted thermogravimetric analyses allowed obtaining TG and DTG curves of the tested epoxy materials, which present the process of their thermal decomposition.

As a result of performed thermogravimetric analyses combined with a spectrophotometer in infrared, spectra in IR have been obtained of the gaseous phase generated as an effect of combustion of the tested epoxy materials. The obtained data presenting the degree of absorbance of specified chemical compounds and grouped bonding in the gaseous phase of thermal decomposition, in the function of wave number for the given decomposition time. Depending on the tested material 430 - 530 spectra have been recorded. For needs of the comparative analysis spectra were selected at determined temperatures (times of thermal decomposition), and namely:

- spectra obtained at a temperature that correspond with the beginning of thermal decomposition for the given material,
- spectra recorded at a temperature that corresponds with the maximum mass loss on TG curves and concurrently at a temperature at which occurred the maximal value of release of the gaseous phase from the given material,
- spectra at a temperature at the end of thermal decomposition for the selected material.

The presented spectra have been abstracted from Gram-Schmidt diagrams in defined times (temperatures) characteristic for the given material. The Gram-Schmidt diagrams (diagram of the intensity of release of volatile combustion products in the time of thermal decomposition) show times of spectra presented in the paper for each tested epoxy material. The diagram (fig. 1) presents the intensity of release of volatile decomposition products during combustion of Epidian 5 in the function of time (Gram-Schmidt).

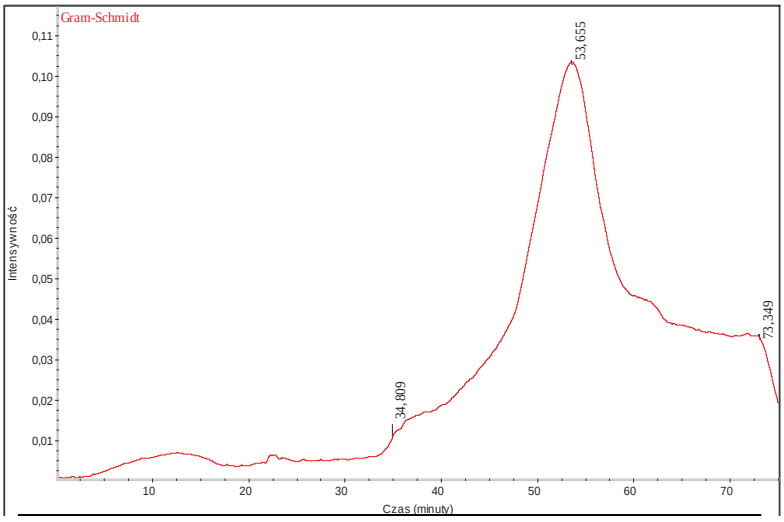

Fig. 1: *Gram-Schmidt diagrams for non-modified material.*

Diagram 3-D (figure 2) illustrates the dependence of absorbance in the function of wave numberduring testing. Sample spectra for non-modified material have been presented in those selected times (figure 3 - 5).

Changes in the release of particular compounds for example for CO for tested materials have been shown in the fig. 6.

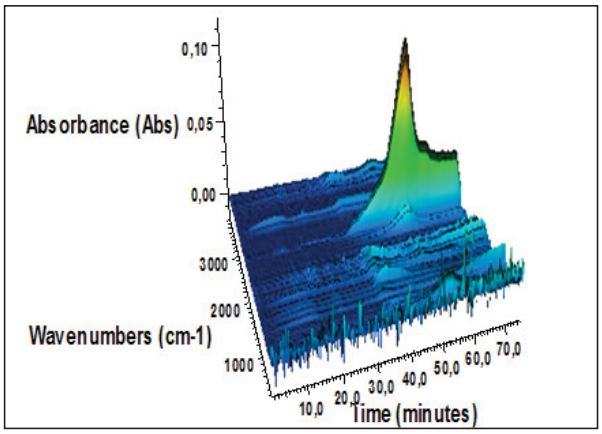

Fig. 2: *Diagram 3-D for unmodified Ep 5*

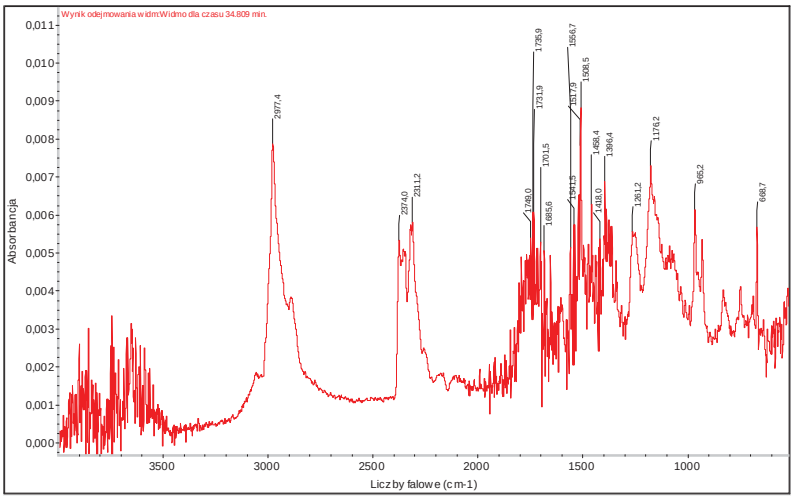

Fig.3: *Sample spectra for non-modified material Ep 5 at time 34,809 min (348 °C)*

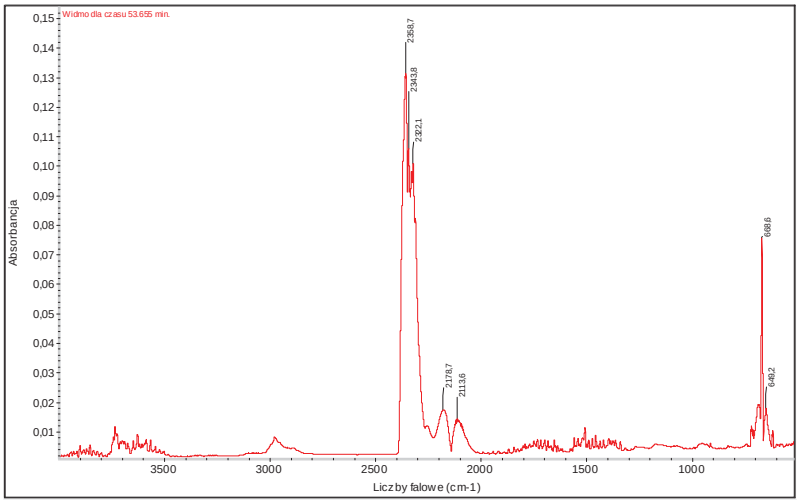

Fig.4: *Sample spectra for non-modified material Ep 5 at time 53,655 min (536 °C)*

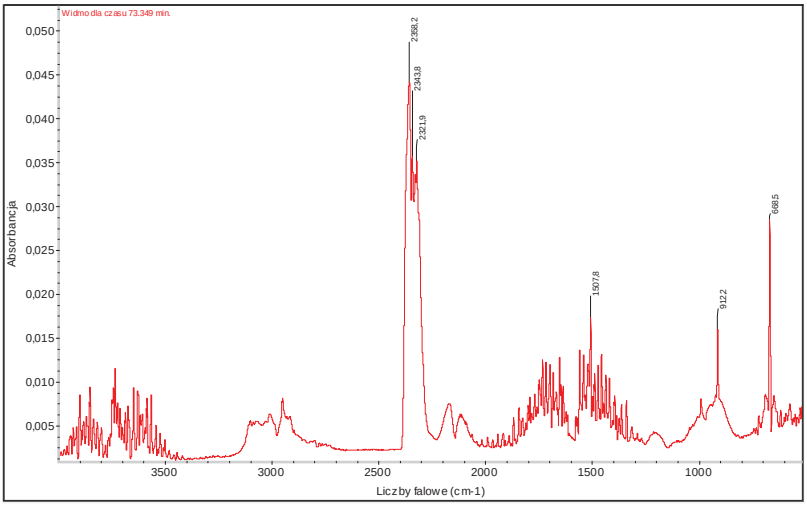

Fig.5: *Sample spectra for non-modified material Ep 5 at time 73,349 min (733 °C)*

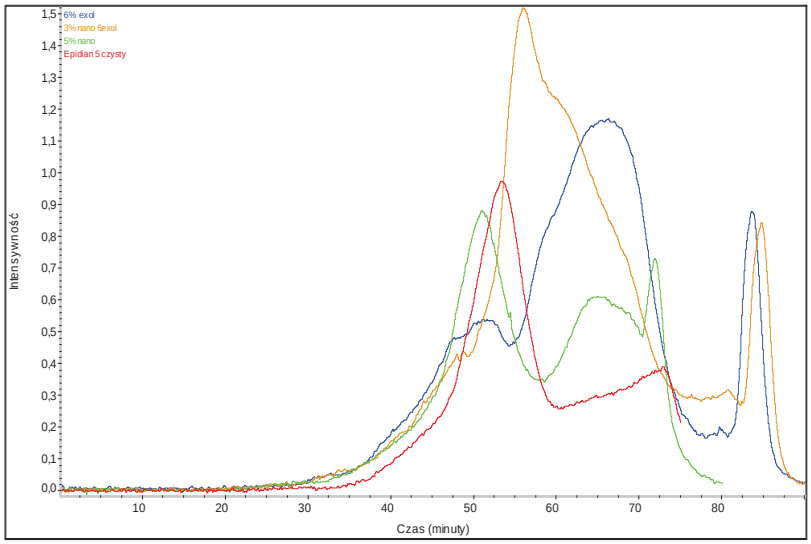

Fig. 6*: Changes in the release of CO from tested materials in function times of combustion.*

Conclusions

Based on the obtained results, the following conclusions may be presented:

- The added flame retardants do not affect in a significant way the beginning of thermal decomposition. Only Exolit introduced to Epidian 5 had a higher temperature of the start of thermal decomposition than Epidian 5.
- Allowing for the TG and DTG curves, Exolit added to Epidian 5 retarded the beginning of thermal decomposition by ca. 2 °C as compared to Epidian 5 and Epidian 5 + 5 % Nanomer and mixed modification, i.e. Epidian 5 + 3 % Nanomer + 6 % Exolit.
- With view to the nature of TG and DTG curves the presumption may be made that adding red phosphorus to Epidian 5 leads to extension of the thermal decomposition process and combustion. Nevertheless, the lowest temperature of the maximum speed of mass loss was recorded for the non-modified Epidian 5 sample with flame

retardant admixtures. Introduction of Nanomer to Epidian 5 increased by ca. 7 °C the value of the maximum rate of mass loss.

- Concurrent addition of Exolit + Nanomer to Epidian 5 hastened the release of 50 % of mass as compared to the release time of 50 % of mass for samples non-modified and modified by Nanomer and separately by Exolit.
- On the basis of the TG and DTG analyses we may conclude that in phase I of thermal decomposition the shape of the curves is similar. However, in phase II of decomposition the curves tend to differ. For mixed modification and for separately added Exolit to Epidian 5 the thermal decomposition of the samples became extended. Most likely the inhibition effects of red phosphorus in the tested epoxy materials comprises inhibition of the decomposition reaction in the solid form of polymer.
- The spectrophotometric analysis of absorbance in IR of released compounds in the function of combustion time of the tested epoxy materials confirmed the correctness of results of the thermogravimetric analysis.
- The added flame retardants did not affect the qualitative composition of the gaseous phase.
- Taking into consideration the Gram-Schmidt spectra (figure 34) it is possible to define the following ranges of temperature values at which volatile products of thermal decomposition were released for the tested epoxy materials:

- hardened Epidian 5: 330 - 760 °C,
- Epidian 5 + 6 % Exolit: 295 - 800 °C,
- Epidian 5 + 5 % Nanomer: 225 - 760 °C,
- Epidian 5 + 3 % Nanomer + 6 % Exolit: 235 - 800 °C.

- On the basis of spectra in IR it became possible to define temperature ranges at which the release of the volatile gaseous phase was of a variable nature and allowed the identification of organic compounds being released. However, in many of the ranges the evoluting volatile products of thermal decomposition are limited to carbon dioxide and water. For this reason in the analysis presented in this study those ranges have been omitted. Ranges of temperature values, for which the dominating products of thermal decomposition were CO_2 and H_2O, are as follows for the tested volatile products of thermal decomposition:

- hardened Epidian 5: 450 - 750 °C,
- Epidian 5 + 6 % Exolit: 470 - 840 °C,
- Epidian 5 + 5 % Nanomer: 430 - 760 °C,
- Epidian 5 + 3 % Nanomer + 6 % Exolit: 500 - 860 °C. An analysis of Chemigrams and Correlation maps (figures 35-38) has shown that all the applied fire resistance modifications led as an effect to considerable hastening in carbon dioxide release. As regards carbon oxide, Bisphenol A and phenol no such changes have been observed. The applied flame retardant admixtures affected the nature of carbon dioxide and oxide release. In samples containing modifications it was found that the release of CO and CO_2 proceeds in two stages, while Epidian 5, in which no flame retardants were used, shows no such correctness. For Bisphenol A and phenol no such changes have occurred.

- In the gaseous phase of Epidian 5 + 6 % Exolit and Epidian 5 + 3 % Nanomer + 6 % Exolit no volatile organic phosphorus compounds were identified, which means that red phosphorus contained in the tested epoxy materials has inhibitory effects in the solid state.

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