

THERMOGRAVIMETRIC STUDY OF RUBBER WASTE-POLYURETHANE COMPOSITES

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Abstract

Granulated rubber obtained from used tyres, below 1.5 mm granularity (fine rubber) and polyurethane prepolymers (Chemolan M, Chemolan M50 and Chemolan B3) were used for the synthesis of rubber waste-polyurethane composites, containing 90, 85, 80, 75 and 70% *w/w* of fine rubber. The influence of the kind of polyurethane resin on hardness, elasticity, glass transition temperature and thermal stability of composites was studied. Kinetic parameters of the thermal degradation process of composites were calculated from thermogravimetric analysis (TG) data.

Keywords: rubber waste, rubber waste-polyurethane composites, thermal analysis, used tyres

Introduction

More than 140 000 Mg of rubber wastes are produced in Poland in a year. Used tyres account for about 75% of rubber waste. 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 reclaim consumption *vs.* virgin rubber consumption, depending on the country, is only 1–10%. We observe that the demand for rubber reclaim has decreased in the world [1–3].

The solution of the rubber waste utilisation problem has been prepared by the European Community. The simplest method for its utilisation is combustion with energy recovery. Used rubber may replace conventional fuel due to its low price. It was found that the combustion of 1 Mg of tyres gives 800 kg of steam or 1200 kW of electric energy. The combustion process allows for rapid management of this kind of materials [2, 3].

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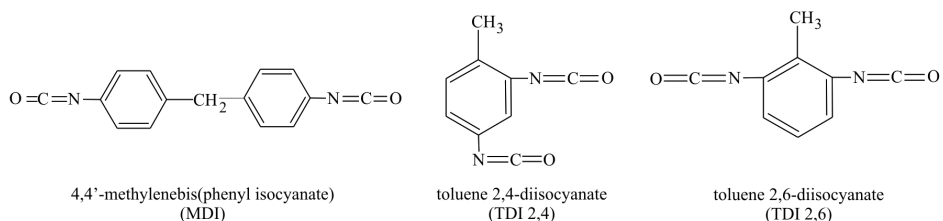
One of the method of the rubber waste management is to break the rubber waste up and use the obtained granulate, fine rubber or rubber dust as a valuable raw material. The increase of the application of products obtained from waste rubber granulate or fine rubber mixed with a small amount of elastomer is observed. These products do not need additional vulcanisation. A thin elastomer layer covering rubber grain polymerises under suitable conditions giving a stable composite. However, the possibility of using this material depends on its properties and stability. Rubber granulates and cast polyurethane elastomers are used for the production of synthetic running tracks in sport and of carpets for foot therapy and foot massage. The waste rubber-polyolefine composites are used for porous element extrusion. Pipes, obtained from these composites can be used for field fertilisation and watering and porous tapes find application for thermal insulation and for vibration damping [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 [3–27]. Regarding the problem of rubber waste management the influence of isocyanate structure on properties of the rubber waste-polyurethane composites was studied.

Experimental

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 car tyres waste,
- polyurethane prepolymers, 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), 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) and Chemolan B-3 (obtained from 4,4'-methylenebis(phenyl isocyanate) and polyoxypropylene 2000) (from Interchemol sp. z o.o., Oborniki Śląskie, Poland).



The rubber waste-polyurethane composites contain 10, 15, 20, 25 or 30 mass% of the suitable polyurethanes (Chemolan M, Chemolan M-50 or Chemolan B-3) and 90, 85, 80, 75 or 70 mass% of fine rubber. Then the obtained mixtures were

transferred into moulds. The prepared profiles of compositions were kept at 363 K under pressure of $2.50 \cdot 10^6$ Pa, of $3.05 \cdot 10^6$ Pa or of $6.10 \cdot 10^6$ Pa for one and a half hour for all compositions. They were cooled under pressure in the air.

Strength testing of the obtained composite profiles was performed according to Polish standards (elasticity PN-88/C-04255 – PN ISO 3383 standard – Shore's method and hardness PN-80/C-04255 – DIN 53505 standard – Schob's method).

Glass transition temperature (T_g) of the rubber waste-polyurethane composites profiles was found by differential scanning calorimetry (DSC). Investigations were carried out on Perkin Elmer Pyris DSC calorimeter at 20 K min^{-1} heating rate, in temperature range 200–370 K for ca. 20 mg mass of sample. 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. The mass of the sample was measured continuously as a function of temperature and the rate of mass loss (DTG) was automatically recorded.

Results and discussion

The rubber waste-polyurethane composites were prepared from granulated rubber (from used tyres) below 1.5 mm granularity (fine rubber) and one component polyurethane prepolymers Chemolan M, Chemolan M-50 and Chemolan B-3 with the hardness similar to the hardness of a fine rubber. Profiles were obtained for each series of composites. Physicochemical properties i.e. strength testing and kinetic parameters of degradation of the obtained compositions were studied.

Mechanical properties of waste rubber-polyurethane composites

The hardness of used rubber before granulation was 60°Shore A. The determined hardness of polyurethanes are the following: 70°Shore A – Chemolan M, 75°Shore A – Chemolan M-50, 80°Shore A – Chemolan B-3. The hardness of most composites was between 55 and 79°Shore A (Table 1–3). The samples containing more of the suitable polyurethane show the highest hardness, closer to that of pure polyurethane (Fig. 1). This suggests that hardness of these composites increases with the decrease of fine rubber concentration. The hardness of the composites prepared from polyurethane prepolymers obtained from different isocyanates depends on their structure and follows the pattern: MDI>MDI/TDI>TDI.

A higher increase of hardness with the rise of polyurethane prepolymer concentration for the composites prepared under lower pressure was observed. This suggests that the composites prepared under higher pressure exhibit a better filling of space between rubber grains in these samples with polyurethane than those prepared under lower pressure. Therefore, the effect of the pressure on the hardness of the composites is observed more distinctly for samples with the lowest concentration of polyurethane prepolymer.

Table 1 Hardness, elasticity and glass transition temperature of rubber waste, polyurethane and rubber waste-polyurethane composites obtained from rubber granulate (fine rubber) below 1.5 mm granularity and pressure $2.50 \cdot 10^6$ Pa

Chemolan B3	Fine rubber/%	Hardness ^a (°Shore A)	Elasticity/% ^b	Glass transition temperature/°C	
0	100	–	–	–59.3	–
10	90	66.0	32.0	–59.2	–36.6
15	85	68.5	26.0	–57.5	–30.2
20	80	71.8	27.5	–59.8	–31.7
25	75	73.6	31.5	–57.6	–30.5
30	70	78.2	32.0	–57.5	–40.7
100	0	80.0	–	–	–39.1
Chemolan M					
0	100	–	–	–59.3	–
10	90	55.7	26.0	–58.5	–41.7
15	85	36.0	35.0	–50.4	–27.6
20	80	61.0	32.0	–49.0	–37.9
25	75	64.0	31.0	–48.6	–37.3
30	70	66.0	44.0	–60.1	–38.7
100	0	70.0	–	–	–43.5
Chemolan M50					
0	100	–	–	–59.3	–
10	90	64.5	30.0	–57.1	–
15	85	70.4	30.0	–59.9	–34.2
20	80	71.5	34.5	–58.7	–42.5
25	75	72.5	30.0	–61.9	–
30	70	73.0	26.0	–59.5	–41.2
100	0	75.0	–	–	–42.1

^amaximum deviation ± 2.3 ^bmaximum deviation ± 2.2

The elasticity defines indirectly the amount of kinetic energy absorbed by the investigated sample. The elasticity values of the rubber waste-polyurethane composites (Table 1–3) are slightly higher than those for pure polyurethane prepared from suitable polyurethane prepolymers [3]. This suggests a presence of a free space or a stress between the grains of fine rubber in composites and shows that these samples temporarily absorb more energy than the homogenous samples. Values of elasticity oscillate in the range of 26–44%. Therefore, the obtained results show that the highest elasticity (average value more than 35%) was found in composites obtained from Chemolan M (TDI based). Composites obtained from Chemolan B3 (MDI based) and Chemolan M50 (mixture of MDI and TDI isomers) showed a lower and similar change of the average value of elasticity, respectively. High value of elasticity of the composites, prepared from polyurethane prepolymers obtained with TDI isomers, was directly connected with their lowest hardness. The increase of the concentration of the polyurethane, prepared from TDI, results in the rise of the composite elasticity. For composites obtained from Chemolan M50 (mixture of MDI and TDI isomers) the

Table 2 Hardness, elasticity and glass transition temperature of rubber waste, polyurethane and rubber waste-polyurethane composites obtained from rubber granulate (fine rubber) below 1.5 mm granularity and pressure $3.05 \cdot 10^6$ Pa

Chemolan B3	Fine rubber/%	Hardness ^a (°Shore A)	Elasticity/% ^b	Glass transition temperature/°C	
0	100	–	–	–59.3	–
10	90	67.5	34.0	–60.1	–29.0
15	85	70.1	38.0	–59.4	–37.9
20	80	71.2	32.0	–57.1	–31.2
25	75	74.1	31.0	–57.3	–36.6
30	70	77.0	29.0	–60.5	–29.7
100	0	80.0	–	–	–39.1
Chemolan M					
0	100	–	–	–59.3	–
10	90	56.8	36.0	–57.5	–
15	85	60.2	32.0	–59.0	–42.6
20	80	62.0	37.5	–58.7	–43.6
25	75	64.0	35.0	–54.2	–40.4
30	70	67.0	38.5	–50.6	–41.9
100	0	70.0	–	–	–43.5
Chemolan M50					
0	100	–	–	–59.3	–
10	90	65.6	30.5	–57.1	–
15	85	66.6	29.0	–58.3	–30.7
20	80	71.5	32.5	–58.8	–32.6
25	75	71.6	32.0	–59.2	–
30	70	72.6	29.5	–59.3	–
100	0	75.0	–	–	–42.1

^amaximum deviation ± 2.3 ^bmaximum deviation ± 2.2

effect of MDI (60 mass% with isocyanate mixture) on the elasticity is observed. The composites obtained with Chemolan M50 and Chemolan B3 show a very similar elasticity. The reduction of elasticity with the increase of MDI concentration in the composites is found.

Differential scanning calorimetry

The DSC technique was used for glass transition temperature (T_g) determination of pure components and waste rubber-polyurethane composites (Tables 1–3).

The T_g of fine rubber is found at -59.3°C . For pure polyurethanes prepared from polyurethane prepolymers Chemolan M, Chemolan M50 and Chemolan B3, T_g amounts to -43.5 , -42.1 and -39.1°C , respectively. It can be seen from the DSC data that the T_g value of the polyurethane, obtained from MDI (Chemolan B3), is higher than those obtained from TDI (Chemolan M) and the mixture of MDI and TDI (Chemolan M50). Therefore two explanations seem to be possible, one that the for-

Table 3 Hardness, elasticity and glass transition temperature of rubber waste, polyurethane and rubber waste-polyurethane composites obtained from rubber granulate (fine rubber) below 1.5 mm granularity and pressure $6.10 \cdot 10^6$ Pa

Chemolan B3	Fine rubber/%	Hardness ^a (°Shore A)	Elasticity/% ^b	Glass transition temperature/°C	
0	100	–	–	–59.3	–
10	90	68.0	31.5	–58.2	–43.1
15	85	70.5	31.0	–60.2	–29.6
20	80	72.0	30.0	–59.9	–29.8
25	75	74.6	32.5	–59.7	–36.0
30	70	77.0	28.5	–60.7	–36.8
100	0	80.0	–	–	–39.1
Chemolan M					
0	100	–	–	–59.3	–
10	90	60.4	38.0	–58.9	–40.1
15	85	61.8	39.0	–59.3	–34.0
20	80	62.6	38.0	–59.2	–46.8
25	75	65.5	40.0	–60.6	–42.8
30	70	65.9	43.0	–58.6	–46.3
100	0	70.0	–	–	–43.5
Chemolan M50					
0	100	–	–	–59.3	–
10	90	64.6	30.0	–56.8	–
15	85	68.0	30.0	–57.5	–
20	80	68.3	34.5	–60.2	–
25	75	71.8	30.0	–63.3	–
30	70	72.0	29.0	–63.0	–
100	0	75.0	–	–	–42.1

^amaximum deviation ± 2.3 ^bmaximum deviation ± 2.2

mer exhibits higher molecular mass or that the other is less flexible than the polyurethanes obtained from TDI or its mixture with MDI. However, considering the elasticity data the latter suggestion seems to be less probable.

Two values of T_g were found for the rubber waste-polyurethane composites obtained from fine rubber (Tables 1–3).

The results point to the non-homogeneous structure of the composites. Since two T_g values of waste rubber-polyurethane composites are close to those of homopolymers it seems that in the obtained composites the rubber and polyurethane exist separately. The T_g values of the composites close to those of polyurethanes are higher than the T_g for virgin ones. In polymers, the increase of T_g might be connected with the growth of their molecular mass. The T_g values, observed above T_g of polyurethane and rubber point to a probable reaction of polyurethane with rubber. The mechanism of this reaction is not clear yet. Probably high temperature of the process and used pressure may cause the bonds to scission and in this way allow for the reaction

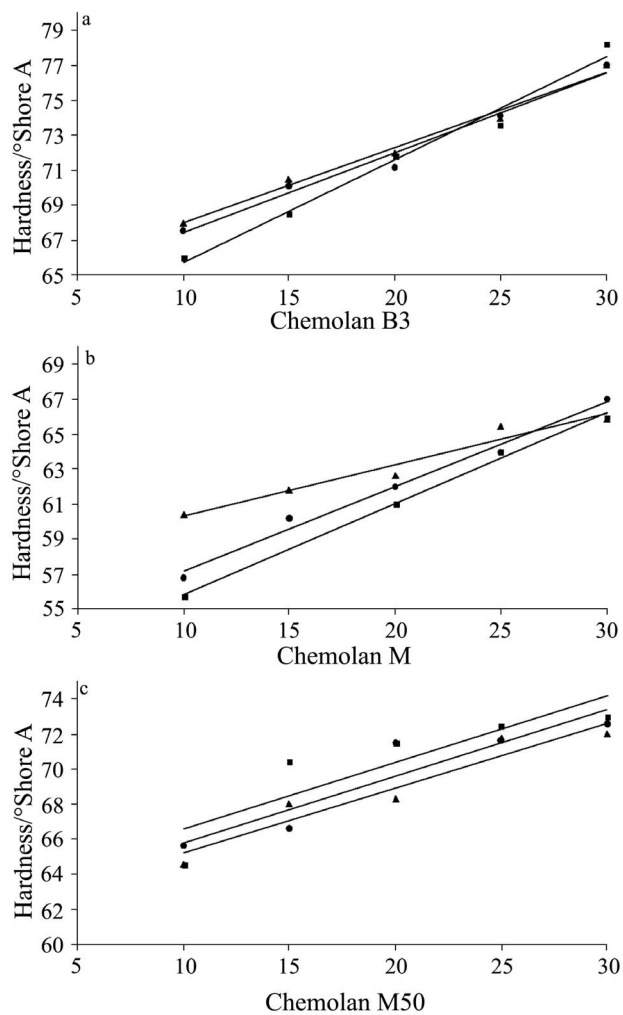


Fig. 1 Dependence of hardness on polyurethane content in the composites. a – Chemolan B3; b – Chemolan M; c – Chemolan M50; ■ – pressure $2.50 \cdot 10^6$ Pa; ● – pressure $3.05 \cdot 10^6$ Pa; ▲ – pressure $6.10 \cdot 10^6$ Pa

of rubber with polyurethane. A similar mechanism was described for rubber granulate vulcanisation with the DeLink agent [3, 4].

There is no dependence between T_g and the pressure used for the composite preparation and therefore between pressure and composite structure, as well.

Thermogravimetric analysis

The TG curves of the fine rubber, the polyurethane prepolymers, and the composites, prepared under pressure of $6.10 \cdot 10^6$ Pa, represent results for the four heating rates

used (Figs 2–4). The temperature of maximum rate of mass loss for two main peaks of the DTG curves and the intermediate temperatures for fine rubber and the majority of compositions were determined (Tables 4–6). The points at which the temperatures

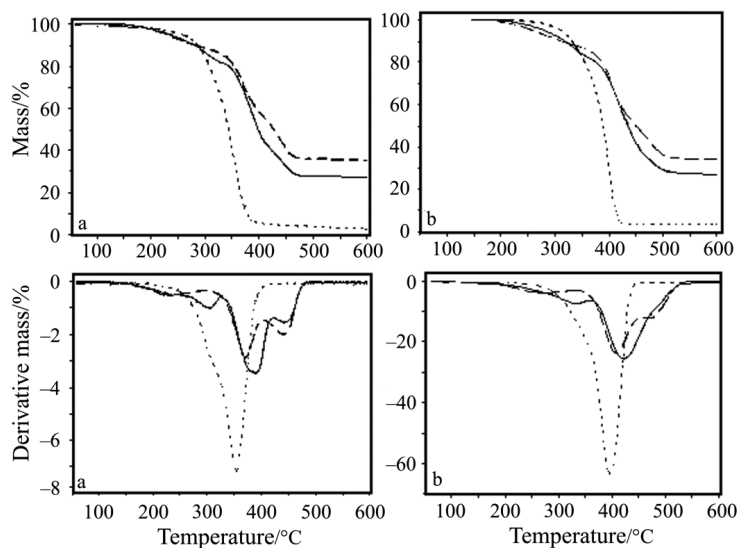


Fig. 2 TG and DTG curves at a 5 K min^{-1} and b 40 K min^{-1} heating rate; --- fine rubber, — rubber waste-polyurethane composite with 20 mass% polyurethane, ... Chemolan B3

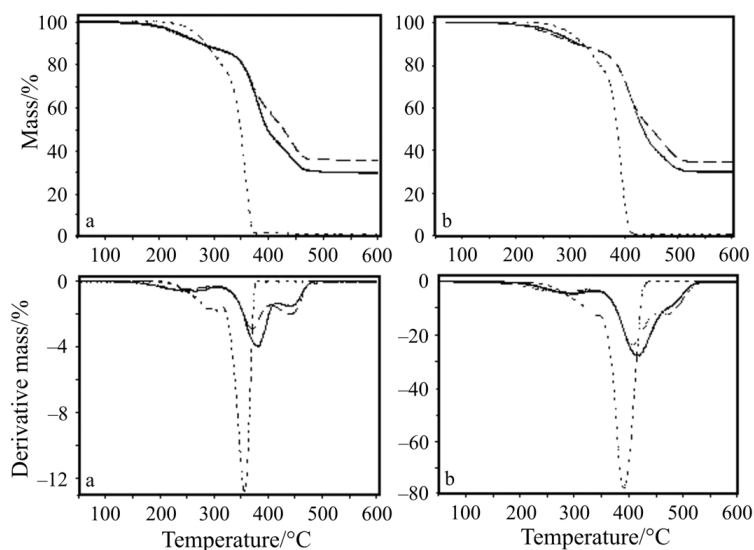


Fig. 3 TG and DTG curves at a 5 K min^{-1} and b 40 K min^{-1} heating rate; --- fine rubber, — rubber waste-polyurethane composite with 20 mass% polyurethane, ... Chemolan M

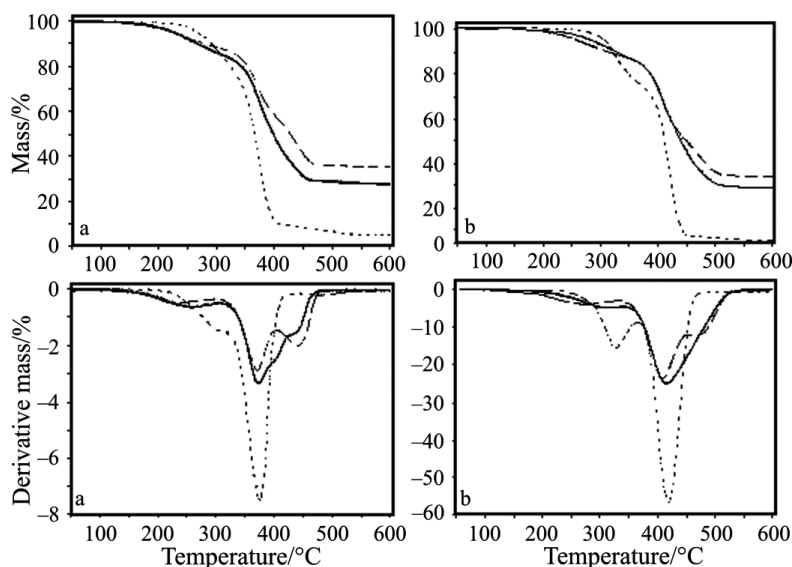


Fig. 4 TG and DTG curves at a 5 K min^{-1} and b 40 K min^{-1} ; heating rate; --- fine rubber, — rubber waste-polyurethane composite with 20 mass% polyurethane, ... Chemolan M50

were assigned are shown in Fig. 5. Precise assignment of T_1 is difficult, owing to the problem of deciding when the major mass loss begins, whereas $T_{\max 1}$ and $T_{\max 2}$ are easier to determine. The mass loss below $\sim 250^\circ\text{C}$ on the TG curve of fine rubber probably corresponds to the decomposition of an oil fraction [10–13]. From the TG data it can be seen that the thermal decomposition for fine rubber and all the composites starts above 250°C . This is followed by two major losses of mass for fine rubber and the majority of the compositions, and thermal decomposition is essentially complete at about 550°C . In the case of two composites, prepared from polyurethane prepolymer containing 25 and 30 w/w% of Chemolan M50 and having the heating

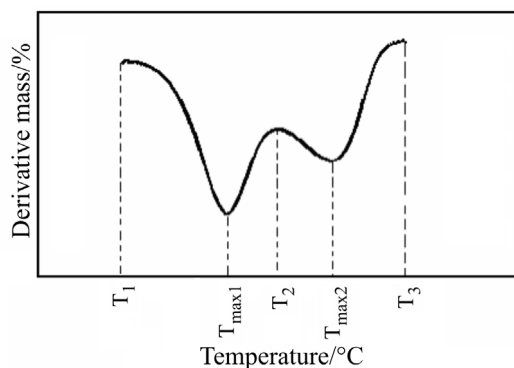


Fig. 5 DTG nomenclature for Tables 1, 2 and 3

Table 4 Temperature characteristic and kinetic parameters for thermal decomposition of fine rubber (I), Chemolan B3 (II) and rubber-urethane composites samples by TG (nomenclature defined in Fig. 4), pressure $6.10 \cdot 10^6$ Pa

I/%	II/%	Heat rate/K min^{-1}	Temperature/ $^{\circ}\text{C}$					Pre-exponential factor A/s^{-1}			Activation energy $E/\text{kJ mol}^{-1}$	
			T_1	$T_{\text{max}1}$	T_2	$T_{\text{max}2}$	T_3	low	high	low	high	
100	0	5	300	369	404	441	492	$1.1 \cdot 10^{12}$	$6.2 \cdot 10^{10}$	156.5	155.9	
		10	315	383	417	458	415	$2.3 \cdot 10^{13}$	$8.2 \cdot 10^8$	172.4	129.0	
		20	328	394	431	464	425	$4.4 \cdot 10^{13}$	$3.7 \cdot 10^7$	175.7	107.9	
		40	337	406	451	478	445	$2.8 \cdot 10^{12}$	$2.8 \cdot 10^7$	160.9	103.8	
90	10	5	315	377	417	443	494	$3.2 \cdot 10^{12}$	$5.9 \cdot 10^{11}$	164.9	170.1	
		10	331	387	434	450	510	$9.8 \cdot 10^{11}$	$3.1 \cdot 10^9$	158.8	136.9	
		20	330	394	443	463	526	$4.7 \cdot 10^{11}$	$2.1 \cdot 10^7$	152.5	104.0	
		40	347	410	458	477	540	$2.0 \cdot 10^{12}$	$2.3 \cdot 10^7$	160.6	102.1	
85	15	5	324	375	418	443	496	$3.9 \cdot 10^{12}$	$6.6 \cdot 10^{10}$	166.4	156.8	
		10	331	389	429	456	509	$6.6 \cdot 10^{12}$	$2.2 \cdot 10^{10}$	168.5	149.0	
		20	342	399	446	467	518	$3.5 \cdot 10^{12}$	$1.0 \cdot 10^7$	164.4	99.0	
		40	347	418	458	477	527	$2.2 \cdot 10^{12}$	$1.9 \cdot 10^6$	161.4	84.4	
80	20	5	331	391	421	442	490	$3.2 \cdot 10^{12}$	$3.2 \cdot 10^{12}$	165.75	187.8	
		10	333	386	430	452	496	$5.7 \cdot 10^{12}$	$5.7 \cdot 10^{12}$	167.4	145.0	
		20	353	401	453	475	519	$1.0 \cdot 10^{12}$	$1.5 \cdot 10^{12}$	160.9	95.0	
		40	362	419	466	485	545	$3.3 \cdot 10^{12}$	$3.3 \cdot 10^{12}$	164.0	82.3	
75	25	5	339	399	428	447	494	$2.1 \cdot 10^{12}$	$1.7 \cdot 10^{12}$	165.3	176.2	
		10	342	391	432	449	482	$8.2 \cdot 10^{12}$	$1.0 \cdot 10^9$	170.0	112.0	
		20	355	403	450	468	506	$3.3 \cdot 10^{12}$	$3.2 \cdot 10^6$	165.1	89.7	
		40	371	422	470	489	536	$10.0 \cdot 10^{11}$	$1.5 \cdot 10^6$	158.4	83.9	
70	30	5	326	375	415	440	480	$2.2 \cdot 10^{13}$	$4.0 \cdot 10^{12}$	175.1	165.0	
		10	340	390	440	460	513	$1.3 \cdot 10^{13}$	$1.3 \cdot 10^{12}$	160.8	89.9	
		20	355	410	459	476	520	$2.4 \cdot 10^{11}$	$2.1 \cdot 10^{12}$	151.5	89.1	
		40	367	421	469	490	538	$6.2 \cdot 10^{11}$	$6.8 \cdot 10^{12}$	155.6	49.3	
0	100	5	325	354	414	—	—	$2.8 \cdot 10^8$	—	109.8	—	
		10	337	373	421	—	—	$4.2 \cdot 10^{12}$	—	160.0	—	
		20	348	386	435	—	—	$1.0 \cdot 10^{13}$	—	164.4	—	
		40	359	398	446	—	—	$8.0 \cdot 10^{12}$	—	161.8	—	

Table 5 Temperature characteristic and kinetic parameters for thermal decomposition of fine rubber (I), Chemolan M (III) and rubber-urethane composites samples by TG (nomenclature defined in Fig. 4), pressure $6.10 \cdot 10^6$ Pa

I/%	III/%	Heat rate/K min^{-1}	Temperature/ $^{\circ}\text{C}$					Pre-exponential factor A/s^{-1}			Activation energy $E/\text{kJ mol}^{-1}$	
			T_1	T_{max1}	T_2	T_{max2}	T_3	low	high	low	high	
100	0	5	300	369	404	441	492	$1.1 \cdot 10^{12}$	$6.2 \cdot 10^{10}$	156.5	155.9	
		10	315	383	417	458	515	$2.3 \cdot 10^{13}$	$8.2 \cdot 10^8$	172.4	129.0	
		20	328	394	431	464	525	$4.4 \cdot 10^{13}$	$3.7 \cdot 10^7$	175.7	107.9	
		40	337	406	451	478	545	$2.8 \cdot 10^{12}$	$2.8 \cdot 10^7$	160.9	103.8	
90	10	5	304	373	409	434	494	$6.3 \cdot 10^{11}$	$2.0 \cdot 10^7$	154.6	108.8	
		10	317	390	430	451	503	$1.1 \cdot 10^{12}$	$1.4 \cdot 10^{12}$	158.4	174.1	
		20	323	399	441	462	516	$5.8 \cdot 10^{11}$	$4.9 \cdot 10^7$	153.5	108.3	
		40	332	412	545	474	522	$3.0 \cdot 10^{13}$	$1.1 \cdot 10^{10}$	143.0	103.6	
85	15	5	310	377	410	444	484	$3.6 \cdot 10^{13}$	$6.5 \cdot 10^{13}$	176.7	194.5	
		10	319	388	426	450	505	$2.8 \cdot 10^{13}$	$1.8 \cdot 10^9$	175.2	133.2	
		20	321	397	438	453	497	$3.9 \cdot 10^{11}$	$1.5 \cdot 10^{10}$	151.7	141.0	
		40	339	412	456	477	533	$2.8 \cdot 10^{12}$	$3.5 \cdot 10^7$	161.8	105.3	
80	20	5	309	380	414	446	486	$1.4 \cdot 10^{14}$	$4.1 \cdot 10^{10}$	172.3	140.2	
		10	320	388	431	451	506	$4.5 \cdot 10^{12}$	$9.3 \cdot 10^9$	166.3	143.5	
		20	328	404	449	469	524	$1.2 \cdot 10^{12}$	$1.5 \cdot 10^{10}$	159.0	122.6	
		40	339	415	459	481	536	$1.4 \cdot 10^{12}$	$4.1 \cdot 10^{12}$	158.6	105.3	
75	25	5	310	348	421	448	490	$4.9 \cdot 10^{12}$	$1.3 \cdot 10^{12}$	168.1	174.7	
		10	328	398	434	462	513	$2.1 \cdot 10^{13}$	$2.0 \cdot 10^8$	175.5	120.6	
		20	332	407	446	461	503	$2.8 \cdot 10^{12}$	$2.5 \cdot 10^{10}$	163.2	144.8	
		40	345	418	459	478	523	$5.5 \cdot 10^{12}$	$4.5 \cdot 10^8$	166.3	87.3	
70	30	5	319	394	420	447	478	$5.7 \cdot 10^{13}$	$4.1 \cdot 10^{14}$	181.1	206.8	
		10	323	408	434	461	501	$1.5 \cdot 10^{13}$	$1.0 \cdot 10^{10}$	173.7	143.4	
		20	341	420	455	474	521	$5.1 \cdot 10^{12}$	$1.8 \cdot 10^{10}$	168.3	131.5	
		40	348	426	466	482	527	$4.8 \cdot 10^{12}$	$2.1 \cdot 10^7$	166.5	99.9	
0	100	5	318	357	380	—	—	$7.1 \cdot 10^{22}$	—	279.3	—	
		10	332	371	408	—	—	$3.5 \cdot 10^{16}$	—	206.6	—	
		20	338	383	419	—	—	$7.3 \cdot 10^{17}$	—	223.7	—	
		40	355	394	431	—	—	$4.7 \cdot 10^{15}$	—	196.7	—	

Table 6 Temperature characteristic and kinetic parameters for thermal decomposition of fine rubber (I), Chemolan M50 (VI) and rubber-urethane composites samples by TG (nomenclature defined in Fig. 4), pressure $6.10 \cdot 10^6$ Pa

I/%	IV/%	Heat rate/K min^{-1}	Temperature/ $^{\circ}\text{C}$					Pre-exponential factor A/s^{-1}				Activation energy $E/\text{kJ mol}^{-1}$	
			T_1	$T_{\text{max}1}$	T_2	$T_{\text{max}2}$	T_3	decomposition stage		low	high		
								low	high				
100	0	5	300	369	404	441	492	$1.1 \cdot 10^{12}$	$6.2 \cdot 10^{10}$	156.5	155.9		
		10	315	383	417	458	515	$2.3 \cdot 10^{13}$	$8.2 \cdot 10^8$	172.4	129.0		
		20	328	394	431	464	525	$4.4 \cdot 10^{13}$	$3.7 \cdot 10^7$	175.7	107.9		
		40	337	406	451	478	545	$2.8 \cdot 10^{12}$	$2.8 \cdot 10^7$	160.9	103.8		
90	10	5	306	375	424	443	469	$4.0 \cdot 10^4$	$8.7 \cdot 10^{10}$	76.1	158.8		
		10	317	387	434	453	509	$1.1 \cdot 10^{11}$	$9.0 \cdot 10^7$	146.4	114.9		
		20	325	393	436	464	514	$5.7 \cdot 10^{12}$	$2.7 \cdot 10^8$	165.0	118.7		
		40	340	410	437	470	535	$3.6 \cdot 10^{13}$	$1.2 \cdot 10^9$	173.6	126.9		
85	15	5	308	372	417	443	489	$1.9 \cdot 10^{11}$	$2.8 \cdot 10^{11}$	149.8	165.2		
		10	317	386	434	458	508	$3.6 \cdot 10^{10}$	$5.8 \cdot 10^8$	143.8	126.6		
		20	332	399	440	461	531	$2.8 \cdot 10^{12}$	$2.1 \cdot 10^{10}$	162.6	90.5		
		40	338	409	454	478	552	$4.6 \cdot 10^{11}$	$5.3 \cdot 10^5$	151.5	78.8		
80	20	5	306	371	423	444	480	$2.5 \cdot 10^{10}$	$1.4 \cdot 10^{11}$	139.9	159.3		
		10	322	388	440	460	509	$7.3 \cdot 10^{12}$	$6.1 \cdot 10^7$	143.5	82.6		
		20	332	402	453	473	523	$7.2 \cdot 10^{10}$	$3.6 \cdot 10^8$	144.1	121.6		
		40	348	411	470	494	540	$5.6 \cdot 10^{10}$	$6.0 \cdot 10^7$	141.9	107.8		
75	25	5	307	374	430	444	486	$6.8 \cdot 10^{10}$	$8.7 \cdot 10^{11}$	135.5	172.0		
		10	316	387	442	460	498	$1.6 \cdot 10^{10}$	$6.4 \cdot 10^{10}$	137.2	154.5		
		20	332	398	452	471	507	$8.9 \cdot 10^{10}$	$1.1 \cdot 10^{10}$	144.6	141.0		
		40	342	408	—	—	512	$1.6 \cdot 10^8$	—	111.0	—		
70	30	5	308	375	390	399	475	$1.3 \cdot 10^{10}$	$5.8 \cdot 10^5$	180.0	84.6		
		10	326	391	405	465	503	$1.4 \cdot 10^{15}$	$8.4 \cdot 10^{12}$	193.6	113.9		
		20	332	400	420	436	459	$2.1 \cdot 10^{10}$	$1.1 \cdot 10^{19}$	138.0	129.0		
		40	340	412	—	—	542	$6.0 \cdot 10^6$	—	192.6	—		
0	100	5	310	377	424	—	—	$6.7 \cdot 10^{10}$	—	142.4	—		
		10	342	394	442	—	—	$7.7 \cdot 10^{12}$	—	169.0	—		
		20	354	408	462	—	—	$5.0 \cdot 10^{12}$	—	167.2	—		
		40	365	421	470	—	—	$2.3 \cdot 10^{14}$	—	188.0	—		

rate 40 K min^{-1} , we can only see one loss of mass (Table 6). Two-stage decomposition of the tyre rubber was found. 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. A similar dependence is described in [13]. It was also found that the decomposition of polyurethanes occurs at a temperature range characteristic for low-temperature decomposition of tyre rubber ($\pm 10^\circ\text{C}$). 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 the 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 polyurethane prepolymers it can be seen that the thermal decomposition starts at about the same temperature as fine rubber and composites and only one-stage loss of mass is observed. The mass loss below this temperature probably corresponds to the decomposition of low molecular mass fractions, probably present in the polyurethane. Since the shape of the TG curves hardly changes below the low-temperature decomposition on the TG of composites one can suggest that these molecules do not take part in the formation of the composite.

The char residue was 35.9% for fine rubber. This value for the composites containing 10, 15, 20, 25 and 30 mass% of polyurethane was 31.3–33.0, 30.6–31.60, 30.13–28.0, 25.5–27.7 and 24.6–26.5%, respectively (Fig. 6). Char residue was high due to the presence of carbon black added during tyre manufacturing and the experimental conditions of thermogravimetric analysis (the use of nitrogen as the purge gas) [13, 23]. It can be seen that char residue decreases with the polyurethane concentration in the composites. The residue was essentially unaffected by the heating rate.

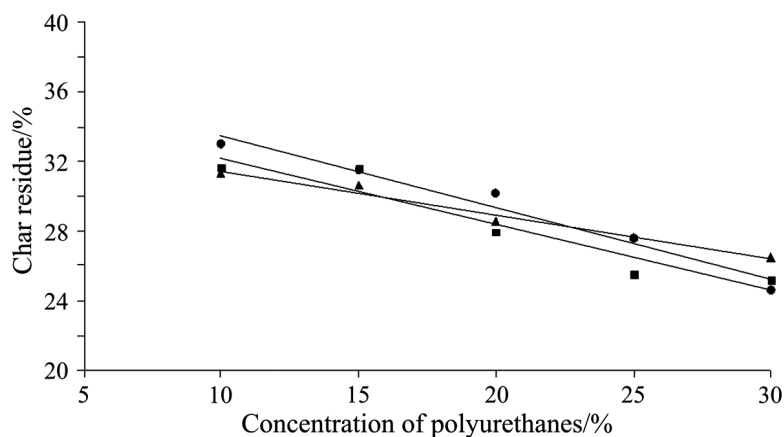


Fig. 6 Dependence of char amount, determined at 500°C - TG curves, on polyurethane content in the composites; ■ - Chemolan B3, ◆ - Chemolan M, ▲ - Chemolan M50

As the heating rate increases, the mass loss is shifted to higher temperatures and the corresponding dw/dt is higher, the process takes place faster as in the case of the majority of materials. A shift of $T_{\max 1}$ and $T_{\max 2}$ on the TG curves to higher temperatures with the increase of the heating rate was observed (Tables 4–6). The DTG curves (Figs 2–4) and the data (Tables 4–6) show that there are clearly two areas of mass loss, giving two peaks on the DTG curves. As the heating rate was increased, two peaks merged progressively and $T_{\max 1}$ and $T_{\max 2}$ values also increased. The shift to higher temperatures of thermal degradation has been attributed to the combined effects of the heat transfer at different heating rates and to the kinetics of the decomposition, resulting in delayed decomposition [14, 21]. Heat transfer from the furnace to the sample has been shown to be a problem in the determination of the kinetic parameters [22], and close contact between the thermocouple and the sample is desirable. In our studies the thermocouple was used to measure the temperature of the sample boat. Consequently, the observed shift in the curves with increasing heating rate is deemed to be due to the changes of the kinetics of the thermal decomposition and again suggest the possibility of chemical interaction between fine rubber and polyurethane.

Kinetic parameters

The decomposition of polymers and rubber, and their composites, comprises a large number of reactions occurring in a parallel and series manner. TG measurements show on overall mass loss due to these reactions. The basic thermal degradation of polymers has been described as a generalised chemical bond scission process consisting of primary and secondary decomposition events. Using TG curves and basing on net mass loss and simplifying assumptions, which do not necessarily correspond to the complex chemical reactions in the thermal degradation of the sample, kinetic parameters of the degradation reaction were calculated. The analysis of the kinetics of a thermal degradation process must be performed using the differential form of kinetic law. The normal procedure is to use the DTG curve in the fitting of data, so a small change in the mass loss curve is reflected in the derivative curve.

The approach adopted by many workers in kinetic analysis of TG data for materials is to assume a first-order reaction for devolatilisation [15–19].

The rate of decomposition is given by:

$$dw/dt = -k(w-w_i) \quad (1)$$

where w is the mass of material before decomposition, w_i is the mass of residue at the end of the reaction, and k is the rate constant, which is also defined by the Arrhenius equation:

$$k = Ae^{-E/RT} \quad (2)$$

where A is the pre-exponential factor and E is the activation energy of the decomposition reaction.

Logarithmic form of this equation is the following:

$$\ln k = \ln A - E/RT \quad (3)$$

The TG continuous record of mass loss vs. time and temperature enables dw/dt and k to be determined from Eq. (1). A plot of $\ln k$ vs. $1/T$ gives a straight line of slope $-E/R$. Two values of activation energy and pre-exponential factor were calculated for the curves for the two stages of reaction indicated by the DTG curves (Tables 4–6). In general, the activation energy of higher-temperature decomposition decreased with increasing heating rate. The activation energy of lower-temperature decomposition usually increased with increasing heating rate similarly as the activation energy of decomposition of pure polyurethanes. The calculated activation energy was 109.8–164.4 kJ mol⁻¹ for Chemolan B3, 196.7–279.3 kJ mol⁻¹ for Chemolan M, 142.4–188.0 kJ mol⁻¹ for Chemolan M50 and 156.5–175.7 and 103.8–155.9 kJ mol⁻¹ for lower- and higher-temperature decomposition of fine rubber respectively. The calculated activation energy for lower-temperature decomposition was between 152.5–175.1 kJ mol⁻¹ for composites obtained from Chemolan B3, 143.0–181.1 kJ mol⁻¹ for composites obtained from Chemolan M, and 76.1–193.6 kJ mol⁻¹ for composites obtained from Chemolan M50. The value of activation energy of fine rubber and composites are similar to the one reported in the papers [13, 24–26]. The average value of overall activation energies of lower-temperature and higher-temperature decomposition of composites was 281.3 kJ mol⁻¹ for Chemolan B3 (MDI) composites (the value calculated from the determined data of activation energy of fine rubber and polyurethane and from the amount of these components in composites – 262.2 kJ mol⁻¹), 301.2 kJ mol⁻¹ for Chemolan M (TDI isomers) composites (the calculated value – 277.6 kJ mol⁻¹) and 278.4 kJ mol⁻¹ for Chemolan M50 (MDI+TDI isomers mixture) components (the calculated value – 265.6 kJ mol⁻¹). Differences between determined and calculated results could suggest again a possible reaction of polyurethane with rubber during the composite formation. Composites obtained from Chemolan M (TDI isomers) showed the highest determined and calculated average activation energy whereas composites obtained from Chemolan M50 and Chemolan B3 containing MDI isocyanate exhibited lower ones but nearly the same.

Summary and conclusions

Stable, non-homogeneous waste rubber-polyurethane composites, obtained from polyurethane components with different isocyanate constituents (MDI, TDI isomers or MDI and TDI isomers mixture), with good mechanical properties were obtained.

Results of hardness and elasticity showed the direct relation between data obtained and the structure of composite components as well. Decrease of elasticity is observed with the increase of MDI concentration in the composites.

Two values of T_g determined by DSC reflect the non-homogeneous structure of the composites. Values of T_g above T_g of polyurethane and rubber point to a probable reaction of polyurethane with rubber.

The obtained results indicate that any exact dependence between pressure of the prepared composites and their constitution, mechanical and thermal properties cannot be postulated.

In TG examination of thermal decomposition of obtained composites the increase in heating rate produced a shift to higher temperatures of thermal degradation. Majority of composite samples, similarly to fine rubber sample, showed two distinct areas of mass loss. Two-stage decomposition shown by composites suggests that the lower-temperature decomposition is mainly due to the rubber waste and polyurethane components whereas the higher-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 the heating rate. The higher-temperature activation energy decreases with increasing heating rate. The differences between the determined and calculated values of average activation energies suggest a possible reaction of polyurethane with rubber during composite formation.

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