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# Thermal degradation kinetics of polyurethane–siloxane anionomers

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ABSTRACT

A series of polyurethane–siloxane anionomers (PU–PDMS), synthesised from isophorone diisocyanate (IPDI), poly(oxytetramethylene)diol (PTMO), polydimethylsiloxane-diol (PDMS), 2,2-bis(hydroxymethyl)propionic acid (DMPA), ethylenediamine (EDA), and triethylamine (TEA), have been submitted to thermal stability investigations under inert or oxidizing atmosphere. The polymers had different amounts of dimethylsiloxane units in their elastic segments (0–15 wt.%). It was observed that siloxanes influenced thermal stability of PU–PDMS anionomers mainly at the second step of degradation. The kinetic degradation studies by Ozawa–Flynn–Wall and Friedman methods revealed that the activation energy ($E_a$) and pre-exponential factor ($A$) increased as a result of siloxane introduction into PU anionomers. The best approximation of the $f(\alpha)$ function was found for the D2 Cn models.

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## 1. Introduction

In recent years great interest has been observed in polyurethane–siloxane polymers obtained in the form of linear copolymers, interpenetrating polymer networks (IPN) as well as classical polymer blends. This results from the fact that these new materials combine main advantages of both comonomers used, i.e. good elasticity and tensile strength which is specific for polyurethane, and great elasticity (especially at low temperatures) and good thermal, chemical and biological stability which are contributed to the system by polysiloxanes. The influence of different polydimethylsiloxane species on lowering the value of free surface energy of polyurethanes is significant [1,2]. The possibility of adding ionomer structures to these polymers allows additionally for the production of waterborne dispersions and – because of that – one may avoid using toxic organic solvents when applying these polymers as varnishes, which is essential from the ecological point of view [3].

Polyurethanes are commonly known to be thermally stable up to 250 °C, and those based on polyesters are more stable than those based on polyethers. Thermal decomposition is initiated in hard segments where urethane linkages are predominant and it terminates in elastic segments which comprise ether bonds [4]. Polyurethane ionomers, however, demonstrate a slightly different behaviour during the thermal degradation, as compared to classical linear polyurethanes, because of the presence of additional ionomer centres in their chains [5,6].

As regards the other component, polysiloxanes are known to offer high thermal stability up to 300 °C. That stability results from the presence of Si–O bonds, for which the dissociation energy is higher (ca. 460.5 kJ/mol) in relation to C–O (358.0 kJ/mol) and C–C (304.0 kJ/mol) bonds [7–11].

Thermal degradation of polydimethylsiloxanes in the inert gas atmosphere, e.g. in $N_2$, or under vacuum, proceeds with the formation of cyclic oligomers and hexamethylcyclosiloxane is formed in most cases [9]. This reaction proceeds until the siloxane chain is too short to undergo further cyclisation, or until evaporation of the products which are formed during chain degradation is easier than chain cyclisation [8]. In addition to cyclic compounds, the presence of aromatic structures, including benzene, was confirmed in degradation products of poly(diphenyldimethyl)siloxanes [10,12]. It was also demonstrated that the heating rate influenced the structures of the cyclic siloxanes formed [8,9].

There are some research studies concerning thermal degradation of polyurethane-siloxanes, but there are no papers available on PU–SI anionomers. Thermal decomposition of polyurethane-siloxanes was reported to proceed in two stages [13–19], whereby one-stage process was observed for interpenetrating polymer networks obtained from those comonomers [20]. The first stage of thermal degradation of polyurethane–siloxane copolymers begins at 175–250 °C, depending on the structure, and it is related to the destruction of the weakest linkage in the chain, i.e. urethane bond [13–15]. Madhavan and Reddy [14] observed that the second stage of degradation occurred at 180–470 °C, and it was associated with decomposition of PDMS elastic segments. They noted that polyurethane–siloxane copolymers synthesised from MDI exhibited higher thermal stability than their analogues obtained from TDI or HMDI. It should be explained by a higher crystal phase con-

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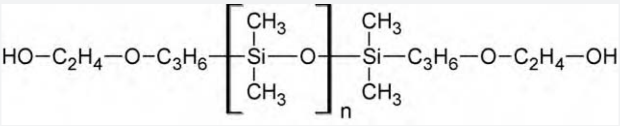
**Table 1**
Structures of polydimethylsiloxanes.

| PDMS symbol | Structure | Number average molecular weight ($M_n$) [g/mol] |
|---|---|---|
| X22-160AS |  $HO{-}C_2H_4{-}O{-}C_3H_6{-}[Si(CH_3)_2{-}O]_n{-}Si(CH_3)_2{-}C_3H_6{-}O{-}C_2H_4{-}OH$ | ≈1000 |

tent in PUs produced from MDI diisocyanate, with more symmetric structures which are favourable for the formation of crystalline structures.

The studies on thermal stability of PU–PDMS obtained from MDI, hydroxyl group terminated polydimethylsiloxane and butane-1,4-diol, have been performed by Chuang et al. [21]. Decomposition of these copolymers occurs at two stages which have been divided into 10 so-called 'sub-stages' related to particular thermolysis reactions. The first main step proceeds at 250–410 °C, and it is connected with destruction of urethane bond and formation of the following decomposition products: $CO_2$, $H_2O$, carbodiimides, tetrahydro-furane, cyclic ethers and linear PDMS oligomers. The second stage, which occurs at 406–650 °C, proceeds with degradation of polysiloxanes to smaller chains and cyclic systems which then undergo thermolysis to form volatile organic compounds, $SiO_2$ and char residue. It has been demonstrated that the initial degradation temperature for those stages is 250 °C and 410 °C, respectively, and that it generally does not depend on the content of hard segments in this copolymer. Nevertheless, the maximum rate of thermal decomposition at the first stage increased with an increase of the content of hard segments, while it was distinctly lower at the second stage.

Decomposition of PU–SI in air results in the formation of char residue; its amount increases with the increasing contribution of siloxane in the copolymer chain [13,15,22]. Wang et al. [13] studied the surface of polyurethane–siloxane copolymer, obtained from MDI, PTMO and PDMS, having both ends terminated with secondary $NH_2$ groups, with X-ray Photoelectron Spectroscopy (XPS), before and after thermal oxidation at 700 °C. Their research confirmed the presence of complex silicate structures which acted as the insulating layer and protected against further oxidation on the surface.

Park et al. [23] compared thermooxidative stability of polyurethane polymers with that of PU–PDMS copolymers, both comprising only α,ω-diaminepolydimethylsiloxane, as well as comprising PDMS with other polyol compounds. It was found that the amount of char was highest at the final temperature of 600 °C for polyurethane comprising only polydimethylsiloxane in soft segments. Moreover, thermal stability of that type of polymer was highest above 450 °C. PU–PDMS copolymers comprising also other polyols demonstrated improved thermal stability at low polydimethylsiloxane contents in relation to polyether (0.2:1), as compared to virgin polyurethane. The increase in stability was more noticeable for PU–PDMS copolymers obtained from poly(oxyethylene)glycol and poly(oxypropylene)glycol than from poly(oxytetramethylene)diol or type *Pluronic* PEG–PPG–PEG block terpolymer.

There are, moreover, reports showing the influence of the type of the siloxane chain extender on thermal stability of linear PU synthesised from MDI and different-molecular-weight PTMO [16] and also those PUs which were moisture cured [24].

So far, no papers can be found for detailed studies on thermal stability of urethane anionomers modified with siloxane. Hence, the aim of this work is to investigate thermal stability, including detailed kinetic studies, of linear polyurethane–siloxane anionomers.

## 2. Experimental

### 2.1. Materials

Isophorone diisocyanate (IPDI), poly(oxytetramethylene)diol (PTMO, $M_n$ = 1000 g/mol), 2,2-bis(hydroxymethyl)propionic acid (DMPA) and dibutyltin dilaurate (DBTDL) were purchased from Aldrich. Poly(dimethylsiloxane)diol (PDMS) X22-160AS (Table 1) was kindly donated by Shin-Etsu (Japan). All the reagents were used as obtained. Triethylamine (TEA), ethylenediamine (EDA) and *N*-methyl-pyrrolidone (NMP) were acquired from Aldrich and dried over 4 Å molecular sieves one week before being used.

#### 2.1.1. Preparation of poly(urethane-siloxane) anionomers

PU–PDMS anionomers were obtained in four-stage method as follows:

*Stage I: Synthesis of urethane–siloxane prepolymer*. Molten PTMO or alternatively PTMO mixed with PDMS were added drop by drop to the flask containing adequate amount of IPDI. Then the catalyst (DBTDL) was added and the reaction was allowed to proceed at 60 °C till the theoretical content of free isocyanate groups reached its end-point. The content of –NCO groups in the mixture was analysed every 30 min.
*Stage II: Incorporation of 2,2-bis(hydroxymethyl)propionic acid into the polymer chain*. Adequate amount of DMPA dissolved in NMP was added drop by drop to the mixture of urethane prepolymers as obtained at stage I, over 10 min, at 85 °C. Then the DBTDL catalyst was added. The total content of the catalyst was about 0.3 wt.% in relation to polyols introduced.
*Stage III: Synthesis of quaternary ammonium salts with the use of TEA*. In order to obtain the quaternary ammonium salts, after the content of free –NCO groups was analysed, the mixture was cooled down to 60 °C. Then TEA was added and the mixture was reacted for 30 min. The number of moles of TEA which was added to the mixture corresponded to the number of moles of the build-in DMPA acid.
*Stage IV: Dispersion step and extension of the isocyanate anionomers with the use of ethylenediamine (EDA) in aqueous medium*. Deionised water was added to isocyanate anionomers with rapid stirring at room temperature over 5 min. Then EDA (dissolved in water) was added drop by drop to the dispersion over 5–7 min in order to extend the isocyanate anionomer chains. The amount of water was so selected to obtain a dispersion comprising about 30% of solids.

The general compositions of PU–PDMS anionomers were shown in Table 2.

### 2.2. Techniques

#### 2.2.1. Determination of –NCO group content

Excess of unreacted amine was titrated with the HCl solution, and bromophenol blue was used as an indicator [25].

**Table 2**
Composition of PU-PDMS anionomers.

| Sample | wt.% of compound in anionomer | | | | | |
|---|---|---|---|---|---|---|
| | IPDI | PTMO | PDMS | DMPA | EDA | TEA |
| I1,5S0% | 34.0 | 50.9 | 0 | 6.8 | 3.1 | 5.2 |
| I1,5S1% | | 49.9 | 1 | | | |
| I1,5S3% | | 47.9 | 3 | | | |
| I1,5S5% | | 45.9 | 5 | | | |
| I1,5S10% | | 40.8 | 10.1 | | | |
| I1,5S15% | | 35.6 | 15.3 | | | |

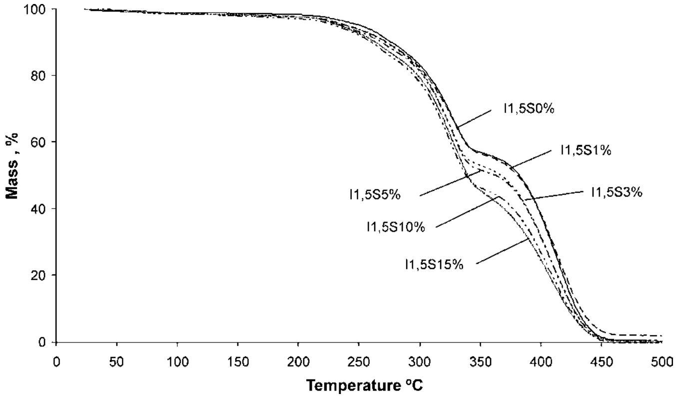


**Fig. 1.** TG profiles for series I1,5Sy, recorded in nitrogen.

### 2.2.2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed using a Mettler Toledo TGA/DSC1 in the temperature range of 25–500 °C when in nitrogen, or at 25–700 °C when in air. The heating rates of 2.5, 5, 10 and 20°/min were used. The measurement conditions were as follows: sample weight ~2.5 mg, gas flow – 50 cm$^3$/min, aluminium pan.

The raw data were converted to ASCII files and the kinetic analysis was carried out with the use of the Netzsch Thermokinetic Program. For *F*-test 400 points were applied and confidence probability of 95% was assumed.

## 3. Results and discussion

### 3.1. Thermal decomposition in nitrogen

TG profiles were presented in Fig. 1; these were taken for PU–PDMS anionomers at the heating rate of 10°/min, in nitrogen, Table 3 provides interpretation of DTG profiles. The DTG profiles for the anionomer samples which were tested in nitrogen reveal basically four peaks, which suggests that the degradation process is composed of four stages. However, only two basic degradation stages can be distinguished in the TG curves. That may suggest that the first basic degradation stage may comprise a few processes (parallel reactions, subsequent reactions or "overlapping" reactions, and possibly evaporation of remaining solvent which has been occluded).

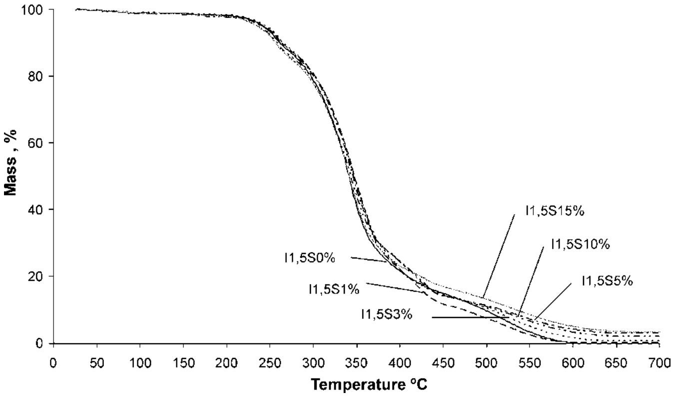


**Fig. 2.** TG profiles for series I1,5Sy, recorded in air.

The mass loss at the first stage of degradation amounts to 43–53 wt.% which corresponds to disintegration of rigid segments. The maximum rate of the degradation process at the first stage is observed at temperature $T_{\max1}$ = 327–331 °C, while no clear dependence can be observed for the maximum degradation rate on the amount of PDMS charged. As distinguished from the second stage of degradation, which involves decomposition of flexible segments, and in which the relation as mentioned above is apparent – for increasing PDMS content in the PU anionomer, the temperature which is specific for the maximum rate of degradation drops down from 417 °C for the sample with no PDMS to 409 °C for the sample with 15% PDMS. The mass loss at the second stage of degradation amounts to 46–56 wt.%.

Decomposition of PU–PDMS anionomers, in terms of 5% mass loss, takes place in the temperature range of 234–255 °C for all series of anionomers which were synthesised at the NCO/OH rate = 1.5.

Thermolytic decomposition ends at the temperature ($T_k$) which is above 450 °C. Nearly all anionomers, irrespective of their siloxane content, undergo 100% decomposition. No solid residue found after degradation may confirm formation of volatile cyclic siloxane compounds.

### 3.2. Thermal decomposition in air

Thermal decomposition of PU–PDMS anionomers in air follows a more complex pattern. Fig. 2 presents TG curves which were recorded for PU–PDMS anionomers at the heating rate of 10°/min, in air, while Table 4 provides interpretation of DTG profiles. Under such conditions, the 5% mass loss appears at 235–245 °C for all anionomers which were produced at NCO/OH = 1.5. The effect of siloxanes on the course of degradation is clearly revealed at the second stage – for decomposition exceeding 50%. The temperature for the 50% mass loss is the lowest one for PU anionomer with no siloxanes, and its value is 340 °C. The addition of PDMS (up to 3 wt.%) increases that temperature as high as even by 7 °C, which

**Table 3**
Decomposition temperatures (DTG) of PU-PDMS anionomers at 10 K/min under nitrogen.

| Sample | $T_{\max1}$ [°C] | Mass loss at stage I of degradation [%] | $T_{\max2}$ [°C] | Mass loss at stage II of degradation [%] |
|---|---|---|---|---|
| I1,5S0% | 330 | 43.0 | 417 | 56.2 |
| I1,5S1% | 330 | 43.2 | 415 | 54.4 |
| I1,5S3% | 327 | 47.1 | 409 | 52.9 |
| I1,5S5% | 328 | 48.0 | 410 | 51.3 |
| I1,5S10% | 327 | 52.5 | 409 | 47.6 |
| I1,5S15% | 331 | 53.5 | 409 | 45.7 |

**Table 4**
Decomposition temperatures (DTG) of PU–PDMS anionomers at 10 K/min under air.

| Sample | $T_{max1}$ [°C] | Mass loss at stage I of degradation [%] | $T_{max2}$ [°C] | Mass loss at stage II of degradation [%] | $T_{max3}$ [°C] | Mass loss at stage III of degradation [%] | $T_{max4}$ [°C] | Mass loss at stage IV of degradation [%] |
|---|---|---|---|---|---|---|---|---|
| I1,5S0% | 255 | 9.7 | 341 | 58.9 | 417 | 16.4 | 519 | 14.6 |
| I1,5S1% | 262 | 10.0 | 349 | 62.1 | 418 | 16.1 | 528 | 11.2 |
| I1,5S3% | 262 | 9.8 | 346 | 63.1 | 391 | 12.0 | 528 | 13.9 |
| I1,5S5% | 258 | 10.7 | 346 | 58.8 | 418 | 16.2 | 544 | 12.4 |
| I1,5S10% | 259 | 13.3 | 346 | 55.3 | 421 | 16.5 | 531 | 12.2 |
| I1,5S15% | 259 | 14.0 | 345 | 59.2 | 432 | 13.0 | 531 | 10.6 |

is the case for the sample I1,5S1%. Further increase of the siloxane content makes $T_{50\%}$ go down.

The TG profiles (Fig. 2) of the tested anionomer samples, for decomposition in air, demonstrate basically four maximum peaks, which may suggest that the degradation process is composed of four stages.

The end-of-degradation temperature in air is lower for the anionomer which has not been modified with siloxanes, and it is about 600 °C. The amount of solid residue after degradation for those series of anionomers increases to follow the increasing contents of siloxanes in the polymer chain, while decomposition of non-modified anionomers is complete in practice. Those findings seem to make the evidence for the formation of complex silicon-based structures in the pyrolysis process. They structures are formed on the surface and probably create the insulating layer which slows down further decomposition of the polymer, as it was observed for polyurethane–siloxane copolymers [13].

### 3.3. *Kinetic analysis of the decomposition process*

Having in mind that the poly(urethane-siloxanes) synthesised in the course of this work offer similar thermal resistance features when investigated by the TG method, we found it advisable to go into further analyses which would make it possible to define more precisely the effects of the synthesis method and polysiloxane content on thermal stability of PU–PDMS copolymers. Kinetic analysis of the observed thermal decomposition processes of those polymers turned out useful for that purpose. In some cases, it is just kinetic analysis that may provide additional information on the mechanism of thermal decomposition of anionomers.

The general expression for the kinetic description of degradation of solids has the form [26]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where $\alpha$ is the conversion degree, $k(T)$ is the reaction rate constant, and $f(\alpha)$ is the kinetic model function.

After substitution of the Arrhenius equation [27]:

$$k(T) = A\ \exp\left(\frac{-E_a}{RT}\right) \tag{2}$$

to (1), one arrives at

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E_a}{RT}\right)f(\alpha) \tag{3}$$

Under non-isothermal conditions, when an expression responsible for the heating rate is added:

$$\beta = \frac{dT}{dt} \tag{4}$$

and after arranging the variables properly, one obtains the final relationship:

$$g(\alpha) = \int_o^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^T \exp\left(-\frac{E_a}{RT}\right)dT \tag{5}$$

where $A$ is the frequency factor, $E_a$ is the activation energy, $R$ is the universal gas constant and $T$ is the absolute temperature.

Isoconversional methods were employed to analyse the degradation kinetics of the synthesised PU–PDMS systems: the Ozawa–Flynn–Wall (OFW) method [28,29] and the Friedman method [30], which make it possible to determine kinetic parameters in thermal decomposition of polymers under dynamic conditions. These methods may be used to determine and to monitor changes in the activation energy as the degradation process proceeds, irrespective of the assumed reaction model. The Ozawa–Flynn–Wall method is based on the Doyle approximation [31] and it resolves itself to the use of the following equation:

$$\ln\ \beta = \ln\left(\frac{A\cdot E_a}{R}\right) - \ln g(\alpha) - 5.3305 + 1.052\frac{E_a}{RT} \tag{6}$$

In order to find the activation energy value $E_a$ for a given degree of conversion $\alpha$, one should take a series of measurements for different heating rates $\beta$. Then, for a fixed degree of conversion ($\alpha$ = const), straight lines are obtained in the diagram $\ln\beta = f(1/T)$ for which the slope is defined as $m = 1.052(E_a/R)$ [32,33].

Another isoconversional method is the Friedman method [30] based on the following equation:

$$\ln\ \frac{d\alpha}{dt} = \ln A + \ln f(\alpha) - \frac{E_a}{RT} \tag{7}$$

In order to find the activation energy value $E_a$ for a given degree of conversion $\alpha$, one should take a series of measurements for different heating rates $\beta$. Then, for a fixed degree of conversion ($\alpha$ = const), straight lines are obtained in the diagram $\ln(d\alpha/dt) = f(1/T)$ for which the slope is defined as $n = -E_a/R$ [32,33].

After the values have been established for kinetic parameters with the above mentioned methods, one needs to define the form for the function $f(\alpha)$ from the Eq. (1). Table 5 presents the specification of models which are most frequently used to describe thermal degradation of polymers.

The kinetic analysis covered the samples of anionomers within the whole series I1,5Sy; these were synthesised in the four-stage method, at the ratio NCO/OH = 1.5, and then subjected to thermal degradation under dynamic conditions, at the heating rates of 2.5, 5, 10 and 20°/min, in nitrogen. The values for the activation energy and frequency factor, for the PU–PDMS anionomer samples in series I1,5Sy calculated by the Friedman and Ozawa–Flynn–Wall methods, were presented in Figs. 3 and 4.

The “wavy” profile for the Friedman plot (two main peaks) and two ranges in the activation energy diagram (Fig. 3) suggest that the thermal degradation process of the investigated samples must pass through at least two stages. Moreover, at the first stage – i.e. at low conversion degrees, lower angles of inclination are observed for the curves which have been calculated from measurements in relation to the isoconversional lines. That may be indicative for the diffusion-controlled character of the processes which take place at the first stage of the decomposition process. At the initial phase of the second stage, however, the measurement-derived curves go much more steeply and they are partially overlapped the isoconversional lines. Hence, one may deduct that the autocatalytic

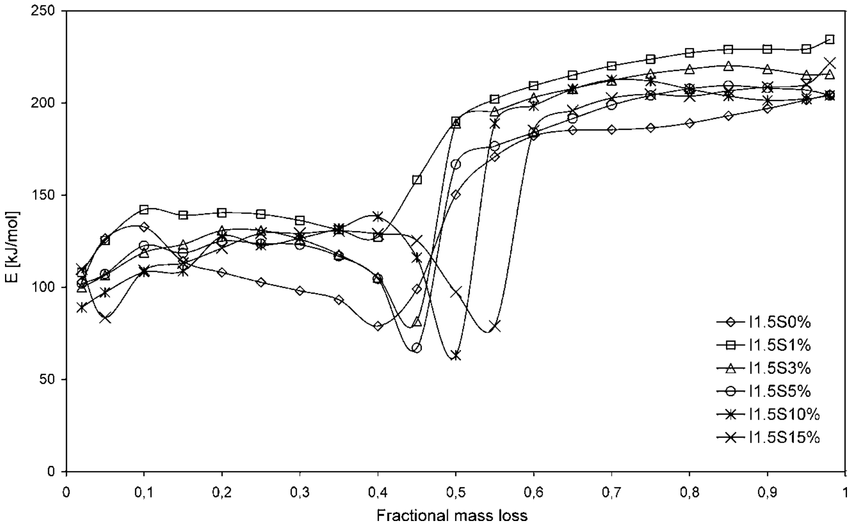


**Fig. 3.** Activation energy values calculated from the Friedman analysis of the degradation process of PU–PDMS anionomers.

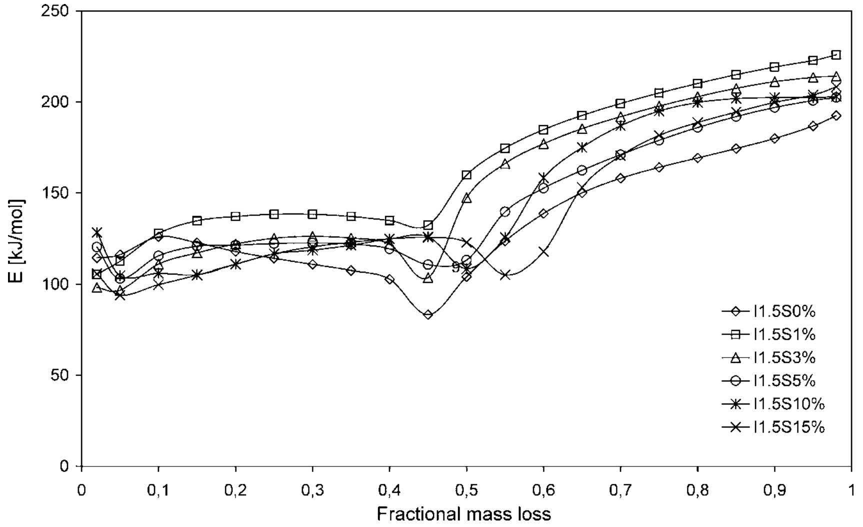


**Fig. 4.** Activation energy values calculated from the Ozawa–Flynn–Wall analysis of the degradation process of PU–PDMS anionomers.

or *n*-order reaction kinetic model will be dominant at the second stage.

The diagrams for changes in activation energy and in frequency factor *versus* conversion degree, those changes having been found by the Friedman method, reveal a minimum at about 0.41 for the unmodified sample. That minimum moves towards higher conversion degrees for the increasing PDMS content, up to about 0.56 for the sample which contains 15% PDMS. The minimum makes a proof for a change in the reaction mechanism in that area (and also for a change in the model which describes that mechanism) – for increasing amounts of PDMS, the conversion degree increases at which the reaction mechanism changes (the degradation process enters stage 2).

Similar relations can be observed in plots which result from the analysis of the studied anionomers with the use of the Ozawa–Flynn–Wall method. The angles of inclination change for the isoconversion lines, which may be evidence for the change in the reaction mechanism. The diagrams for changes

**Table 5**
Kinetic models for thermal degradation of polymers [32,33].

| Model | Symbol | $f(\alpha)$ |
|---|---|---|
| Reaction of *n*th order | Fn | $(1-\alpha)^n$ |
| Phase boundary-controlled reaction (contracting area) | R2 | $2(1-\alpha)^{1/2}$ |
| Phase boundary-controlled reaction (contracting volume) | R3 | $3(1-\alpha)^{2/3}$ |
| *n*-Dimensional nucleation (Avrami–Erofeev equation) | An | $n(1-\alpha)[-\ln(1-\alpha)]^{(1-1/n)}$ |
| One-dimensional diffusion | D1 | $1/2\alpha$ |
| Two-dimensional diffusion | D2 | $1/[-\ln(1-\alpha)]$ |
| Three-dimensional diffusion (Jander equation) | D3 | $3(1-\alpha)^{2/3}/2[1-(1-\alpha)^{1/3}]$ |
| Three-dimensional diffusion (Ginstling–Brounshtein) | D4 | $3/2[(1-\alpha)^{-1/3}-1]$ |
| Prout–Tompkins equation | Bna | $(1-\alpha)^n\alpha^a$ |
| Reaction of *n*th order with autocatalysis | Cn | $(1-\alpha)^n(1+K_{\mathrm{kat}}\,\alpha)$ |

**Table 6**
Average activation energy obtained on the basis of isoconversional methods.

| Sample | Average activation energy calculated from Friedman analysis, $E_a$ [kJ/mol] | | Average activation energy calculated from OFW analysis, $E_a$ [kJ/mol] | |
|---|---|---|---|---|
| | I stage | II stage | I stage | II stage |
| I1,5S0% | 109.7 | 178.7 | 114.6 | 158.3 |
| I1,5S1% | 132.7 | 213.9 | 129.5 | 200.8 |
| I1,5S3% | 117.7 | 210.1 | 115.9 | 192.2 |
| I1,5S5% | 115.9 | 196.1 | 118.5 | 178.3 |
| I1,5S10% | 116.6 | 203.8 | 116.2 | 185.0 |
| I1,5S15% | 116.1 | 204.3 | 113.5 | 179.7 |

in activation energy *versus* conversion degree, as found by the Ozawa–Flynn–Wall method (Fig. 4), show the minima in similar regions as it was in the case of the Friedman analysis. Hence, the multiple nonlinear regression method was employed at the following stage to adjust the model for $f(\alpha)$ to the profile of the actual TG curve. The point in which the reaction model changes was assumed to be the degree of conversion corresponding to the minimum of activation energy in the diagrams for activation energy values *versus* conversion degrees which had been calculated by isoconversion methods.

The average value of activation energy for each decomposition step is presented in Table 6. The degree of matching was determined with the use of *F*-test. The results of those calculations were presented in Table 7 and Fig. 5. The best match between the experimental data and the models considered was obtained for the two-stage degradation mechanism.

After analysis of the results of average activation energy from isonversional methods (Table 6), shape of profiles and isoconversional lines from Friedman plots, as well as data from multiple nonlinear regression, the most probable kinetic models for ther-

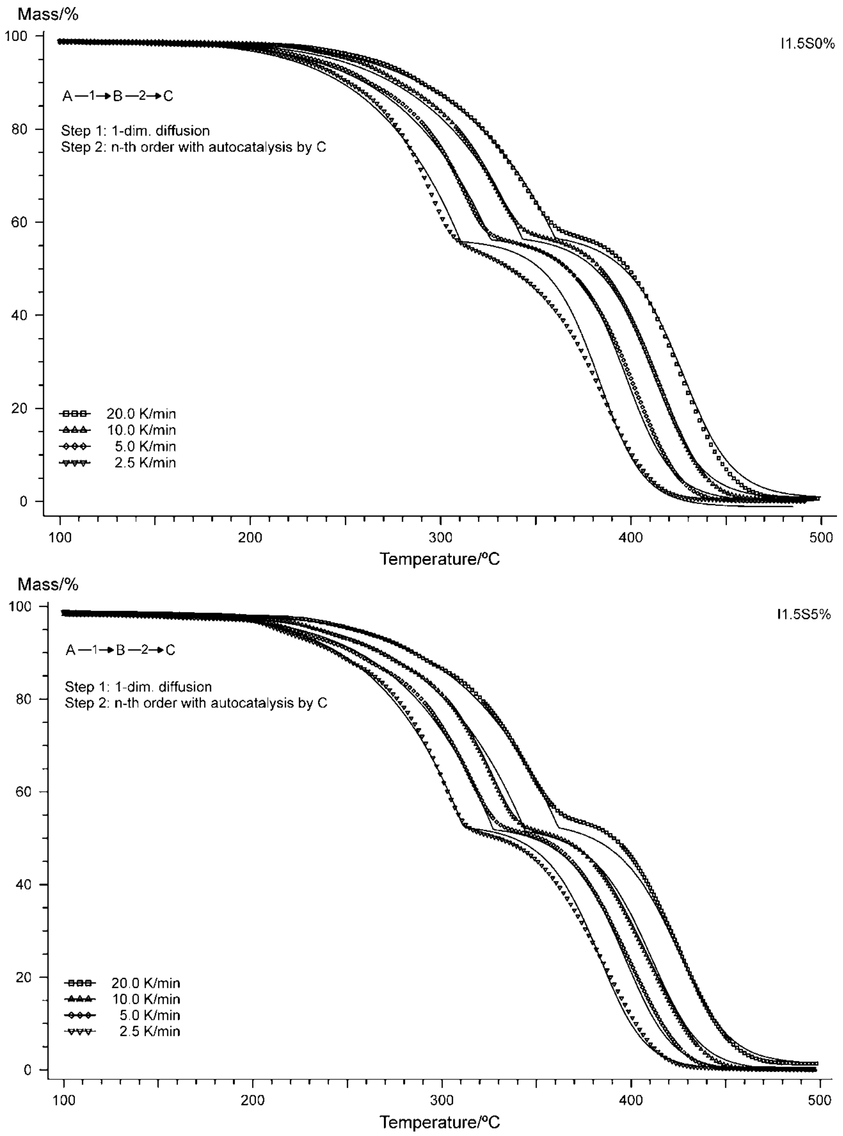


**Fig. 5.** Best fit of kinetic models of the thermal decomposition of PU–PDMS.

**Table 7**
Results of kinetic analysis.

| Sample | Stage I | | | | | Stage II | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $E_{a1}$ [kJ/mol] | $\log A_1$ | Order | Dimension | Model | $E_{a2}$ [kJ/mol] | $\log A_2$ | Order | Dimension | Model | *F*-test |
| I1,5S0% | 110.6 | 7.59 | – | 0.86 | An | 164.3 | 10.21 | 1.26 | – | Cn | 1.00 |
| | 110.7 | 7.60 | – | 0.85 | An | 163.1 | 10.28 | 1.12 | – | Bna | 1.01 |
| | 110.8 | 7.60 | – | 0.85 | An | 166.8 | 10.46 | - | 1.0210 | An | 1.06 |
| | 118.3 | 7.9 | – | – | D1 | 171.4 | 10.70 | 1.61 | – | Cn | 1.06 |
| I1,5S1% | 138.2 | 9.56 | – | – | D2 | 199.5 | 13.04 | 0.84 | – | An | 1.00 |
| | 127.4 | 8.73 | – | – | D1 | 197.2 | 12.95 | 1.39 | – | Cn | 1.07 |
| | 137.7 | 9.51 | – | – | D2 | 194.6 | 12.75 | 1.34 | – | Cn | 1.15 |
| I1,5S3% | 123.7 | 8.41 | – | – | D1 | 192.8 | 12.63 | 1.36 | – | Cn | 1.00 |
| | 120.7 | 8.12 | – | – | D1 | 192.6 | 12.62 | 1.35 | – | Bna | 1.17 |
| | 127.0 | 8.71 | – | – | D1 | 178.6 | 11.43 | – | – | F1 | 1.61 |
| I1,5S5% | 118.2 | 7.83 | – | – | D1 | 177.9 | 11.34 | 1.52 | – | Cn | 1.00 |
| | 122.1 | 8.19 | – | – | D1 | 181.2 | 11.73 | 1.28 | – | Bna | 1.04 |
| | 119.9 | 8.00 | – | – | D1 | 174.9 | 11.13 | – | – | F1 | 1.16 |
| I1,5S10% | 124.8 | 8.27 | – | – | D2 | 190.6 | 12.48 | 1.34 | – | Fn | 1.00 |
| | 125.1 | 8.30 | – | – | D2 | 191.9 | 12.57 | 1.34 | – | Bna | 1.00 |
| | 124.6 | 8.25 | – | – | D2 | 190.9 | 12.50 | 1.36 | – | Cn | 1.00 |
| | 115.0 | 7.53 | – | – | D1 | 197.0 | 12.99 | 1.40 | – | Fn | 1.01 |
| I1,5S15% | 122.6 | 8.05 | – | – | D2 | 182.1 | 11.86 | 1.33 | – | Fn | 1.00 |
| | 122.6 | 8.05 | – | – | D2 | 183.8 | 12.00 | 1.35 | – | Cn | 1.00 |
| | 123.0 | 8.09 | – | – | D2 | 183.0 | 11.94 | 1.33 | – | Bna | 1.01 |

mal degradation of investigated samples were marked in Table 7 in grey. The findings from isoconversion studies, based on Friedman and OFW methods, suggested the diffusion-controlled nature of the first degradation stage for the all samples (models D1 or D2). For the second stage of decomposition for the unmodified sample and samples with PDMS content up to 5% the most probable kinetic model is the *n*th order reaction with autocatalysis (Cn), while for samples with PDMS content 10 and 15% it is *n*th order reaction (Fn).

To understand better the physicochemical meaning of these models let us assume that a chemical reaction occurs at the planar boundary between two media and that the geometric system consists of large spherical particles of one phase surrounded by substantially finer particles of the other phase. This system can be described by one of the two approaches: a continuous (non-stationary) model and a discontinuous (stationary) model of the shrinking core of particles. If the mass transport becomes rate-controlling, a diffusion process is encountered and the main process is the gradual growth of the product layer. The shrinking interface model has become a basis for the description of most reactions of solids. Diffusion and chemical reaction are two possible pathways of a reaction of spherical particles which are covered with a thin surface layer of the products in an amount that is usually experimentally undetectable. The reacting components diffuse through this layer to the reaction boundary in which they chemically react. The slower of the two principal processes then becomes the rate-controlling process [34].

One may thus infer that at the first stage of degradation (degradation of hard segments), when one deals with a solid or with high viscosity melt, the mass transfer processes are rate-determining for the whole process. Degradation of hard segments takes place in the bulk of the material [continuous (non-stationary) model] and the decomposition products must diffuse to the surface to be evaporated (degradation is a faster process, while it is diffusion of the volatile products to the surface which is rate-controlling process for the first stage). At the second stage (degradation of flexible segments), there is material which has been already subjected to partial degradation, probably with a porous structure. That creates more convenient conditions for the mass transfer processes. Resulting from that, the degradation reaction itself of flexible segments makes the process which is rate-determining for the second stage.

Similarly, the first stage of degradation for all PU–PDMS anionomers follows the mono-dimensional (D1) or two-dimensional (D2) diffusion mechanism. The activation energy at that stage is the lowest for the sample with no siloxanes and it is only 110.6 kJ/mol. Anionomers which have been modified with siloxane require the activation energy value which is higher on average by 10 kJ/mol for that stage. That difference between the unmodified sample and that modified with PDMS is as high as twofold at the second stage.

From our results it can be concluded that the most probable kinetic model for unmodified sample and samples with lower PDMS content is D1Cn, while for higher PDMS content it is D1Fn or D2Fn. At the second stage, degradation involves flexible segments, where siloxane structures are present. The maximum values for the activation energy and for log *A* at both stages were established for the anionomer I1,5S1% which contained only 1 wt.% of siloxane in its chain. These values are 127.4 kJ/mol and 8.73 and 197.2 kJ/mol and 12.95, respectively.

## 4. Conclusions

The synthesised PU–PDMS anionomers undergo two-stage degradation in nitrogen; the temperature peak for the maximum mass loss is 327–331 °C for the first stage and 409–417 °C for the second stage. The DTG results show that the degradation mechanism for PU–PDMS in air is more complex. In that case, the maximum mass loss at stage I was shifted towards lower temperatures – 255–262 °C. The measurements justify the observation that the presence of polysiloxanes in PU–PDMS copolymers improves thermal stability of those polymers, which becomes visible more clearly in the case of oxidative degradation (in air). However, no clear evidence was obtained for improved thermal stability which would result from the chemical structure and that may be inferred from structural stability in the neutral atmosphere only.

In that case, it was found advisable to conduct more advanced research within kinetics of decomposition in nitrogen. The investigations were based on the Ozawa–Flynn–Wall method and they revealed that the incorporation of siloxanes into PU–PDMS anionomer chains increased the activation energy values in both stages of thermal degradation, by 10 kJ/mol on average for stage I and by about 20 kJ/mol for stage II. The unmodified polyurethane ionomer (I1,5S0%) showed the activation energy values for decomposition stages I and II of 110.6 and 164.3 kJ/mol, respectively, which is enough to declare the advantageous effect of siloxanes on thermal stability of anionomers tested.

The best compliance of experimental data to the considered models was obtained for the two-stage degradation mechanism. The results of the isoconversion studies, which utilised the Friedman and OFW methods, were indicative for the diffusion nature of the first degradation stage and for the autocatalytic behaviour at the second stage. Thus, thermal degradation of PU–PDMS anionomers may be generally assumed to follow the D2Cn models.

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