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KINETIC PARAMETERS FROM THERMOGRAVIMETRIC STUDY OF USED RUBBER GRANULATES–POLYURETHANE COMPOSITES

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From the TG data of rubber granulates, different polyurethane and composites it can be seen that the thermal decomposition for the rubber granulate and all of the composites start above 520 K. Two major mass losses for the rubber granulates and majority of the composites were observed and thermal decomposition is essentially complete by ~820 K. The changes of activation energies of lower and higher temperature decomposition, calculated according to the different equations were observed for a priori assumed first-order reaction for devolatilisation. Differences between determined and calculated results could suggest a possible reaction between polyurethane agents and rubber granulate during the composites formations.

Keywords: *activation energy, decomposition, kinetic parameters, rubber waste-polyurethane composites, thermal analysis*

Introduction

The production of rubber materials rises every year. Therefore, the processing of waste rubber and its management must be treated as a global problem. The index of rubber reclaims consumption *vs*. virgin rubber consumption, depending on the country, is only 1–10% [1–3]. One of the methods of the rubber waste management is to break the rubber waste up and use obtained granulate, fine rubber or rubber dust as a valuable raw material. The increase of the application of products obtained from waste rubber granulate or fine rubber mixed with a small amount of an elastomer is observed. These products do not need additional vulcanisation. A thin polymer layer covering rubber grain polymerises under suitable conditions giving a stable composite. However, the possibility to use this kind of material depends on its properties and stability [3, 4].

Different thermal techniques are used for the study of the properties of polymers, rubber and composites and to determine the kinetic parameters of their stability and decompositions processes. The use of thermogravimetric data to evaluate kinetic parameters of solid-state reactions involving mass loss has been investigated by number of scientists and have stated some advantages of this method over conventional isothermal studies [5–9]. A priori knowledge of the value of the order of reaction is assumed in most derivations, while the method which allows for the determination of both the activation energy and the order of reaction suffers from a number of disadvantages.

The structure of polyurethane supermolecular structure of the waste rubber granulates–polyurethane composites are discussed on the basis of thermogravimetric measurements and previous studies [5].

Experimental

Materials and methods

For preparation of rubber waste-polyurethane composites the following substrates were used:

- granulated rubber (fine rubber) of granularity below 1.5 mm received from the cars tyres waste,
- polyurethanes, i.e. Chemolan M (obtained from the mixture of toluene 2,4-diisocyanate – 80 mass% and toluene 2,6-diisocyanate – 20 mass% and polyoxypropylene 2000) with 5.6–5.9% free NCO groups; Chemolan M-50 (obtained from mixture of 4,4’-methylenebis(phenyl isocyanate) – 60 mass% and mixture of toluene 2,4-diisocyanate – 80 mass% and toluene 2,6-diisocyanate – 20 mass% – 40 mass% and polyoxypropylene 2000) with 8.0% free NCO groups and Chemolan B-3 (obtained from 4,4’-methylenebis(phenyl isocyanate) and polyoxypropylene 2000) with 10.0% free NCO groups (from Interchemol sp. z o.o., Oborniki Śląskie, Poland).

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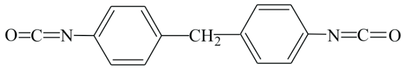
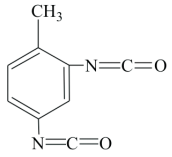
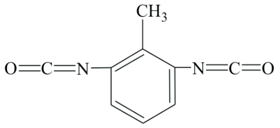


4,4'-methylenebis(phenyl isocyanate) (MDI)



toluene 2,4-diisocyanate (TDI 2,4)



toluene 2,6-diisocyanate (TDI 2,6)

The rubber waste-polyurethane composites contained 10, 15, 20, 25 or 30 mass% of suitable polyurethanes (Chemolan M, Chemolan M-50 or Chemolan B-3) and 90, 85, 80, 75 or 70 mass% of fine rubber. To obtain proper compositions the polyurethanes were mixed in proportion listed above, with fine rubber and transferred into moulds. The prepared profiles of compositions were kept at a temperature of 363 K under pressure of $6.10\cdot10^6$ Pa during one and half hours for all compositions. After this time they were kept cooled still under pressure on the air.

Thermogravimetric analysis (TG) of the samples was conducted using Perkin-Elmer TGA Pyris 1 thermal analyser. For TG analysis a ca. 0.5 mg sample was heated to 900 K at 5, 10, 20 or 40 K min^{-1}, using nitrogen as the purge gas (Fig. 1). The mass of the sample was continuously measured as a function of temperature and the rate of mass loss (DTG) was automatically recorded.

Results and discussion

Stable, non-homogeneous waste rubber granulates–polyurethane composites, obtained from polyurethane components with different isocyanate constituent (MDI, TDI isomers or MDI and TDI isomers mixture), with good mechanical properties were obtained. The composites as well as the polyurethane agents and granulated used rubber pyrolysed.

The TG curves of the fine rubber, the polyurethane prepolymers, and the composites, prepared under pressure $6.10\cdot10^6$ Pa, represent results for the four heating rates. An example of TG and DTG curves for fine rubber, fine rubber+polyurethane composite with 20 mass% Chemolan B3 and pure Chemolan B3 is shown in Fig. 1 for two heating rates (5, 40 K min^{-1}). For all DTG curve temperatures T_1, T_{max1}, T_2, T_{max2}, T_3 were assigned. The points at which the temperatures

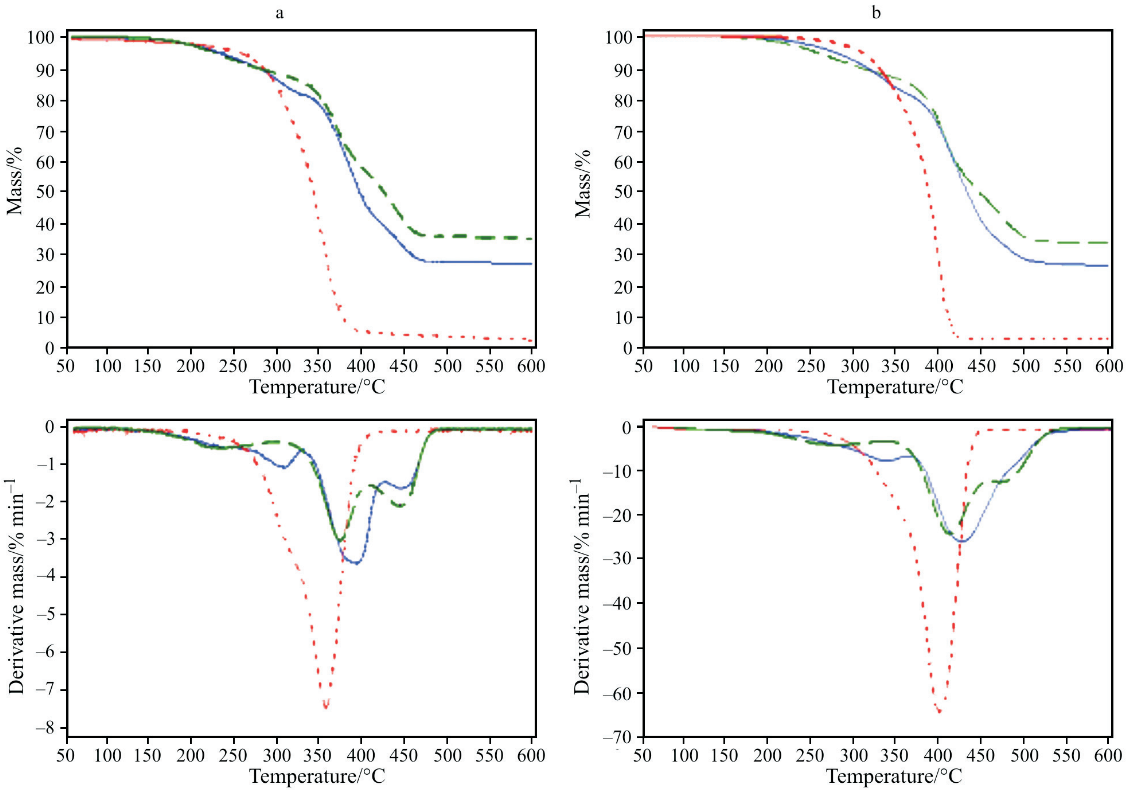


Fig. 1 TG and DTG curves at a – 5 and b – 40 K min^{-1} heating rate; --- – fine rubber, —– – urethane rubber composite with 20% polyurethanes, ··· – Chemolan B3 [5]

were assigned are shown in Fig. 2. Precise assignment of the T_1 is difficult, owing to the problem of deciding when the major mass loss begins, whereas T_{max1}, T_{max2}, T_2 and T_3 are easier to determine.

According to TG data it was found that two-stage decomposition of the tyre rubber was observed. The results of our investigation suggest that the low-temperature and high temperature decompositions occurred due to the decomposition of natural rubber (NR) and styrene-butadiene rubber (SBR) and/or polybutadiene rubber (BR), respectively [5]. It was also found that the decomposition of suitable polyurethane occurs at a temperature range characteristic for low-temperature decomposition of tyre rubber (±10°C). Therefore, one can suppose that the low-temperature decomposition, recorded for the studied composites, reflected the decomposition of NR, which is probably a component of tyres and adequate polyurethane. The high-temperature decomposition found for the studied composites is only related to the decomposition of the rubber waste. For all polyurethane polymers prepared from the suitable polyurethane prepolymers it can be seen that the thermal decomposition starts at about the same temperature as fine rubber and composites decompositions, and only the one-stage mass loss is observed.

To assume a first-order reaction for devolatilisation activation energy for composites were calculated [5]. Average value of overall activation energies of lower-temperature and higher-temperature decom-

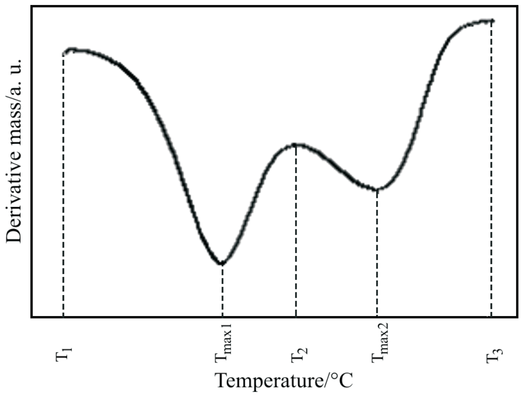


Fig. 2 DTG terminology for Table 1. The points at which the temperatures (T_1, T_{max1}, T_2, T_{max2}, T_3) were assigned

Table 1 Example temperature characteristic and kinetic parameters for thermal decomposition fine rubber, Chemolan B3 and composites samples by TG, pressure 6.10·10^6 Pa, reaction order 1/2

n=2		Heating rate/ K min^{-1}	Temperature/°C					Decomposition stage			
Fine rubber/%	M/%							Pre-exponential factor, A/s^{-1}		Activation energy, E_a/kJ mol^{-1}	
			T_1	T_{max1}	T_2	T_{max2}	T_3	low	high	low	high
100	0	5	300	369	404	441	492	$7.7\cdot10^5$	$2.6\cdot10^{11}$	233.18	433.44
		10	315	383	417	458	515	$3.9\cdot10^6$	$3.9\cdot10^{11}$	258.06	446.86
		20	328	394	431	464	525	$6.1\cdot10^6$	$2.3\cdot10^{11}$	269.02	447.45
		40	337	406	451	478	545	$1.1\cdot10^6$	$5.6\cdot10^{11}$	252.71	471.10
90	10	5	304	373	409	434	494	$6.4\cdot10^5$	$1.4\cdot10^{10}$	231.78	394.15
		10	317	390	430	451	503	$7.0\cdot10^5$	$5.6\cdot10^{13}$	239.49	520.79
		20	323	399	441	462	516	$2.9\cdot10^5$	$4.6\cdot10^{13}$	231.99	523.98
		40	332	412	445	474	522	$1.4\cdot10^5$	$1.9\cdot10^{12}$	225.57	482.49
85	15	5	310	377	410	444	484	$9.7\cdot10^6$	$1.4\cdot10^{13}$	266.55	488.36
		10	319	388	426	450	505	$3.8\cdot10^6$	$4.5\cdot10^{12}$	260.17	482.85
		20	321	397	438	453	497	$2.0\cdot10^5$	$5.1\cdot10^{16}$	226.55	616.43
		40	339	412	456	477	533	$5.9\cdot10^5$	$6.6\cdot10^{13}$	246.42	540.55
80	20	5	309	380	414	446	486	$5.0\cdot10^6$	$9.2\cdot10^{13}$	259.04	515.67
		10	320	388	431	451	506	$2.1\cdot10^6$	$7.8\cdot10^{13}$	253.86	525.51
		20	328	404	449	469	524	$6.3\cdot10^5$	$1.6\cdot10^{13}$	243.59	514.41
		40	339	415	459	481	536	$4.7\cdot10^5$	$4.4\cdot10^{13}$	244.26	536.06
75	25	5	310	348	421	448	490	$2.6\cdot10^6$	$1.5\cdot10^{13}$	252.81	494.59
		10	328	398	434	462	513	$7.6\cdot10^6$	$2.3\cdot10^{12}$	271.94	478.32
		20	332	407	446	461	503	$1.1\cdot10^6$	$4.3\cdot10^{16}$	251.53	619.45
		40	345	418	459	478	523	$1.1\cdot10^6$	$7.4\cdot10^{13}$	255.90	539.94
70	30	5	319	394	420	447	478	$3.9\cdot10^7$	$4.3\cdot10^{16}$	286.77	600.07
		10	323	408	434	461	501	$3.3\cdot10^6$	$5.5\cdot10^{14}$	261.24	552.56
		20	341	420	455	474	521	$3.0\cdot10^6$	$2.6\cdot10^{15}$	266.59	589.43
		40	348	426	466	482	527	$3.1\cdot10^6$	$3.3\cdot10^{15}$	270.70	600.19
0	100	5	318	357	380			$4.8\cdot10^{16}$		522.43	
		10	332	371	408			$1.3\cdot10^{19}$		601.77	
		20	338	383	419			$3.8\cdot10^{15}$		512.94	
		40	355	394	431			$2.9\cdot10^{17}$		578.76	

positions of composites was 281.3 kJ mol^{-1} for Chemolan B3 (MDI) composites (calculated from determined data of activation energy of fine rubber and suitable polyurethane and amount of these components in composites – 262.2 kJ mol^{-1}), 301.2 kJ mol^{-1} for Chemolan M (TDI isomers) composites (calculated – 277.6 kJ mol^{-1}), and 278.4 kJ mol^{-1} for Chemolan M50 (MDI+TDI isomers mixture) components (calculated – 265.6 kJ mol^{-1}). Differences between determined and calculated results could suggest a possible reaction of polyurethane with rubber during the composites formation. The highest determined and calculated average activation energy showed composites obtained from Chemolan M (TDI isomers) but the differences between determined and calculated activation energy showed composites obtained from Chemolan B3 with highest value of free NCO groups.

Using the same thermogravimeric data and assume the orders of the reaction of devolatilisation of 1/2, 1, 3/2 and 2, activation energy for composites were calculated [10].

In the reaction $\mathrm{aA_{(s)} \rightarrow bB_{(s)} + cC_{(g)}}$ the rate of disappearance of A may be expressed by:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(1-\alpha)^{\mathrm{n}} \tag{1}$$

where α=fraction of A decomposed at time t, n=order of reaction and k=rate constant given by Arrhenius equation:

$$k = A\mathrm{e}^{-\mathrm{E_a/RT}} \tag{2}$$

where A=the pre-exponential factor and E_a=activation energy of the reaction.

For the linear heating rate of, say, a, K min^{-1}:

$$a = \mathrm{d}T/\mathrm{d}t \tag{3}$$

Combining Eqs (1)–(3), rearranging and integrating we get:

$$\int_0^\alpha \frac{\mathrm{d}\alpha}{(1-\alpha)^{\mathrm{n}}} = \frac{A}{a}\int_0^{\mathrm{T}} \mathrm{e}^{-\mathrm{E_a/RT}}\mathrm{d}T \tag{4}$$

After resolving Eq. (4) and taking logs we get for all n values except n=1:

$$\log\left[\frac{1-(1-\alpha)^{1-\mathrm{n}}}{T^2(1-n)}\right] = \log\frac{AR}{aE_\mathrm{a}}\left(1-\frac{2RT}{E_\mathrm{a}}\right) - \frac{E_\mathrm{a}}{2.3RT} \tag{5}$$

for n=1

$$\log\left[-\log\frac{(1-\alpha)}{T^2}\right] = \log\frac{AR}{aE_\mathrm{a}}\left(1-\frac{2RT}{E_\mathrm{a}}\right) - \frac{E_\mathrm{a}}{2.3RT} \tag{6}$$

thus a plot of either

$$\log\left[\frac{1-(1-\alpha)^{1-\mathrm{n}}}{T^2(1-n)}\right] \quad vs. \quad \frac{1}{T}$$

or, where n=1

$$\log\left[-\log\frac{(1-\alpha)}{T^2}\right] \quad vs. \quad \frac{1}{T}$$

should result in a straight line of slope $-E_\mathrm{a}/2.3R$ for the correct value of n, since it may be shown that for most values of E_a and for the temperature range over which reactions generally occur the expression

$$\log\frac{AR}{aE_\mathrm{a}}\left(1-\frac{2RT}{E_\mathrm{a}}\right)$$

is sensibly constant.

The activation energy values and pre-exponential factors for the respective assumed just the same reaction orders of primary and secondary processes of the thermal destruction of fine rubber, Chemolan M50, M and B3 and rubber-polyurethane composites were determined from TG data using described above equations. Example – results were presented in the Table 1.

Determination of activation energy and analysis of results for every from of reaction order one ought to drive separately.

For so inhomogeneous materials as rubber and polyurethane composites seems that comparing of results of calculations makes sense only for average value of the activation energy of decomposition processes. Calculated on the ground of TG data the activation energy values for polyurethanes and fine rubber were averaged and presented in the Table 2. Activation energy values of the decomposition process of pure polyurethane plastics, for the reaction order 1, 3/2 and 2, decrease in the following order:

Chemolan M (TDI)>Chemolan B3 (MDI)>Chemolan M50 (MDI+TDI)

for reaction order

1	321.43 kJ mol^{-1}	228.07 kJ mol^{-1}	216.53 kJ mol^{-1}
3/2	424.40 kJ mol^{-1}	326.96 kJ mol^{-1}	284.53 kJ mol^{-1}
2	553.98 kJ mol^{-1}	448.66 kJ mol^{-1}	369.81 kJ mol^{-1}

For the reaction order 1/2 this relation changes to following relation:

Chemolan M (TDI)>	Chemolan M50 (MDI+TDI)>	Chemolan B3 (MDI)
(252.65 kJ mol^{-1})	(170.21 kJ mol^{-1})	(168.56 kJ mol^{-1})

Previously, making calculations according to other equations [5], for assumed first-order reaction one obtained the relation:

Chemolan M (TDI)>	Chemolan M50 (MDI+TDI)>	Chemolan B3 (MDI)
(226.6 kJ mol^{-1})	(166.7 kJ mol^{-1})	(149.0 kJ mol^{-1})

as for present driven calculations for assumed reaction order equal 1/2.

For composites with the fine rubber, the activation energy values for assumed values of devolatilization reaction orders were estimated from TG data.

Table 2 Range and average activation energies (E_a) of fine rubber and polyurethanes: Chemolan B3, Chemolan M and Chemolan M50

Reaction order		E_a/kJ mol^{-1} of decomposition stage			
		Low	Average	High	Average
1/2	fine rubber	158.98–178.79	169.66	147.88–180.00	157.59
	Chemolan B3	133.60–185.92	168.56		
	Chemolan M	222.00–289.43	252.65		
	Chemolan M50	136.27–197.04	170.21		
1	fine rubber	179.30–203.42	192.50	213.91–246.84	227.18
	Chemolan B3	178.73–254.78	228.07		
	Chemolan M	288.11–359.92	321.43		
	Chemolan M50	173.02–248.79	216.53		
3/2	fine rubber	204.09–233.50	220.39	316.47–332.58	325.49
	Chemolan B3	261.98–368.79	326.96		
	Chemolan M	387.46–457.28	424.40		
	Chemolan M50	226.16–325.91	284.53		
2	fine rubber	233.18–269.02	253.24	433.44–471.10	449.71
	Chemolan B3	367.73–513.89	448.66		
	Chemolan M	512.94–601.77	553.98		
	Chemolan M50	292.51–422.80	369.81		

Table 3 Average activation energies (E_a) of rubber–polyurethane composites prepared from fine rubber and suitable polyurethane

Reaction order		E_a/kJ mol^{-1}		
		Det.	Calc.	Diff.
1/2	Chemolan B3	178.56	170.26	8.30
	Chemolan M	178.13	186.26	–8.13
	Chemolan M50	169.37	169.77	–0.40
1	Chemolan B3	232.00	200.69	31.31
	Chemolan M	230.67	218.28	12.39
	Chemolan M50	217.73	197.30	20.43
3/2	Chemolan B3	306.60	243.07	63.53
	Chemolan M	302.39	261.19	41.20
	Chemolan M50	281.54	233.21	48.33
2	Chemolan B3	399.65	294.02	105.63
	Chemolan M	391.56	313.39	78.17
	Chemolan M50	361.49	277.00	84.49

det. – determined, calc. – calculated, diff. – differences

These values were also calculated from the percentage of these composites, from suitable component values of the activation energy and from their fraction. For these composites one calculated also average values of the activation energy from all measurements and calculations and the results are presented in the Table 3.

Between average values of the activation energy determined from all measurement for composites and calculated values from the percentage appear differences which can point on reactions between the fine rubber and the polyurethane what one showed already previously [3, 5, 11, 12].

It is clear that values determined from measurement and calculated are different. For the reaction order 1, 3/2 and 2 the highest averaged value of the activation energy one observes for composites obtained from Chemolan B3 (MDI) (for all reaction order). Differences between the experimental activation energy and the theoretical for composites decrease following:

Chemolan B3 (MDI)>Chemolan M50 (MDI+TDI)>Chemolan M (TDI)

for reaction order:

1	31.31 kJ mol^{-1}	20.43 kJ mol^{-1}	12.39 kJ mol^{-1}
3/2	63.53 kJ mol^{-1}	48.33 kJ mol^{-1}	41.20 kJ mol^{-1}
2	105.63 kJ mol^{-1}	84.49 kJ mol^{-1}	78.17 kJ mol^{-1}

previously [5]

Chemolan M (TDI)>Chemolan B3 (MDI)>Chemolan M50 (MDI+TDI)
(28.6 kJ mol^{-1}) (18.9 kJ mol^{-1}) (12.5 kJ mol^{-1})

For average values of the decomposition activation energy determined from TG measurement of composites prepared from the fine rubber the following dependence is observed:

Chemolan B3 (MDI)>Chemolan M (TDI)>Chemolan M50 (MDI+TDI)

for reaction order:

1/2	178.56 kJ mol^{-1}	178.13 kJ mol^{-1}	169.37 kJ mol^{-1}
1	232.00 kJ mol^{-1}	230.67 kJ mol^{-1}	217.73 kJ mol^{-1}
3/2	306.60 kJ mol^{-1}	302.39 kJ mol^{-1}	281.54 kJ mol^{-1}
2	399.65 kJ mol^{-1}	391.56 kJ mol^{-1}	361.49 kJ mol^{-1}

previously [5]

Chemolan M (TDI)>Chemolan B3 (MDI)>Chemolan M50 (MDI+TDI)
(301.2 kJ mol^{-1}) (281.3 kJ mol^{-1}) (278.4 kJ mol^{-1})

For the values of the decomposition activation energy calculated from composites composition prepared from the fine rubber and values of the activation energy estimated for components one observes other relation:

Chemolan M (TDI)>Chemolan B3 (MDI)>Chemolan M50 (MDI+TDI) for reaction order:

1/2	186.26 kJ mol^{-1}	170.26 kJ mol^{-1}	169.77 kJ mol^{-1}
1	218.28 kJ mol^{-1}	200.69 kJ mol^{-1}	197.30 kJ mol^{-1}
3/2	261.19 kJ mol^{-1}	243.07 kJ mol^{-1}	233.21 kJ mol^{-1}
2	313.39 kJ mol^{-1}	294.02 kJ mol^{-1}	277.00 kJ mol^{-1}

previously [5]

Chemolan M (TDI)>Chemolan M50 (MDI+TDI)>Chemolan B3 (MDI)
(277.6 kJ mol^{-1}) (265.6 kJ mol^{-1}) (262.2 kJ mol^{-1})

Described relations are just the same for every from assumed reaction orders.

TG studies and results of calculations of the activation energy values obtained previously [5] and at present show clearly that the manner of making calculations, more than the assumed order of primary and secondary devolatilization reactions has the influence on obtained results and possibilities of their interpretation. The disagreement of calculation results performed according to other equations need explanation. For composites the ascertainment in every case of the difference between activation energy values estimated from TG measurements and calculated from the amount of the components in composites, shows only on reaction of the polyurethane with the fine rubber. Because of this, one should have to consider which from assumed reaction order and manners of conducting calculation of the activation energy best reflect the investigated processes of composites devolatilization. This analysis was conducted by the comparison of correlation coefficients values calculated from the equation (Table 4).

$$\ln k \quad vs. \quad \frac{1}{T}$$

Table 4 Average correlation factors for fine rubber and polyurethanes

Reaction order		Correlation factors of decomposition stage	
		Low	High
1/2	fine rubber	0.9487	0.7981
	Chemolan B3	0.8430	
	Chemolan M	0.9215	
	Chemolan M50	0.9058	
1	fine rubber	0.9724	0.9209
	Chemolan B3	0.9446	
	Chemolan M	0.9781	
	Chemolan M50	0.9689	
3/2	fine rubber	0.9798	0.9788
	Chemolan B3	0.9884	
	Chemolan M	0.9800	
	Chemolan M50	0.9900	
2	fine rubber	0.9681	0.9803
	Chemolan B3	0.9757	
	Chemolan M	0.9379	
	Chemolan M50	0.9694	

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] \quad vs. \quad \frac{1}{T}$$

$$\log\left[-\log\frac{(1-\alpha)}{T^2}\right] \quad vs. \quad \frac{1}{T}$$

For Chemolan B3, M and M50 the best fitting of straight line appears in the case, when the assumed reaction order amounted 3/2. Similarly for the first range of fine rubber decomposition the highest value of the correlation coefficient was reached for n=3/2. The best fit to straight line on graphs prepared for the second range of fine rubber decomposition was reached at the assumed reaction order equal to 2. Just the same dependences as for the fine rubber was observed for all composites. Average values of composites correlation coefficients in the dependence of the reaction order are presented in the Table 5. For low temperature range decomposition of every from received composites the best fit to straight line was reached at the reaction order equal to 3/2. Values of the correlation coefficient for the high-temperature decomposition range are close to unities when the reaction order amounts 2. The calculated reaction order of the styrene-butadiene rubber or suitable range of low-temperature decomposition was 1.3 and for high-temperature was equal 1.9 [13].

Lowest values of correlation coefficients for fine rubber, Chemolan M, M50, B3 and for all composites were in the case when assumed reaction order was 1/2, what can explain the values of decomposition activation energy presented in Table 3 for this reaction order. Great differences of correlation coefficient values may be the source of the lack compliance of results of preceding calculations with these presented now. Results obtained at present and presented previously [5] can show however on the more exact calculation of the activation energy calculation value according to nowa-

Table 5 Average correlation factors for rubber–polyurethane composites

Reaction order		Correlation factors of decomposition stage	
		Low	High
1/2	Chemolan B3	0.8774	0.7674
	Chemolan M	0.9483	0.7823
	Chemolan M50	0.9363	0.7781
1	Chemolan B3	0.9528	0.8893
	Chemolan M	0.9742	0.9032
	Chemolan M50	0.9664	0.9032
3/2	Chemolan B3	0.9722	0.9634
	Chemolan M	0.9813	0.9691
	Chemolan M50	0.9760	0.9601
2	Chemolan B3	0.9683	0.9771
	Chemolan M	0.9666	0.9820
	Chemolan M50	0.9627	0.9697

days accepted rules and on the acceptance of the devolatilization reaction order equal 3/2. Results of previously performed mechanical research, DSC and DMTA show on this also [5, 11, 12]. In compliance with these researches the best to preparing the polyurethane-rubber composites was found Chemolan B3 polyurethane prepolymer, having highest content of free isocyanate groups, prepared with the use of the isocyanate MDI.

One ought however to ascertain that aside from the manner of the activation energy calculations the results of TG research clearly show on reacting of the polyurethane with the rubber in received composites.

Conclusions

According to the TG measurements, the thermal degradation of the composites shifted to higher temperatures with increasing heating rate. Majority of the composites, as the fine rubber sample, showed two distinct mass loss steps. Two-stage decomposition shown by composites suggests that the low-temperature decomposition is due mainly rubber waste and suitable polyurethane components whereas the high-temperature decomposition is due to the decomposition of rubber waste. The thermal decomposition of the composites could be related to the structure of the isocyanate components of the polyurethane.

The kinetic parameters (pre-exponential factor and activation energy) were determined for components and composites in relation to heating rate to assume 1/2, 1, 3/2 and 2 order reaction for devolatilisation. At higher temperatures activation energy decreases with increasing heating rate. Differences between determined and calculated results of average of overall activation energies could suggest a possible reaction of polyurethane with rubber during the composites formation too what was postulated before as well. One can suppose that the more stable composites obtained from Chemolan B3 with highest value of free NCO groups.

On the base of presented results it seems that the possibility of drawing correct conclusions from thermogravimetric studies and from performed calculations of the activation energy depends in the less degree on the accepted manner of calculations and on established, in well-founded limits, of the reaction order. Higher dependence was found on the straight line correlation coefficients values used to the calculation of the activation energy value.

Nomenclature

T_1	temperature of the first stage of decomposition (low-temperature decomposition) when mass loss starts
$T_{\max1}$	temperature at which the low-temperature decomposition has the highest rate
T_2	temperature of the second stage of decomposition (high-temperature decomposition)
$T_{\max2}$	temperature at which the high-temperature decomposition has the highest rate
T_3	end temperature of decomposition

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