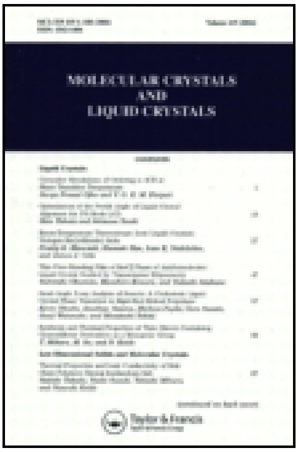

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Thermogravimetric Analysis of Composites Obtained from Polyurethane and Rubber Waste

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The thermogravimetric analysis was applied for indication of the thermal stability of polyurethane-rubber composites received from polyurethane and rubber waste. The results of the thermogravimetric analysis show that the decomposition of rubber granulate depends on the speed of heating. It starts within the temperature range from 320°C to 360°C and is completed at the temperature range from 500°C to 550°C. The evaporation of small-molecular substances probably takes place below 300°C. At temperatures above 320°C, two-stage decomposition of rubber and polyurethane-rubber waste composites was observed. The low temperature decomposition of rubber probably corresponds to the decomposition of natural rubber (NR) while the high temperature decomposition corresponds to decomposition of styrene-butadiene rubber (SBR) or/and butadiene rubber (BR). The thermogravimetric studies of the polyurethanes obtained from different isocyanates showed that the increase of thermal stability depends on the isocyanate used. The one-stage decompositions of different polyurethanes were observed. Polyurethane-rubber composites undergo two-stage decomposition. Thus, the low temperature decomposition of composites may be connected to the decomposition of suitable polyurethane and NR, and the high temperature decomposition may be connected to the decomposition of SBR or/and BR as it was observed for rubber granulate.

Tested samples of composites contained polyols of the trade name Recypol® 201 and Recypol®601 received from used polyurethane foam and of rubber recyclate received from tyres in the form of a granulate of dimensions ranging from 1.5 to 2.0 mm. The percentage ratio of polyurethane glue/rubber granulate: 5/95; 7.5/92.5; 10/90 was chosen. The profiles of composites were held at the temperature of 90°C for 90 min under the load of and $2 \cdot 10^6$ Pa. Thermogravimetric analysis of the samples was conducted using Perkin Elmer TGA PYRIS. Measurements were performed at the temperatures from 25°C to 900°C, with heating rates of 20°C/min, 40°C/min, 80°C/min using nitrogen as the purge gas. The value of the apparent activation energy of decomposition processes of the composites is reported.

Keywords Polyurethane; polyurethane-rubber composites; thermogravimetric analysis (TGA); thermal stability

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Introduction

The thermogravimetric analysis (TGA) allows us to determine the thermal stability of polymeric materials, which is one of the criteria needed in the designing and manufacturing of goods whose thermal stability is required. The thermal stability of a material is described as the limit temperature, and means that the material can be used with no damage to its usable properties [1]. Due to the large range of polyurethane applications, e.g. the components of composites, specific emphasis was given to their analyses, and in particular to their thermogravimetric analysis [2–5].

Analyses on thermal decomposition of polyurethanes showed that, in most cases, it is a complex and heterogeneous, two-phase or three-stage process, during which only a few partial reactions occurred [6–12]. The first stage of thermal decomposition of polyurethanes is connected to the degradation of hard segments. The rate of this phase depends on a number of soft segments. A large number of hard segments in the polyurethane structure results in a slowing down of this stage. The second and the third stages are considerably slower than the first one, and they are connected with the decomposition of soft polyurethane segments. The polyurethanes with a larger share of soft segments initially shows a lower mass loss and a higher temperature at the beginning of the decomposition process [13].

It was noticed that the temperature at the beginning of polyurethane decomposition process depends on the isocyanate structure and a type of diol used to obtain them. It was stated that the polyurethanes synthesised from aromatic diisocyanates, like toluene diisocyanate (TDI) and 4,4′-methylenebis (phenyl isocyanate) (MDI) have a thermal stability that is worse than polyurethanes synthesised from m-xylene diisocyanate (XDI) [14].

The thermogravimetric analysis of polyurethanes obtained with glycolysates of polyurethane foams as a component showed that, in contrast to the polyurethanes obtained by means of commercial diols, the former are characterised by a somewhat lesser thermal stability [15,16]. The deterioration of polyurethane properties starts at the temperature range of 274°C and 292°C, whereas at 300°C, a 10% loss in mass of the sample occurs.

Analyses of the thermal stability of goods obtained from the recyclable car tyres were also conducted. Rubber mixes, which are usually used in the production of car tyres, are a mixture of two or three types of rubber; natural rubber (NR), styrene-butadiene rubber (SBR) and butadiene rubber (BR). The thermogravimetric analysis shows that there is more than one temperature at which the decomposition process takes place with a maximum rate for rubber obtained from these types of mixes [17–19].

The thermogravimetric analyses of three samples of car tyres, with the pre-defined content of NR, SBR i BR, heated at the rate of 5 to 80 K min^{-1}, proved that along with the increase in heating rate, a shift of decomposition process towards higher temperatures also occurs. It was also stated that the temperature at which the rate of decomposition process for different rubbers had the highest value was higher for SRB and lower for NR. In the case of BR, decomposition is a two-stage process. Thus, one may notice two temperatures at which the rubber decomposition process is proceeding at the highest rate [20].

The thermogravimetric analysis of rubber-polyurethane composites obtained with recyclable car tyres and various polyurethane glues showed that decomposition is a two-stage process. Processes taking place at a lower temperature correspond to the decomposition of rubber and polyurethane, whereas decomposition processes proceeding at a higher temperature probably correspond to rubber decomposition only. Furthermore, it was stated that the course of thermal decomposition may depend on the structure of the isocyanate, which is one of the components of polyurethane glues [21,22].

Table 1. The polyurethane glues

% quantity of polyol		Isocyanate (MDI) index NCO
Recypol®201	Recypol®601	
30	70	150
50	50	175
70	30	

Since the structure of the polyurethane used for obtaining of rubber-polyurethane composites may have a significant impact on their properties and thermal resistance, it is recommended to carry out thermogravimetric analyses of composites received with tyre crumb and polyurethane glues obtained from diols received from recyclable polyurethane foams and MDI.

Experimental

Materials and Methods

Samples of rubber-polyurethane composites, of defined contents, were used for the analyses. At the first stage, polyurethane glues were received from the mix of Recypol®201 and Recypol®601 polyols (obtained through the chemical recycling of chips of recyclable polyurethane goods, by means of glycolysis developed by Rampf Ecosystems GmbH from Germany) and 4,4′-diphenylmethane diisocyanate (MDI) from the Elastogran company. An excess of isocyanate marked with NCO index was adopted (Table 1).

At the second stage, rubber-polyurethane composites were obtained. The composites were obtained from polyurethane glues (obtained at the first stage) and granulated rubber with a grain size of between 1.5 and 2.0 mm, which were obtained from recyclable car tyres (Table 2).

The prepared mixture of granulated rubber and polyurethane was placed in forms under the 2 MPa load and held at a temperature of 90°C for 90 min.

Thermogravimetric analyses of rubber-polyurethane composites, granulated rubber and polyurethane glues were carried out by means of the PYRIS device by Perkin Elmer. Measurements were made within the temperature range between 30°C and 900°C, with the heating rate of 20 K min^{-1}, 40 K min^{-1}, 80 K min^{-1}, and with nitrogen as carrier gas.

Table 2. The polyurethane-rubber composites

% quantity	
Glue	Rubber granulate
5	95
7,5	92,5
10	90

Table 3. Temperature characteristics for the polyurethane glues by TGA

Name of sample	Heating rate K min^{-1}	Temperatures (°C)				
		$T_{1(10\%)}$	T_{max1}	T_2	T_{max2}	T_3
150[30-70]glue	20	311	—	—	390	433
	40	324	350	368	415	485
	80	338	360	378	425	498
150[50-50]glue	20	313	—	—	390	416
	40	324	323	367	410	460
	80	336	343	379	423	469
150[70-30]glue	20	316	334	348	395	439
	40	327	336	368	415	450
	80	337	343	383	428	489
175[30-70]glue	20	312	336	357	394	450
	40	326	348	369	407	462
	80	341	358	379	424	476
175[50-50]glue	20	308	324	355	396	445
	40	327	346	373	410	468
	80	339	353	379	420	482
175[70-30]glue	20	310	335	358	403	449
	40	321	345	375	410	469
	80	337	355	384	422	490

Results and Discussion

Thermogravimetric Analysis

It was stated, on the basis of thermograms of polyurethane glue samples, with various contents of polyols and MDI, that the beginning of the decomposition process for the assumed 10% of the mass loss of the sample occurs at similar temperatures (Table 3).

It may be stated, on the basis of analysis of granulated rubber thermograms, that decomposition of granulated rubber used for the preparation of the composites, starts, depending on the rate, at a temperature range of between 320°C and 360°C, whereas the end of decomposition falls within the temperature range of 500°C–520°C. The temperatures for the beginning and the end of decomposition rise along with the increase in heating rate (Table 4).

Analysing the course of change to TG and DTG curves of granulated rubber (Fig. 1a, b), two distinct areas of mass loss were noticed, with two maxima on the DTG curves denoting

Table 4. Temperature characteristics for the rubber granulate from tyres by TGA

Name of sample	Heating rates K min^{-1}	Temperatures (°C)				
		$T_{1(10\%)}$	T_{max1}	T_2	T_{max2}	T_3
Rubber granulate of car tyres	20	321	391	431	450	498
	40	335	412	450	471	518
	80	362	428	463	490	519

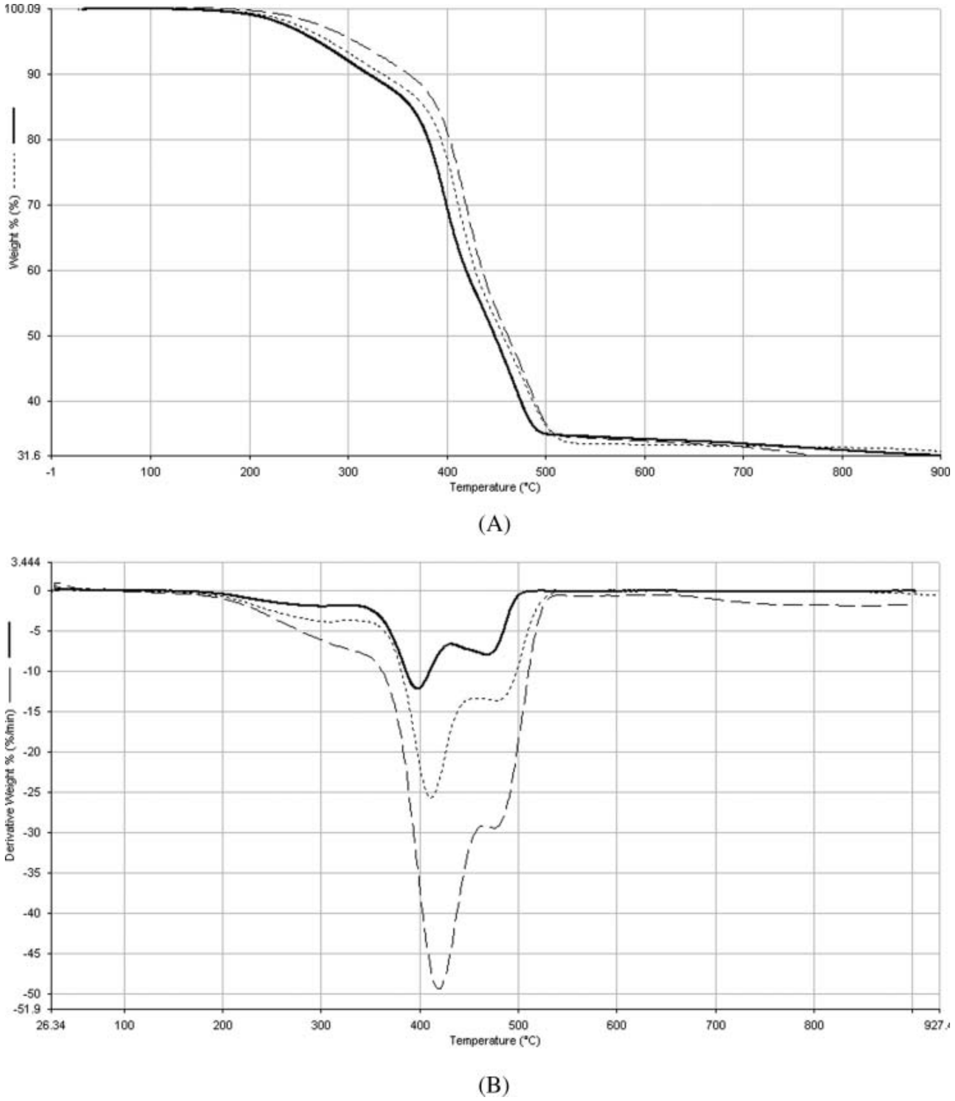
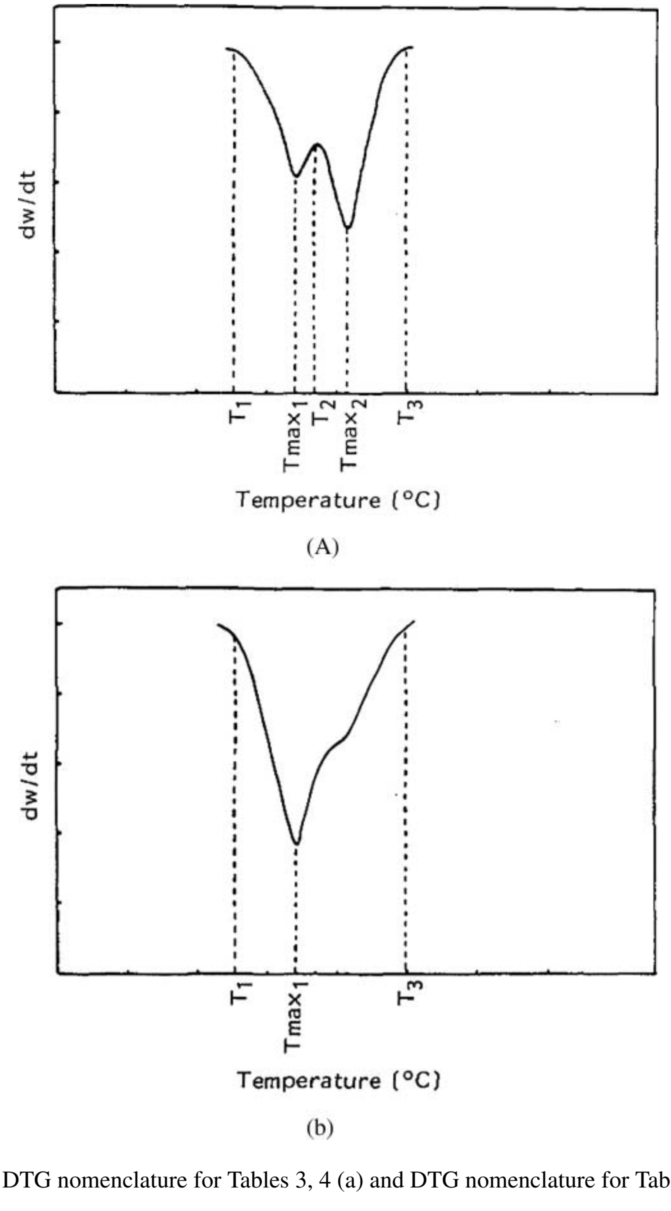


Figure 1. TGA thermograms of rubber granulate (a) and DTG (b) curves at 20°C/min^{-1} (—), 40°C/min^{-1} (···) and 80°C/min^{-1} (**- - -**) heating rate.

temperatures, at which decomposition proceeds with the maximum rate (Fig. 2). The first area of weight-loss during heating, proceeding at lower temperatures, is probably connected to the decomposition of natural rubber (NR). The second area of weight-loss occurs at higher temperatures, and it may be related to the decomposition of butadiene rubber (BR) and/or styrene-butadiene rubber (SBR) [16,19]. The temperatures for the beginning and the end of both decomposition processes were shown in Fig. 2a.

For all analyzed samples of rubber-polyurethane composites within the scope of analyzed heating range, the decomposition process was marked by two areas of mass loss. One distinct area of mass loss occurred at lower temperatures T_{max1} and the second area of mass



(A)

(b)

Figure 2. DTG nomenclature for Tables 3, 4 (a) and DTG nomenclature for Tables 5, 6 (b).

loss occurred at higher temperatures T_{max2} with very unclear inflexions on the DTG line, which hindered the possibility of determining temperatures T_2 and T_{max2}. Thus, the process of composites destruction was marked as a process with one distinct maximum of decomposition rate, and the temperature T_{max} (Fig. 2b), (Tables 5–6). DTG curves of composites may indicate that within the process of composites received, a reaction is occurring between the thiol groups of mechanically granulated rubber and isocyanate groups of polyurethane glues (prepared directly before their application, as a mixture of MDI and polyols obtained through the recycling of polyurethanes) with the formation of a new structure, which was previously suggested [21–24].

Table 5. Temperature characteristics for the polyurethane-rubber composites (NCO150) by TGA

Name of sample	Heating rate K min^{-1}	Temperatures (°C)		
		$T_{1(10\%)}$	T_{max1}	T_3
150[30-70]5/95	20	363	396	503
	40	382	412	535
	80	391	422	560
150[30-70]7,5/92,5	20	365	400	500
	40	376	415	530
	80	388	425	550
150[30-70]10/90	20	361	400	510
	40	373	410	530
	80	386	425	550
150[50-50]5/95	20	372	400	415
	40	373	410	430
	80	389	420	450
150[50-50]7,5/92,5	20	358	400	500
	40	379	410	525
	80	387	425	550
150[50-50]10/90	20	360	400	515
	40	367	415	525
	80	380	425	550
150[70-30]5/95	20	360	395	485
	40	380	410	525
	80	389	420	545
150[70-30]7,5/92,5	20	321	400	515
	40	350	408	525
	80	361	425	560
150[70-30]10/90	20	320	395	485
	40	337	410	525
	80	359	420	560

The beginning of decomposition for the assumed 10% of mass loss for analyzed samples of rubber-polyurethane composites proceeds at higher temperatures than hardened polyurethane glues and granulated rubber, used to obtained the composites, for which the beginning of decomposition process takes place at a lower temperature of around 50°C. This shift in temperature of the beginning of composites decomposition in comparison to the temperature of the beginning of decomposition of pure polyurethane and the decomposition of the granulated rubber may indicate that during the reception of composites, a reaction between thiol groups of mechanically disintegrated rubbers and isocyanate groups of polyurethane glues occurs, which results in the formation of a new more stable structure with the beginning of the decomposition taking place only at higher temperatures (Fig. 3a, b and 4a, b).

Table 6. Temperature characteristics for the polyurethane-rubber composites (NCO175) by TGA

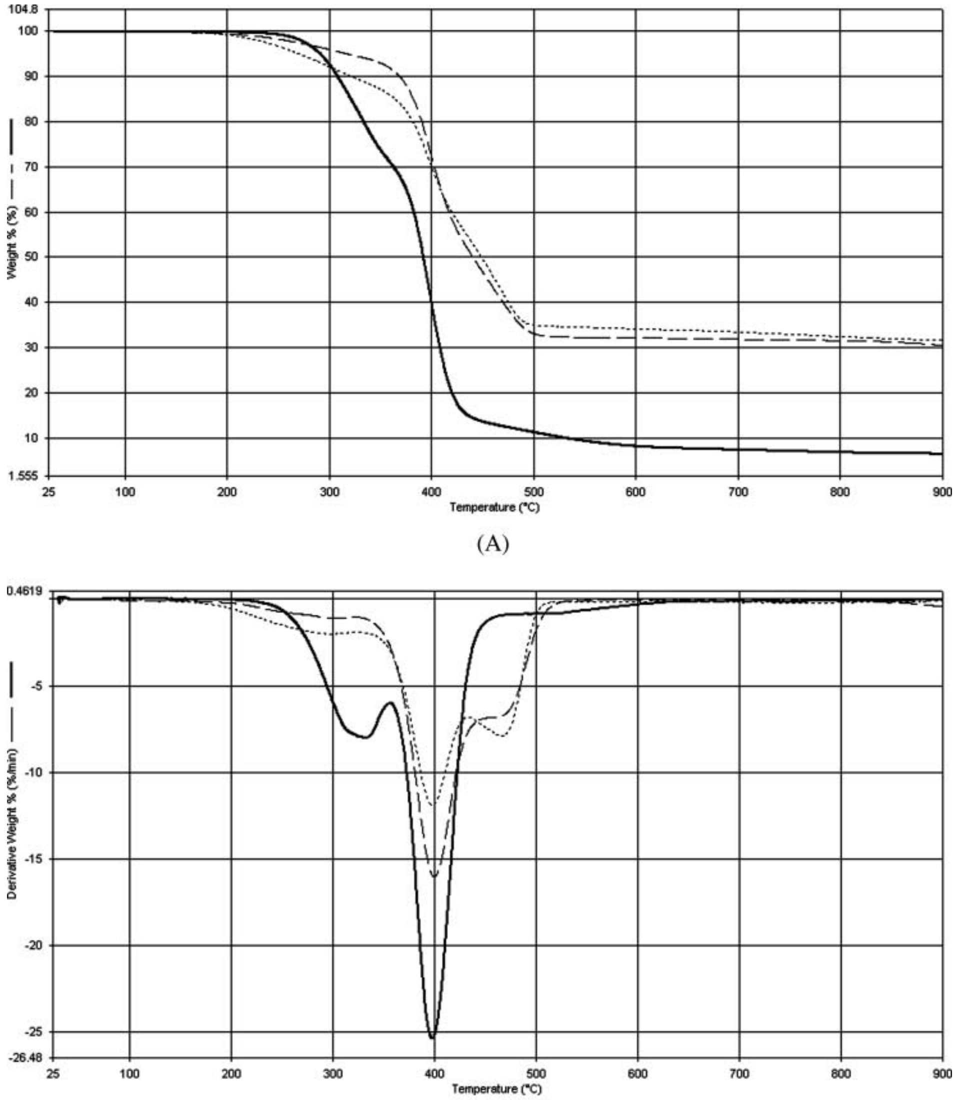
Name of sample	Heating rate K min^{-1}	Temperatures (°C)		
		$T_{1(10\%)}$	T_{max1}	T_3
175[30-70]5/95	20	347	395	485
	40	385	410	515
	80	389	420	545
175[30-70]7,5/92,5	20	358	400	510
	40	373	410	530
	80	382	420	550
175[30-70]10/90	20	347	397	480
	40	373	410	525
	80	377	420	545
175[50-50]5/95	20	368	400	510
	40	377	410	535
	80	390	425	555
175[50-50]7,5/92,5	20	363	400	510
	40	378	410	530
	80	392	420	550
175[50-50]10/90	20	350	400	490
	40	367	410	530
	80	374	425	550
175[70-30]5/95	20	355	400	500
	40	378	410	530
	80	392	420	540
175[70-30]7,5/92,5	20	363	400	490
	40	377	410	525
	80	385	420	545
175[70-30]10/90	20	363	400	515
	40	370	410	530
	80	385	425	550

Kinetics of Thermo-Degradation

The stability of composites made with polyurethane glues and granulated rubber may be estimated on the basis of thermogravimetric measurements of the apparent activation energy of their thermo-degradation process [21–24].

In order to calculate the kinetic parameters of decomposition process, the Kissinger method was used, which relies on the assumption that for different heating rates, the maximum of temperatures equals the greatest heating rate for an analyzed sample, provided that primary and secondary reaction are of n-order [25–27].

The values of apparent activation energies E_a were determined by means of the graphic method, according to the formula (1) on the basis of dependence $ln(\beta/T_m^2)$ on $(1/T_m)$ from the tangent of the line inclination angle. The point of intersection of the straight line with the ordinate corresponds to the values of pre-exponential factor in the Arrhenius equation (2),



(A)

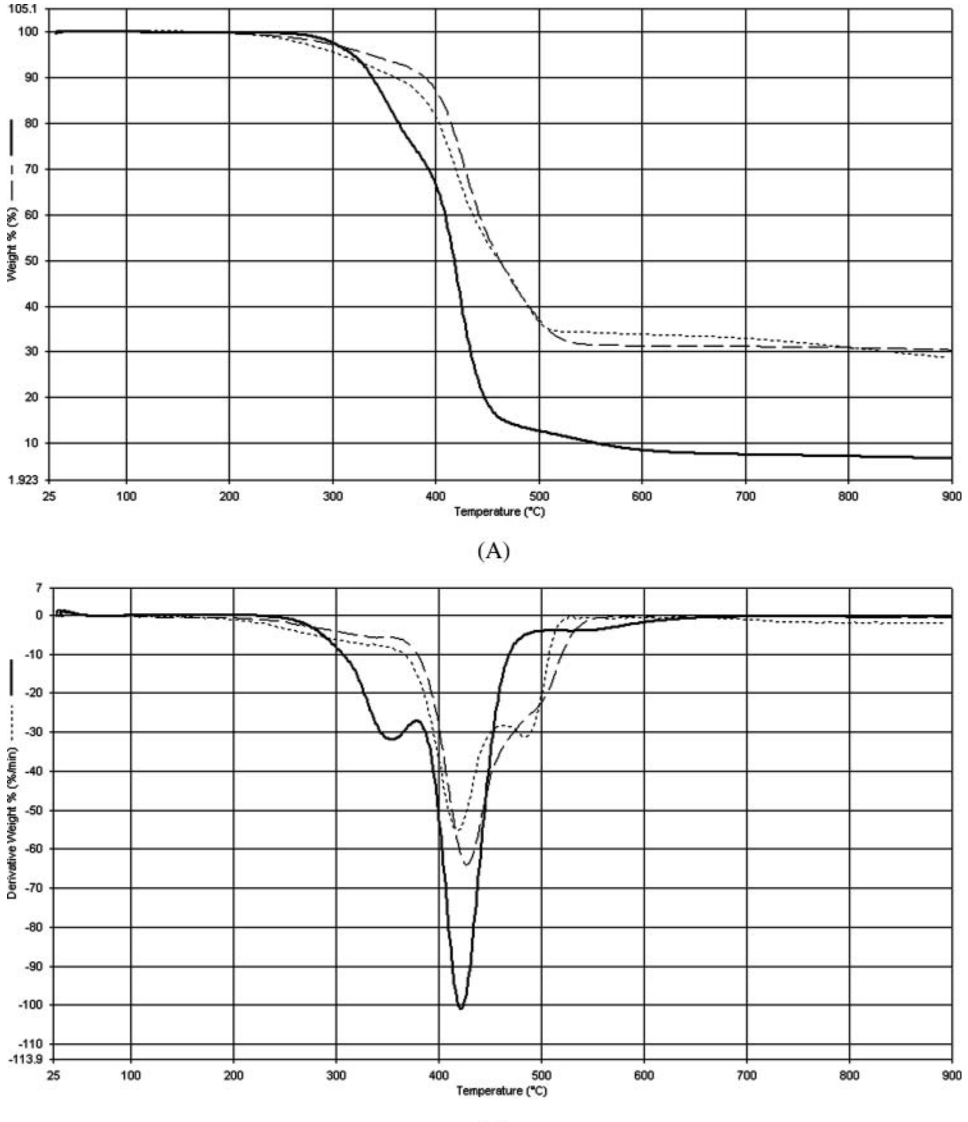
(B)

Figure 3. TGA thermograms (a) and DTG curves (b) at 20 K min^{-1} heating rate ▬ 175[50/50]glue, ⋯ rubber granulate, --- polyurethane-rubber composite 175[50/50]5/95.

which was obtained from the Kissinger equation, under the assumption of the first-order kinetics.

$$\frac{d\left[\ln \frac{\beta}{T_m^2}\right]}{d\left(\frac{1}{T_m}\right)} = \frac{-E_a}{R} \tag{1}$$

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



(A)

(B)

Figure 4. TGA thermograms (a) and DTG curves (b) at 80 K min^{-1} heating rate ━ 175[50/50]glue, ··· rubber granulate, --- polyurethane-rubber composite 175[50/50]5/95.

where β – heating rate of sample, K/min; T_m – temperature, which corresponds to the maximum of the DTG curve for a given heating rate, K; E_a – apparent activation energy, kJ mol$^{-1,}$ R – universal gas constant, (8,3145 J/mol K); k – the Arrhenius rate constant; A – the pre-exponential factor; and T – temperature of measurement, K.

On the basis of the results obtained, one can conclude that the values of apparent activation energies of composites destruction for polyurethane glues increases along with a raise in the isocyanate and polyol Recypol®201 contents in glues (Table 7). The lowest

Table 7. The calculated apparent activation energy E_a (kJ/mol) of thermal degradation By the Kissinger method

Name of sample	Kissinger equation $-E_a/R(1/T) + \ln A$	Correlation factor	Activation energy E_a (kJ mol^{-1})
car tyre rubber granulate	−15934× + 13,958	0,99	132,48
150[30-70]glue	−15815× + 13,803	0,9267	131,49
150[50-50]glue	−17677× + 16,623	0,9792	146,98
150[70-30]glue	−17949× + 16,816	0,9793	149,24
175[30-70]glue	−20030× + 20,049	0,9952	166,54
175[50-50]glue	−25121× + 27,499	0,9877	208,87
175[70-30]glue	−32207× + 37,678	0,9778	267,79
150[30-70]5/95	−22927× + 24,213	0,9775	190,63
150[30-70]7,5/92,5	−214275× + 26,003	0,9828	201,83
150[30-70]10/90	−24391× + 26,265	0,9877	202,80
150[50-50]5/95	−30960× + 35,971	0,9999	257,42
150[50-50]7,5/92,5	−24391× + 26,265	0,9877	202,80
150[50-50]10/90	−24275× + 26,003	0,9828	201,83
150[70-30]5/95	−23911× + 25,744	0,9828	198,81
150[70-30]7,5/92,5	−23688× + 25,273	0,9576	196,95
150[70-30]10/90	−23911× + 25,744	0,9828	198,81
175[30-70]5/95	−23911× + 25,744	0,9828	198,81
175[30-70]7,5/92,5	−30960× + 35,971	0,9999	257,42
175[30-70]10/90	−26423× + 29,390	0,9921	219,69
175[50-50]5/95	−24391× + 26,265	0,9877	202,80
175[50-50]7,5/92,5	−30960× + 35,971	0,9999	257,42
175[50-50]10/90	−24391× + 26,265	0,9877	202,42
175[70-30]5/95	−30960× + 35,971	0,9999	257,42
175[70-30]7,5/92,5	−30960× + 35,971	0,9999	257,42
175[70-30]10/90	−24391× + 26,265	0,9877	202,80

value of apparent activation energy of destruction process 190 kJ mol^{-1} was calculated for composites made from polyurethane glues of the NCO 150 index and the Recypol®201/Recypol®601 polyol contents amounting to 30/70. The highest values of apparent activation energies of destruction process were calculated for composites made from polyurethane glues of the NCO 175 index and the Recypol®201/Recypol®601 polyol contents amounting to 50/50 and 70/30. Therefore, it may be stated that an increase in the participation of free isocyanate groups in polyurethane glues prepared directly before their application (an increase in the NCO index) causes an increase in the value of apparent activation energy. It may thus be assumed that the number of free isocyanate groups has a significant influence on the course of composites receiving process as well as on the properties of the rubber-polyurethane composites.

The impact of free isocyanate groups on properties and stability of rubber-polyurethane composites was previously suggested [21–24]. Thus, the results of conducted analyses may be considered as a confirmation of previous studies.

Conclusions

The results of thermogravimetric analyses of rubber-polyurethane composites show their high thermal stability. This may be connected to the fact that during the reception of composites, a reaction between the thiol groups of mechanically disintegrated rubber and isocyanate groups of polyurethane glues occurs. This reaction is accompanied by the simultaneous creation of a new structure, which results in a considerable shift from the beginning of the decomposition process towards higher temperatures, in comparison with the beginning of the decomposition process of glues and granulated rubber.

The analysis of the values of the apparent activation energy of composites helped us to notice that the lowest apparent activation energy values were calculated for composites made from polyurethane glues with NCO index equal to 150 and the Recypol201/Recypol601 polyol contents amounting to 70/30.

Analyzing the values of the apparent activation energy depending on the amount of isocyanate used for the preparation of polyurethane glues, it was noted that the values for the composites obtained from polyurethane glues of the NCO index equal to 150 were lower than those for composites of polyurethane glues of the NCO index equal to 175. Thus, it is suggested that the amount of the isocyanate affects the apparent activation energy.

Acknowledgments

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References

[1] Fabris, H. J. (1976). *Advances in Urethane Science and Technology*, *4*, 89.
[2] Korah Bina, C., Kannan, K. G., & Ninan, K. N. (2005). *J. Therm. Anal. Cal.*, *78*, 753.
[3] Jasinska, L., Balas, A., Haponiuk, J. H., Nowaczyk, G., & Jurga, S. (2007). *J. Therm. Anal. Cal.*, *88*, 419.
[4] Ginic-Markovic, M., Choudhury, N. R., Matisons, J. G., & Williams, D. R. G. (2000). *J. Therm. Anal. Cal.*, *39*, 469.
[5] Araujo, R. C. S., & Pasa, V. M. D. (2000). *J. Therm. Anal. Cal.*, *67*, 313.
[6] Scaiano, J. C., & Jellinek, H. H. G. (1989). *Elsevier*, *2*, 1.
[7] Lage, L. G., & Kawano, Y. (2001). *J. Appl. Polym. Sci.*, *79*, 910.
[8] Ferguson, J., & Petrovic, Z. (1976). *Eur. Polym. J.*, *12*, 177.
[9] Lee, H. K., & Ko, S. W. (1993). *J. Appl. Polym. Sci.*, *50*, 1269.
[10] Grassie, N., & Mendoza, G. A. P. (1985). *Polym. Degrad. Stabil.*, *11*, 359.
[11] Day, M., Cooney, J. D., & MacKinnon, M. (1995). *Polym. Degrad. Stabil.*, *48*, 341.
[12] Zhang, Y., Shang, S., Zhang, X., Wang, D., & Hourston, D. J. (1995). *J. Appl. Polym. Sci.*, *58*, 1803.
[13] Petrović, Z. S., Zavargo, Z., Flyn, J. H., & Macknight, W. J. (1994). *J. Appl. Polym. Sci.*, *51*, 1087.
[14] Song, Y. M., Chen, W. C., Yu, T. L., Linliu, K., & Tseng, Y. H. (1996). *J. Appl. Polym. Sci.*, *62*, 827.
[15] Datta, J., & Rohn, M. (2007). *J. Therm. Anal. Cal.*, *88*, 437.
[16] Datta, J., & Kacprzyk, M. (2008). *J. Therm. Anal. Cal.*, *93*, 753.
[17] Yang, J., Kaliaguine, S., & Roy, C. (1993). *Rubber Chem. Technol.*, *66*, 213.
[18] Conesa, J. A., & Marcilla, A. (1996). *J. Anal. Appl. Pyrolysis*, *37*, 95.

[19] Lin, J. P., Chang, C. Y., Wu, C. H., & Shih, S. M. (1996). *Polym. Degrad. Stab.*, *53*, 295.

[20] Williams, P. T., & Besler, S. (1995). *Fuel*, *74*, 1277.

[21] Sułkowski, W. W., Mistarz, S., Borecki, T., Moczyński, M., Danch, A., Borek, J., Maciążek, M., & Sułkowska, A. (2006). *J. Therm. Anal. Cal.*, *84*, 91.

[22] Sułkowski, W. W., Danch, A., Moczyński, M., Radoń, A., Sułkowska, A., & Borek, J. (2004). *J. Therm. Anal. Cal.*, *78*, 905.

[23] Danch, A., Sułkowski, W. W., Moczyński, M., Radoń, A., Stezler, F., & Jurga, S. (2004). *J. Appl. Polym. Sci.*, *94*, 1186.

[24] Danch, A., Ilisch, S., Sułkowski, W. W., Moczyński, M., Radoń, A., & Radusch, H. J. (2005). *J. Therm. Anal. Cal.*, *79*, 623.

[25] Bhowmick, A. K., Rampalli, S., Gallagher, K., Seeger, R., & McIntyre, D. (1987). *J. Appl. Polym. Sci.*, *33*, 1125.

[26] Westerhout, R. W. J., Waanders, J., Kuipers, J. A. M., & van Swaaij, W. P. M. (1997). *Ind. Eng. Chem. Res.*, *36*, 1955.

[27] Kissinger, H. E. (1957). *Anal. Chem.*, *29*, 1702.