BEATA GRABOWSKA[1)*)], MARIUSZ HOLTZER[1)], SONJA EICHHOLZ[2)], KRZYSZTOF HODOR[2)], ARTUR BOBROWSKI[1)]

Thermal analysis of a sodium salt of the maleic acid-acrylic acid copolymer used as a polymeric binder

RAPID COMMUNICATION

Summary — Samples of sodium salt of the maleic acid-acrylic acid copolymer used as a binding agent in molding sands were investigated. Methods of thermal analysis (DTG, TG, DSC) were applied to assess the thermal stability of the investigated polymer sample by estimation of temperature and thermal effects of transformations occurring during its heating. Examinations were performed at the temperature range -100—1000 °C. It was found that the total degradation process starts at the temperature about 400 °C. In addition, the analysis of volatile decomposition products was carried out by means of the Fourier transform infrared spectroscopy (FT-IR) and the thermogravimetric (TG) method coupled „on-line" with the mass spectrometry (MS) method. At the temperature range 300—400 °C the signals for small molecular masses were found, which indicates that the degradation process and the fragmentation of polymer chains occurred as well as small particles were formed (molecular weight: 15—55), including, first of all, H_2O and CO_2. Probably during the degradation radicals are also formed, which is indicated by the MS signals.
Keywords: polymer binders, molding sands, thermal analysis, degradation.

ANALIZA TERMICZNA SOLI SODOWEJ KOPOLIMERU KWAS MALEINOWY-KWAS AKRYLOWY STOSOWANEJ JAKO SPOIWO POLIMEROWE

Streszczenie — Analizie termicznej poddano próbki soli sodowej kopolimeru kwas maleinowy-kwas akrylowy stosowanej jako spoiwa w masach odlewniczych. W celu określenia stabilności termicznej badanej próbki polimeru zastosowano metody analizy termicznej (DTG, TG, DSC) i wyznaczono wartości temperatury i efekty cieplne przemian zachodzących podczas ogrzewania. Badania prowadzono w zakresie temperatury -100—1000 °C. Stwierdzono, że pełny proces degradacji rozpoczyna się od temperatury ok. 400 °C. Dodatkowo za pomocą spektroskopii w podczerwieni z transformacją Fouriera (FT-IR) oraz metody termograwimetrycznej (TG) sprzężonej „on-line" ze spektrometrią masową (MS) przeprowadzono analizę lotnych produktów rozkładu. W temperaturze z zakresu 300—400 °C zaobserwowano sygnały odpowiadające małym ciężarom cząsteczkowym, co świadczy o zachodzeniu procesu degradacji, fragmentaryzacji łańcuchów polimerowych i tworzeniu się małocząsteczkowych związków (ciężary cząsteczkowe 15—55), w tym przede wszystkim H_2O i CO_2. Podczas degradacji prawdopodobnie powstają również rodniki alkilowe, na co wskazują sygnały MS.
Słowa kluczowe: spoiwa polimerowe, masy odlewnicze, analiza termiczna, degradacja.

Investigations related to utilizing water soluble polymers as binding agents and to the development of their crosslinking method have been carried out in the Laboratory of Environmental Protection (AGH University of Science and Technology), for many years already [1—4]. The applied polymer material is a sodium salt of maleic acid-acrylic acid copolymer. Methods of crosslinking and hardening of this polymer in molding sands are already developed [5]. A certain fragment of the performed studies related to the determination of the thermal stability of the investigated polymer is presented in this paper. Such determination is essential to the behavior of the binding agent at increased temperatures during liquid metal pouring into the casting mould. Information con-

*) AGH University of Science and Technology, Faculty of Foundry Engineering, Department of Foundry Processes Engineering, Reymonta 23, 30-059 Krakow, Poland.

2) NETZSCH-Gerätebau GmbH, Applications Laboratory Thermal Analysis, Wittelsbacherstr. 42, 95100 Selb/Bavaria, Germany.

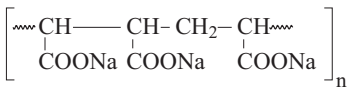
*) Author for correspondence; e-mail: beata.grabowska@agh.edu.pl

cerning the formation of gaseous decomposition products of this polymer, which can enter the atmosphere during the technological process, are essential from the point of view of the environmental protection.

EXPERIMENTAL

Materials

40 wt. % water solution of the sodium salt of maleic acid-acrylic acid copolymer [formula (I)] of a brand name



(I)

Sokalan CP 5, produced by the BASF Company, characterized by: pH = 8, viscosity according to Brookfield 2800 mPa · s and average molecular weight 70 000.

Methods of testing

The Thermo-Microbalance NETZSCH TG 209 F1 Iris® with the effective resolution of 0.1 μg enables highly precise measurements under pure gas atmospheres from the ambient temperature up to 1000 °C. Internal mass flow controllers (MFC) guarantee a highly precise gas flow adjustment of three different gases.

For control of the measurements as well as for data acquisition, modern digital electronics and the well established NETZSCH Proteus® 32-bit Software are employed. Several Advanced Software packages like c-DTA® [calculated differential thermal analysis signal (DTA-signal)], Super-Res® (rate-controlled mass change) or Thermokinetics® are available. Combining both thermogravimetric (TG) and spectroscopic methods such as Fourier transform infrared spectroscopy (FT-IR) and/or mass spectroscopy (MS), enables further identification of the evolved gases.

Data exchange between NETZSCH Proteus® software and Bruker OPUS™ software is done online during the measurement. This guarantees simultaneous start and stop of the measurement as well as the data exchange during the measurement.

The basic parameters of thermal analysis of Sokalan CP 5 are collected in Table 1.

T a b l e 1. Basic parameters of thermal analysis carried out for Sokalan CP 5

Parameters	Sokalan CP 5
temperature range	ambient temperature — 500 °C
heating rate	10 K/min
atmosphere	nitrogen
flow rate	40 cm^3/min
crucible	Al_2O_3
sample mass	about 45 mg

RESULTS AND DISCUSSIONS

The results of thermal analysis of the Sokalan CP 5 sample are presented in Figure 1.

The TG and DTG curves showed four mass loss steps of 9.0 %, 6.9 %, 8.9 % and 18.5 % below ~390 °C and two further steps of 1.6 % and 14.9 % above this temperature. In the temperature range: -100—0 °C polymorphous transformations were not seen. The DSC curve showed several endothermic effects which correlate well with the observed mass loss steps. The thermal curves indicate that the degradation process starts at the temperature 400 °C.

Figure 2 shows the 3D view of FT-IR spectra versus the temperature registered for Sokalan CP 5. Three temperature values, 121, 400 and 461 °C, at which essential structural changes occur (mass changes and thermal effects), were marked out on the basis of the thermal spectra. Then

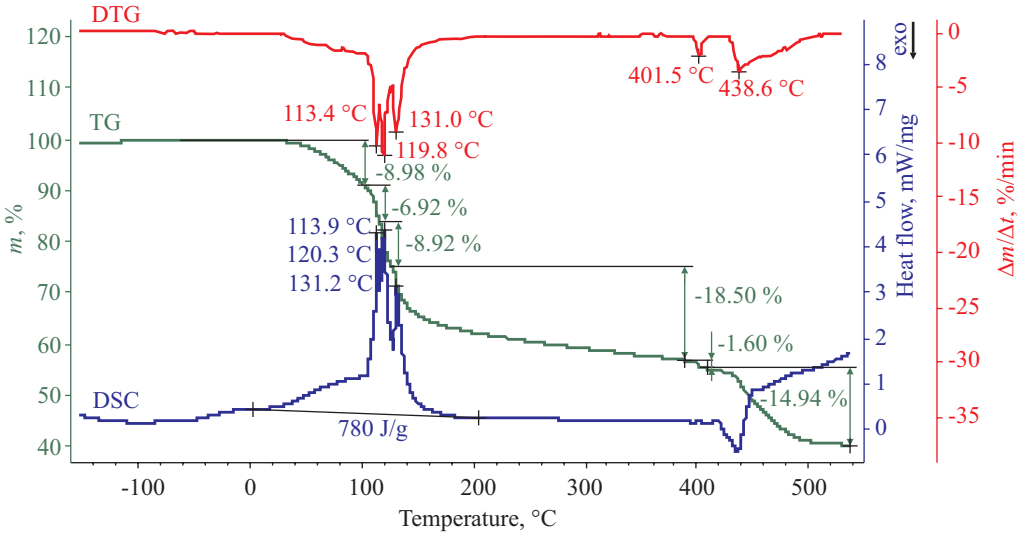


Fig. 1. Temperature-dependent mass change (TG, solid green line), rate of mass change (DTG, dashed green line) and heat flow rate (DSC, solid blue line) of the Sokalan CP5 sample

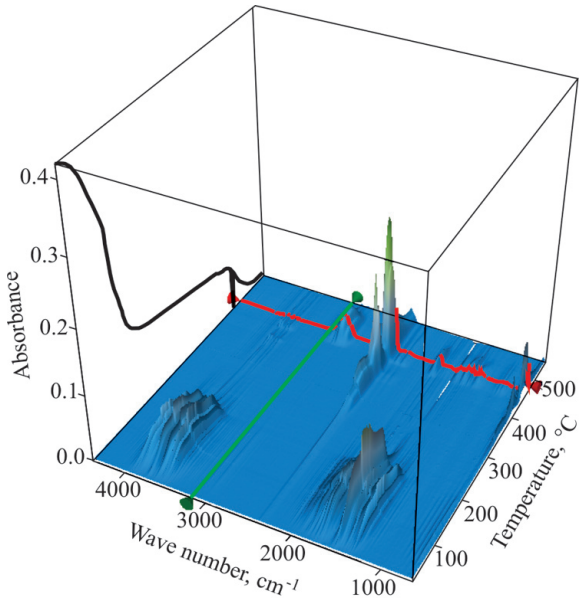


Fig. 2. 3D view of all registered FT-IR spectra versus temperature including the TG results at the side face

the analysis of the FT-IR spectra was performed for these temperatures.

The extracted FT-IR spectra of the Sokalan CP 5 sample are shown in Figure 3. At 121 °C water is released from the sample. At the temperature 400 °C the band 2400 cm^{-1} characteristic to the formation of CO_2 occurs. However, it can be noticed that at the temperature 461 °C the intensity of the band originating from CO_2 decreases. In addition the new band characteristic to the methane formation occurs at the wave number 3000 cm^{-1}. The band characteristic to the formation of CO was not seen.

In order to confirm the proper interpretation of the FT-IR spectra the spectrum library was used and the obtained spectra were compared with the standard ones for CH_4, CO_2 and CO (Fig. 4 and 5).

The water vibrations are negative at 400 °C (Fig. 4) because water was released from the beginning of the measurement and therefore was detected during the background measurement of the IR.

At 461 °C (Fig. 5) methane can be detected. Additionally, saturated C-H stretching vibrations at about

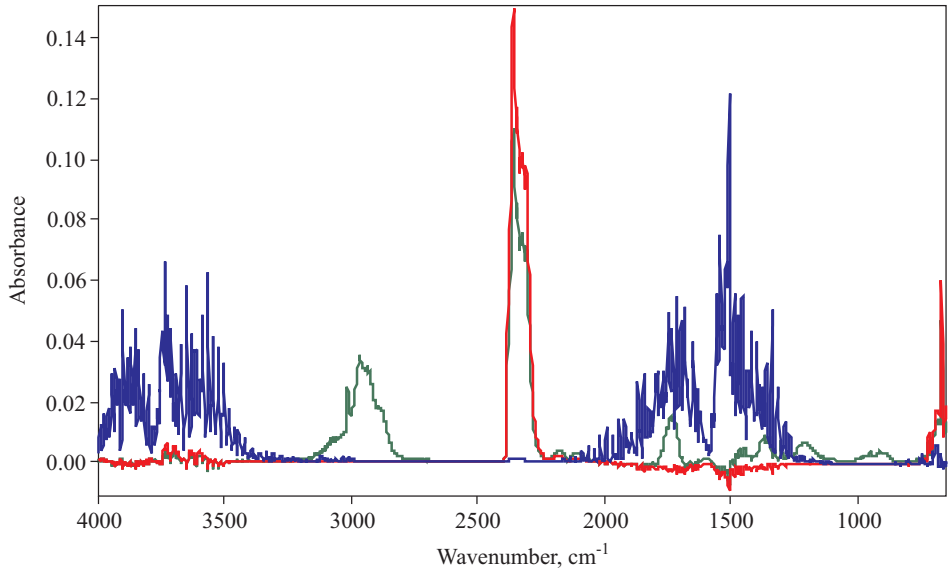


Fig. 3. FT-IR spectra of the specimen at 121 °C (blue), 400 °C (red) and 461 °C (green)

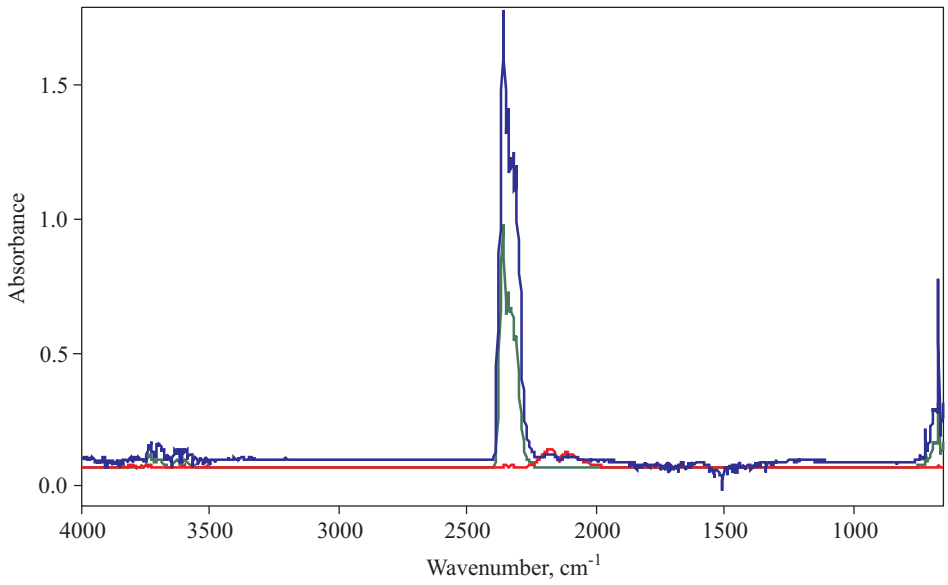


Fig. 4. Comparison of the registered at 400 °C FT-IR spectrum (blue) with the library spectra of CO (red) and CO_2 (green)

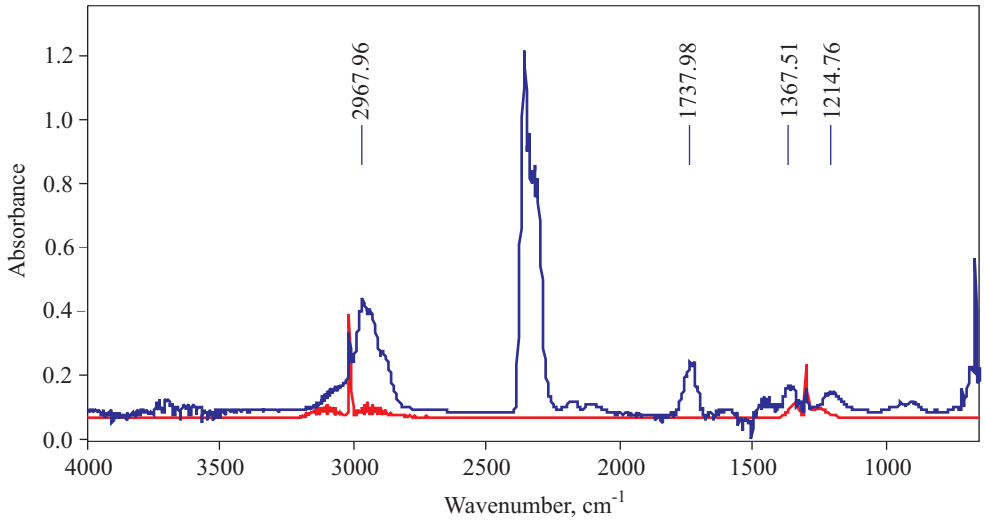


Fig. 5. Comparison of the registered at 461 °C FT-IR spectrum (blue) with the library spectrum of methane (red)

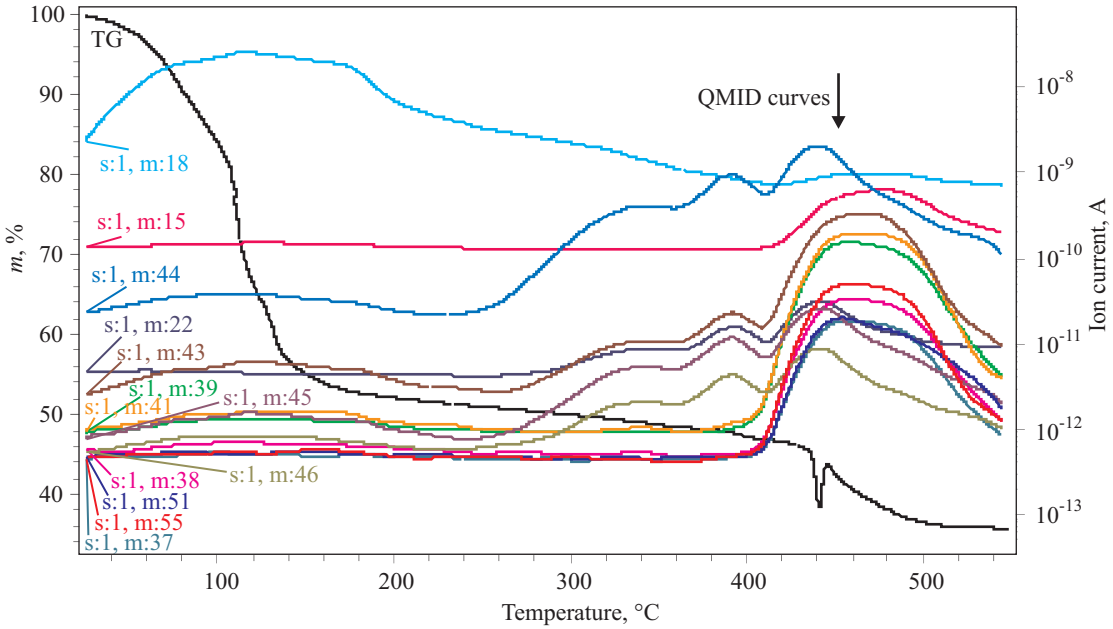


Fig. 6. Mass changes (TG) and MS signals (mass numbers: 15, 18, 22, 37, 38, 39, 41, 43, 44, 45, 46, 51 and 55) of Sokalan CP 5

2970 cm^{-1} are shown, and other vibrations at about 1740 cm^{-1}, 1360 cm^{-1} and 1214 cm^{-1} which should provide an indication of C=O and C-O stretching vibrations.

Figure 6 contains the mass changes and some of the strongest MS signals of Sokalan CP 5. The mass spectrometer signals shown indicate that the mass loss steps are predominantly due to the release of H_2O and CO_2 with mass numbers 18 and 44. The remaining signals for mass numbers 15, 22, 37, 38, 39, 41, 43, 45, 46, 51 and 55 originate probably from alkyl radicals being formed during the degradation process, but carbonyl compounds of short chains can also be formed. However, the obtained results require further studies.

A complete identification of the formed decomposition products on the basis of their molar mass is only possible when supplementary testing with gas chromatography is performed.

CONCLUSIONS

The FT-IR investigations performed at increased temperatures confirmed the thermal analysis results (DSC, TG, DTG) related to the polymer thermostability. In the temperature range -100—0 °C the polymorphous transformations were not found. It was established that the degradation process starts at the temperature approximately 400 °C. On the basis of the performed analysis of volatile products of the polymer decomposition carried out with the FT-IR method and the TG method coupled „on-line" with the MS the signals of small molecular

masses were found, which indicates that the degradation process and the fragmentation of polymer chains occurred as well as small particles and alkyl radicals were formed (molecular weights 15—55), including, first of all H_2O and CO_2.

The obtained molar masses indicate no formation of aromatic compounds, which is essential from the point of view of harmfulness when the polymer tested is used as a binder for molding sands.

To fully identify the maleic acid-acrylic acid copolymer sodium salt decomposition products, examination with the gas chromatography method will be continued.

REFERENCES

1. Grabowska B., Holtzer M.: *Polimery* 2007, **52**, 841.
2. Grabowska B.: *Arch. Foundry Eng.* 2008, **8**, No. 1, 51.
3. Grabowska B., Holtzer M.: *Przegląd Odlewnictwa* 2008, **58**, No. 4, 212.
4. Grabowska B., Holtzer M.: *Polimery* 2008, **53**, 531.
5. Grabowska B., Holtzer M.: *Arch. Metall. Mater.* 2009, **54,** 427.

Received 9 IV 2010.

W kolejnym zeszycie ukażą się m.in. następujące artykuły:

— *J. Wojturska* — Degradacja enzymatyczna poliuretanów. Cz. II. Wpływ budowy chemicznej poliuretanów i warunków hydrolizy enzymatycznej

— *M. Żenkiewicz, P. Rytlewski, R. Malinowski* — Metody i urządzenia stosowane w modyfikowaniu tworzyw polimerowych plazmą niskotemperaturową

— *I. Zarzyka-Niemiec* — Reakcje oksalamidu z węglanem etylenu (*j. ang*.)

— *N. Tudorachi, A. P. Chiriac, R. Lipsa* — Biodegradowalne kopolimery zawierające jednostki sakcynoimidu oraz jednostki kwasu mlekowego. Cz. I. Możliwości syntezy (*j. ang*.)

— *E. Wierzbicka, I. Legocka* — Elastomeryczny kopolimer blokowy styren-izopren-styren (SIS) modyfikowany pochodną borową (9-BBN) jako kompatybilizator mieszanin PE-LD/PS i PP/PS

— *S. Kuciel, A. Liber-Kneć* — Kompozyty na osnowie PHB napełniane włóknami naturalnymi (*j. ang*.)

— *M. Bartkowiak-Jowsa, R. Będziński, J. Chłopek, J. Filipiak, B. Szaraniec* — Analiza porównawcza charakterystyki odkształceniowych polimerów biodegradowalnych rozważanych jako materiał na stenty naczyniowe (*j. ang*.)

— *A. Ahmadzai, A. H. Behravesh* — Wpływ warunków przetwarzania na penetrację wody podczas formowania ABS w procesie wtryskiwania wspomaganego wodą (*j. ang*.)