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# Thermal degradation of some polymaleamides

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This study is an investigation on the thermal stability of some unsaturated polymaleamides with aliphatic and aliphatic-aromatic structure. The polymaleamides were synthesized by ring opening polyaddition of N,N'-hexamethylen-bis-isomaleamide with both an aliphatic-diamine (hexamethylendiamine) and some aromatic diamines (1,4-pheneylenediamine, 4,4'-diaminodiphenyl sulfone, 4,4'-diamino diphenyl methane and 4,4'-diaminodiphenyl ether). The thermal stability of the polymaleamides was examinated in atmospheric air by thermogravimetric analyses, heating the samples from 20 to 600$^0$C with 12$^0$C min$^{-1}$. The thermograms of the studied polymaleamides show a slight increase of the mass samples (0.1-0.5%) with increase of temperature in the interval 30-60 $^0$C. This behaviour was associated with the absorption of oxygen and formation of hydroperoxy structures during the thermal treatment. Thermogravimetric analyses show the presence of three main decomposition stages, which are partial superposed.

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*Keyword:* Polymaleamides, Thermal degradation, Kinetics, Thermal stability

## 1. Introduction

Polyamides represent polymers of the highest interest and are among the first synthesized polymers. Polyamides are used in a diverse range of applications from bicycle to aircraft tyres, including automotive, electrical, construction, household and machinery, as well as thin films and powder coatings. Unsaturated polyamides derived from maleic acid are called polymaleamide. [1,2]

The existence of >C=C< group in a polymer chain offers the possibility of crosslinking reactions which can be utilized for the preparation of insoluble and infusible high temperature laminates. [3] During the curing reactions of these unsaturated groups no volatile products are given off. This fact represents an important advantage because averts voids releasing in the cross-linked polymer. It is the reason for the polymealeamides are recommended as curing agents in thermosetting resins mixtures for the composite materials, as adhesives sealing materials, etc. [4]

These polymers can be easy obtained in the mild condition by ring-opening polyaddition (ROPA) from the corresponding bisisomaleimide and diamine. The present work is a study of the relationship between chemical structure and thermal properties of some polymaleamides, in order to elucidate the mechanism of thermal decomposition on heating. [5]

## 2. Experimental

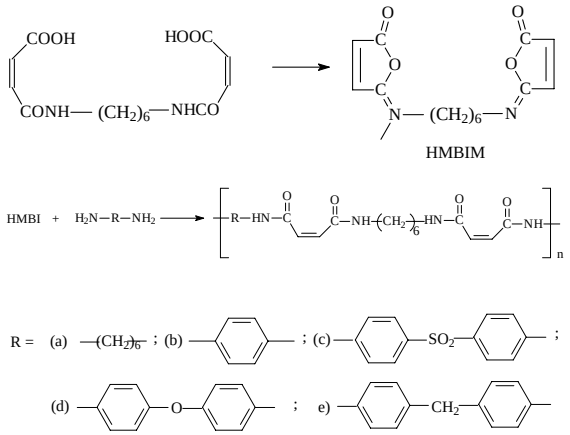
Thermogravimetric analysis was performed using MOM-Budapest (Hungary) derivatograph. Pellet samples were placed in an open vitreous silica pan and heated from 20 to 600 $^o$C with 12 $^o$C min$^{-1}$ heating rate, in atmospheric air. The precision of temperature measurements was ±1.5 $^o$C (Pt-PtRd thermocouple). The reference material was $\alpha$-$Al_2O_3$. In order to obtain comparable data, the analysis was performed for all the samples in the same conditions.

The kinetic analysis was carried out using the Versatile 1.000 program [6] for calculus using the Coats-Redfern integral method [7].

## 3. Result and discussion

Polymaleamides have been synthesized by ROPA of 1, 6-hexamethylene-bismaleimide with some diamines in equimolecular ratio, at room temperature. N-methyl-2-pyrolidin-2-one was used as solvent. Solid polymers were obtained by casting the solution to glass slides by means of o doctor blading and precipitation as solid films with methyl alcohol. At the last the films were immersed in methanol for total removing of the solvent and dried to 70 $^o$C in an oven. Particulars data concerning the synthesis of polymaleamides was elsewhere presented [8,9].

Scheme 1 presents the chemical reactions used for synthesis of polymaleamides:




*Scheme 1. Synthesis of polymaleamides.*

Fig. 1 presents the TG and DTG curves recorded for the synthesized polymaleamides.

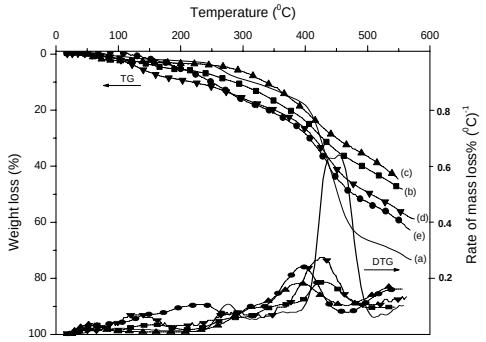
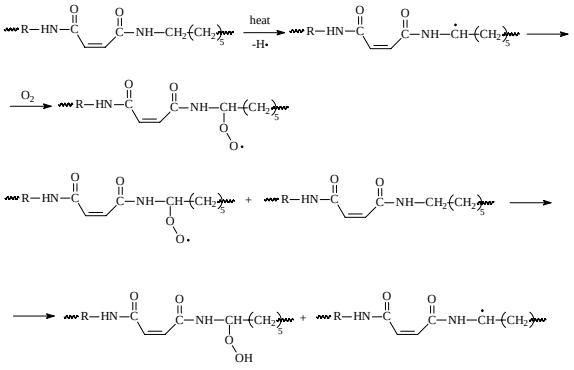



*Fig. 1. TG and DTG curves recorded for synthesized polymaleamides.*

All the thermograms of studied polymaleamides show a slight increase of mass samples between 0.1 and 0.5% with the increase of temperature from 30 to 60 °C. It is a typical behaviour of polyamides with aliphatic structure when are exposed to the thermo oxidative conditions. The observation was associated by some authors with absorption of oxygen by the polyamide macromolecular chains and the formation of peroxides compounds by radical intermediates [10,11]. All the polymaleamides (a-e) can support the reaction with oxygen from air resulting hydroperoxy structures during the thermal treatment as it is presented in Scheme 2.

From Fig. 1 results that the polymaleamide (a) and polymaleamide (e) are more sensible to the oxygen action compared with the other studied polymaleamides. This behaviour can be explained by the full aliphatic structure of polymaleamide (a) and the presence of the methylene group from diamino diphenylmethane radical in polymaleamide (e) respectively.




*Scheme 2. The formation of hydroperoxy structures from (a-e) polymaleamides.*

The TG and DTG curves for the studied polymaleamides show the presence at least three main decomposition stages with different rates, which are partial superposed.

Some others characteristics extracted from the thermograms, such as: the initial decomposition temperature ($T_i$), the temperature corresponding to 10% ($T_{10}$) and 30% ($T_{30}$) weight losses as well as the temperature corresponding to the maximum decomposition rate ($T_{max}$) for each stage of decomposition and the char yields at 550 °C are listed in Table 1.

*Table 1. TG and DTG data which characterize the decomposition of polymaleamides a-e.*

| Poly maleamide | $T_i$ (°C) | $T_{10}$ (°C) | $T_{30}$ (°C) | Thermal decomposition stage ($T_{max}$ (°C)) | | | Char yield in air at 550°C (%) |
|---|---|---|---|---|---|---|---|
| | | | | I | II | III | |
| (a) | 82 | 314 | 424 | 103 | 282 | 464 | 29 |
| (b) | 61 | 287 | 427 | 136 | 263 | 420 | 52 |
| (c) | 60 | 337 | 451 | 147 | 408 | 529 | 55 |
| (d) | 61 | 218 | 414 | 133 | 286 | 433 | 44 |
| (e) | 120 | 251 | 407 | 146 | 237 | 404 | 41 |

Table 1 show that the weight loss corresponding to studied polymaleamides starts at low temperatures (60-120 °C) and are small and dependent on the structure of the sample in the first stage of decomposition (0.1-5% measured at $T_{max}$).

The second decomposition stage is characterized by $T_{max}$ values placed in the 282-333°C temperature interval. During this stage, the weight losses are also dependent by the structure of the samples and there are placed between 7.7% for polymaleamide (a) and 14.6% for the polymaleamide (d).

The other values of weight losses corresponding to polymaleamides (b), (c) and (e) are 10.5, 9.6 and 8.5% respectively.

In the third stage the main decomposition of the studied polymers takes places. The $T_{max}$ values are placed between 401 and 464 °C range and significant weight losses resulted from the TG curves: 58; 32; 21; 36 and 29% correspond to (a)-(e) polymaleamides. There is a higher content of char yield correspondent to polymaleamides (b)-(e) with aliphatic-aromatic structures compared with polymaleamide (a), characterized by the full aliphatic structure.

Table 2 shows some kinetical decomposition parameters of polymaleamides (a)-(e), such as the activation energy ($E_a$), the reaction order (n) and the pre-exponential factor (A).

As can be seen, the activation energies are dependent on the polymaleamide structure. Table 2 shows that small values of the activation energies are necessary to start the thermal decomposition of all polymaleamides. The $E_a$ values corresponding to the first decomposition stage of the samples can be arranged between 36 and 56 kJ·mol$^{-1}$ in the order (c) < (a) < (e) < (b) < (d) samples. The reaction order n also depends by the structure of polymaleamide heaving values between 1 and 2. This fact could be related with a complex mechanism of thermal decomposition which can be due both to the intramolecular transfer and

random scission of the main chain and to the colliding simultaneously of two random polymer segments; such as intermolecular transfer and scission. [12]

*Table 2. Kinetical decomposition parameters of polymaleamides (a)-(e).*

| Poly maleamide | Process ($^0$C) | Kinetical decomposition parameters | | | |
|---|---|---|---|---|---|
| | | $E_a$ (kJ·mol$^{-1}$) | A (sec$^{-1}$) | n | Correlation coefficient |
| (a) | I (82-218) | 46 | $3.770 \cdot 10^2$ | 1.6 | 0.991 |
| | II (219-300) | 200 | $3.805 \cdot 10^{17}$ | 1.7 | 0.990 |
| | III (301-560) | 109 | $3.899 \cdot 10^5$ | 1.6 | 0.990 |
| (b) | I (61-208) | 55 | $5.339 \cdot 10^4$ | 1.5 | 0.986 |
| | II (209-331) | 107 | $8.373 \cdot 10^7$ | 1.8 | 0.991 |
| | III (332-556) | 90 | $1.211 \cdot 10^4$ | 1.5 | 0.986 |
| (c) | I (60-241) | 34 | 5.526·10 | 1.7 | 0.986 |
| | II (242-437) | 89 | $6.387 \cdot 10^4$ | 1.4 | 0.987 |
| | III (438-568) | 172 | $3.250 \cdot 10^9$ | 1.8 | 0.987 |
| (d) | I (61-200) | 56 | $1.129 \cdot 10^5$ | 1.4 | 0.991 |
| | II (201-368) | 99 | $7.578 \cdot 10^6$ | 1.5 | 0.991 |
| | III (369-575) | 159 | $1.032 \cdot 10^9$ | 1.7 | 0.998 |
| (e) | I (120-210) | 50 | $3.352 \cdot 10^3$ | 1.2 | 0.981 |
| | II (211-361) | 94 | $5.267 \cdot 10^6$ | 2.0 | 0.984 |
| | III (362-568) | 139 | $7.025 \cdot 10^7$ | 2.3 | 0.987 |

For all the samples, the second and the third decomposition stages are characterized by higher values of $E_a$ compared with the first stage. The values of the reaction orders indicate also the complex mechanisms of the thermal degradation.

In Fig. 2, the experimental curves and the curves calculated with the kinetic parameters presented in Table 2 are compared.

One observes the very good agreement between experimental and calculated data, especially in the first and the second decomposition stage.

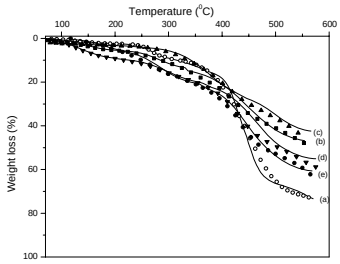



*Fig. 2. Experimental (symbols) and calculated weight losses (full line) as a function of temperature for polymaleamide samples.*

## 4. Conclusions

Some polymaleamides with aliphatic and aliphatic-aromatic structure were synthesized by ring opening polyaddition reaction.

The thermal stability of polymaleamides in atmospheric air was examinated by means of thermogravimetry, at 12 $^o$C min$^{-1}$ heating rate.

Thermogravimetric analysis show presence of least three main decomposition stage, which are partial superposed.

The weight loss corresponding to studied polymaleamides starts at low temperatures (60-120 $^o$C), are small and dependent by the structure of the sample in the first stage of decomposition (0.1-5% measured at $T_{max}$).

The second decomposition stage is characterized by $T_{max}$ values placed in the 282-333$^o$C temperature interval. During this stage, the weight losses are also dependent by the structure of the samples.

In the third stage the main decomposition of the studied polymers takes places. The $T_{max}$ values are placed between 401 and 464 $^o$C range and significant weight losses resulted from the TG curves. There is a higher content of char yield correspondent to polymaleamides (b)-(e) with aliphatic-aromatic structures compared with polymaleamide (a), characterized by the full aliphatic structure.

Some kinetical decomposition parameters of the polymaleamides such are the activation energy ($E_a$), the reaction order (n) and the pre-exponential factor (A) are calculated by Coats-Redfern method.

The $E_a$ values corresponding to the first decomposition stage of the samples can be arranged between 36 and 56 kJ·mol$^{-1}$ in the order (c) < (a) < (e) < (b) < (d) samples.

For all the samples, the second and the third decomposition stages are characterized by higher values of $E_a$ compared with the first stage. The values of the reaction orders indicate the complex mechanisms for all the stages of thermal degradation.

One observes the very good agreement between experimental and calculated data, especially in the first and the second decomposition stage.

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