

# POLIMERY

CZASOPISMO POŚWIĘCONE CHEMII, TECHNOLOGII I PRZETWÓRSTWU POLIMERÓW

## Polyurethane composites with mixture of carbon fibers and glass frit

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DOI: [dx.doi.org/10.14314/polimery.2016.307](https://dx.doi.org/10.14314/polimery.2016.307)

**Abstract:** Polyurethane elastomer (EPU) and polyurethane (PUUR) products are used in many stages of the mining process, such as extraction, transport, processing and storage. In these stages wheels with tires from polyurethane elastomers are used. Tire materials, especially in suspended transport, are exposed to particularly high loads, which results in their destruction and consequently short exploitation period. To solve this problem it was proposed to use for the production of tires polyurethane composites manufactured using fillers in the form of chopped carbon fiber and glass frit. The effect of the mixture of glass frit and carbon fibers on the properties of polyurethane elastomers was measured. The resulting composites were characterized using the techniques of thermal analysis (DSC, TGA and DMTA) and the structure was described using SEM. The results of tribological research and the evaluation of antistatic traits of the obtained polyurethanes were presented.

**Keywords:** polyurethane elastomers, polyurethane composites, glass frit, short carbon fiber.

### Kompozyty poliuretanowe napełnione mieszaniną włókien węglowych i fryty szklanej

**Streszczenie:** Wyroby z elastomerów uretanowych (EPU), w tym uretanomoczników (PUUR), są wykorzystywane w kopalniach (np. jako opony kół transportu podwieszanego) na wielu etapach procesu pozyskiwania kopaliny, zarówno na etapie wydobywania, transportowania, przetwarzania, jak i magazynowania. Opony w transporcie podwieszonym są narażone na szczególnie duże obciążenia, powodujące szybkie zniszczenie i w konsekwencji skrócenie czasu eksploatacji. W związku z tym do produkcji opon zaproponowano wykorzystanie kompozytów poliuretanowych zawierających cięte włókna węglowe i frytę szklaną. Oceniono wpływ mieszaniny fryty szklanej i włókien węglowych na właściwości elastomerów uretanowych. Wytworzone kompozyty scharakteryzowano metodami analizy termicznej (DSC, TGA i DMTA), a ich strukturę – metodą SEM. Przedstawiono wyniki badań trybologicznych oraz dokonano oceny cech antystatycznych otrzymanych uretanomoczników.

**Słowa kluczowe:** elastomery uretanowe, kompozyty poliuretanowe, fryta szklana, krótkie włókno węglowe.

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Polyurethane products are used in many stages of the mining process, such as: extraction, transport, processing and storage. In many of these applications polyurethane elastomers are used [1], e.g. for the production of components subject to abrasive wear such as sifts, pump and chute, hydrocyclones as well as road wheel liners [1]. Changing conditions of coal mining make these devices operate under increasingly higher loads. For their manufacture, materials with higher strength are sought. Many devices used in suspended transport are supplemented with EPU-based wheel tires, which meet the requirements of this application. In the case of work on a continuous basis, EPU strength, as is the case with other groups of elastomers, is not sufficient despite their modifications [2, 3]. Wheel tires undergo considerable strain, especially at the start of the train, which is the reason for the destruction of tires. Also visible is the thermal degradation caused by energy accumulation transformed into heat and EPU abrasive wear [4]. The phenomena occurring during the deformation of these materials, causing their thermal degradation may be described using the DMA analysis on the basis of  $\tan \delta$  changes (loss tangent), whose value is the ratio of loss modulus ( $E''$ ) to the storage modulus ( $E'$ ). Modulus  $E'$  is proportional to the share of the stored energy and the modulus  $E''$  to the share of the energy converted into heat and irreversibly lost [5]. In the case of materials undergoing thermal degradation it is preferred that they manifest low ability to absorb the energy transformed into heat, consequently expressed in low  $E''$  values and possibly low  $\tan \delta$  in the utility temperature range. These characteristics determine those materials whose  $\tan \delta$  in the utility range is  $< 0.3$ . They are the materials which do not have any high ability to suppress vibrations (damping materials) [6, 7].

Elastomers exposed to high permanent loads should also be characterized by high strength, and therefore a method to manufacture EPU composites was proposed. Polyurethane composites, thanks to their characteristics, have a wide range of applications [8]. To strengthen them as well as other polymeric materials, among others, carbon fibers and particles as well as glass are used [9, 10]. Materials designed for mining purposes should also be cheap.

To increase the EPU strength properties and to limit the accumulation of energy in tires, EPU filler introduction was proposed. Within the framework of the study the effect of frit glass and carbon fibers mixture was evaluated on the properties of urethane elastomers designed for continuous operation under high load in road wheels.

## EXPERIMENTAL PART

### Materials

Poly(ethylene adipate) (PAE)  $M_n = 1906$  g/mol and methylene diphenyl diisocyanate (MDI) used in this study were supplied by Sigma-Aldrich.

Dicyandiamide (DYDI) provided by Emerald Performance (USA) was used as chain extender.

Glass frit (FG) (Institute of Ceramics and Building Materials Kraków) and cut carbon fiber (CF) of 60  $\mu\text{m}$  length (Velox, Polska Ltd.) were used as filler. Glass frit is glass recast with silica: ceramic mass or low-melting ceramic glaze component in the form of glass plates of irregular shape.

### Preparation of polyureaurethanes and composites

PUUR's were synthesized in a one-shot method at substrate mole ratio PEA : MDI : DYDI = 2 : 5 : 3 and isocyanate index 1.05. Elastomers contained 28.3 wt % of hard segments (HS). The PEA, DYDI, FG and CF were degassed for 2 h at  $160 \pm 5$  °C and 6 hPa with intense stirring. The mixture was cooled down to  $60 \pm 3$  °C before the MDI was added. The blend was then stirred for 5 min. The prepared mixture was then poured into a duralumin mold and annealed for 8 h at 150 °C. The samples were tested after 14 days of seasoning under ambient conditions. Table 1 shows the composition of prepared polyurethane-glass composites.

**Table 1. Characterization of the obtained PUUR and composites**

Sample	Amount of filler grams per 100 g of PUUR	Filler volume contribution (CF : FG)
PUUR	0	0
FG/CF-0/100	0 FG + 50 CF	0.00 : 0.27
FG/CF-25/75	12.5 FG + 37.5 CF	0.04 : 0.21
FG/CF-50/50	25.0 FG + 25.0 CF	0.09 : 0.14
FG/CF-75/25	37.5 FG + 12.5 CF	0.14 : 0.07
FG/CF-100/0	50 FG + 0 CF	0.19 : 0.00

Composites containing 50 wt % of filler were produced. The filler came in the form of glass frit (FG), carbon fiber (CF) or their mixtures. As a part of the study, five groups of composite materials were manufactured and their properties were compared to those of PUUR (Table 1). The density of the frit is 2.4 g/cm<sup>3</sup> and the density of carbon fibers 1.7 g/cm<sup>3</sup>.

### Methods of testing

– The Fourier transform infrared spectra (FT-IR) were obtained on Nicolet 7600 (Thermo Electron Corporation, USA). The spectra were recorded at spectral range 4000–400 cm<sup>-1</sup>, a resolution of 4 cm<sup>-1</sup> and a count of 64. The data analysis was performed using Omnic software. A baseline correction with CO<sub>2</sub> and H<sub>2</sub>O was performed to eliminate the impact of the compound residues from the analysis.

Based on FT-IR spectra the index of hydrogen bonding ( $R$ ) and degree of phase separation ( $DPS$ ) were analyzed. This value was performed from the bands in the range of 1630–1750 cm<sup>-1</sup> corresponding to the stretching vibrations of the C=O groups.

The  $\text{C=O}$  groups share of urea and urethane groupings linked with hydrogen bonding was defined as below (1) [11, 12]:

$$R_{\text{C=O}} = \frac{A_{\text{B1}} + A_{\text{B2}}}{A_{\text{F1}} + A_{\text{F2}}} \quad (1)$$

where:  $A_{\text{B1}}$ ,  $A_{\text{B2}}$  – the surface areas of the bands from the vibrations bound by the hydrogen bond of the carbonyl groups of urea (B1) (1680–1640  $\text{cm}^{-1}$ ) and urethane (B2) (1727–1705  $\text{cm}^{-1}$ ) respectively,  $A_{\text{F1}}$ ,  $A_{\text{F2}}$  – the surface areas of bands from vibrations unbounded with the hydrogen bond of the carbonyl groups of urea (F1) (1701–1690  $\text{cm}^{-1}$ ) and urethane (F2) (1745–1736  $\text{cm}^{-1}$ ) bonding respectively.

On the basis of the resulting index  $R$  the degree of phase separation  $DPS$  of hard segments was calculated from the following equation (2):

$$DPS = \frac{R_{\text{C=O}}}{1 + R_{\text{C=O}}} \quad (2)$$

The changes in the carbonyl hydrogen bonding and in  $DPS$  affect the properties of the polyurethanes, as presented in the work by Pretsch, Jakob and Muller [13] as well as Ryszkowska [3].

– The thermal degradation was performed via thermogravimetric analysis (TGA) using TA Instruments TGA Q500. Samples of 10 mg were heated from the room temperature to 800 °C at the speed of 10 deg/min. Tests were carried out in nitrogen atmosphere.

– The structure description was carried out using differential scanning calorimetry (DSC), performed on TA Instruments DSC Q1000 calorimeter. Samples of 5–10 mg were placed in a nitrogen atmosphere and examined under a heat. Test cycle consisted of: cooling to -90 °C, soaking for 5 min, heating at the rate of 10 deg/min to about 250 °C. Characteristic temperatures were designated from the first heating cycles.

– The dynamic mechanical thermal analysis (DMTA) was carried out on TA Instruments DMA Q800. This study was conducted using rectangular-shaped samples (60 × 10 × 2 mm) with two-point bending method. Samples were heated at the rate of 3 deg/min from -100 °C to 180 °C, using a constant frequency of 1 Hz and an amplitude of 25  $\mu\text{m}$ .

Based on the results of the analysis of thermal mechanical properties (DMTA) cross-linking density ( $V_c$ ) was determined.  $V_c$  of the ureaurethane and composites, understood as the inverse of the average molecular weight between network nodes, was calculated using an expression based on Flory's rubber elasticity theory Eq. (3) [14, 15].

$$V_c = \frac{E_T}{3\rho RT} \quad (3)$$

where:  $V_c$  ( $\text{mol}\cdot\text{m}^{-3}$ ) – cross-linking density,  $E_T$  (Pa) – storage modulus measured at the rubbery plateau,  $R = 8.31 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  is universal gas constant, and  $T$  (K) is absolute temperature at which the plateau of  $E_T$  was determined.

– Structure description of the CF, FG and composites was performed by scanning electron microscopy (SEM) using a Hitachi TM3000 microscope with an accelerating voltage of 15 kV. A series of SEM images, acquired at different magnifications, were used to study the structures of the filler. Prior to SEM analysis, the samples were coated with gold to increase their conductivity.

– Static tensile tests were performed on a tensile machine of Instron 1115 according to PN-EN ISO 527. The paddle-shaped samples were stretched at a speed of 500 mm/min.

– Density was determined using analytical balance produced by RADWAG with an attachment for measuring the density using Archimedes principle according to the standard PN-C-04215:1983.

– The hardness was measured using a durometer, Durometer A, Wilson Wolpert Company, according to DIN 53505, ASTM D2240 and ISO 7619.

– Resilience was determined using Schob apparatus in conformity with ASTM D1054 Method B (Schob).

– Tribological tests were carried out using two methods. The first method tested abrasive wear resistance applying the Schopper-Schlobach apparatus in conformance with the ISO 4649 standard. Measurements of 5 samples for each PUUR were taken and the results averaged. Calculations using the second method included the pin-on-disk type tester (type T-11). The tribological pair consisted of a tang made out of the tested material and a counter-sample in the shape of a shield of steel with a roughness of  $R_a = 2.2$ ,  $R_z = 18.8$ . The diameter of the tested sample was 3 mm, which enabled to obtain high unit pressure with a low regular load. The friction hub scheme was presented in the study of Auguścik *et al.* [16].

On the basis of preliminary studies and literature reviews the following parameters of tribological research were accepted: testing time – 1 h, pressure – 1 MPa = 7.065 N, linear velocity – 0.264 m/s. The results of 3 measurements for each PUUR were averaged.

– Antistatic features of the tested materials were evaluated using a Eurostat-manufactured Eurostat Volume 600 antistatic ohmmeter. Measurement of volume resistivity was conducted using measuring electrodes of 2.5 kg in accordance with the ASTM D257. At the same time, the measurement of humidity and air temperature as well as resistance were carried out (resistance to  $2\cdot 10^{12} \Omega$  at the voltage reaching 100 V).

## RESULTS AND DISCUSSION

Changes in the chemical structure of the polyurethane matrix were evaluated on the basis of the FT-IR analysis (Fig. 1). On the FT-IR spectra of the tested materials, typical for polyurethane urea bands, were found to be present [17–19]. After the introduction of fillers the intensity of bands varied within the range: 2850–2950  $\text{cm}^{-1}$  ( $\text{CH}_2$  stretching vibration), 1630–1740  $\text{cm}^{-1}$  ( $\text{C=O}$  stretch-

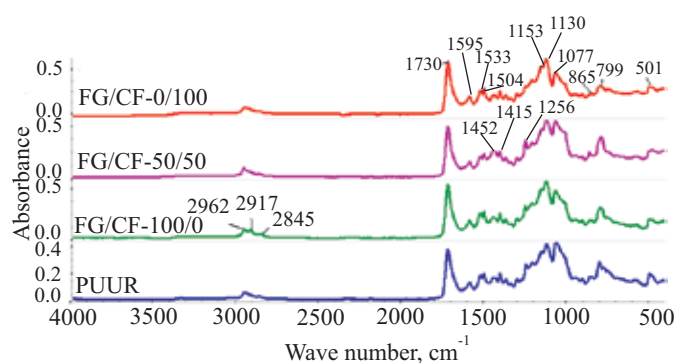
**Table 2.** The results of FT-IR and density analysis of the obtained PUUR and composites

Sample	<i>R</i>	<i>DPS</i> , %	$\rho$ , g/cm <sup>3</sup>	$\rho_T$ , g/cm <sup>3</sup>	$\Delta(\rho - \rho_T)/\rho$ , %
PUUR	0.82	44.9	1.256 ± 0.005	1.256 ± 0.005	
FG/CF-0/100	0.74	42.6	1.385 ± 0.005	1.397	-0.9
FG/CF-25/75	0.71	41.3	1.415 ± 0.003	1.425	-0.7
FG/CF-50/50	0.61	37.8	1.448 ± 0.004	1.455	-0.4
FG/CF-75/25	0.59	37.3	1.481 ± 0.005	1.485	-0.3
FG/CF-100/0	0.58	36.7	1.514 ± 0.007	1.517	-0.2

ing vibration), 1450 cm<sup>-1</sup> (-CH<sub>2</sub>- deformation vibration), 1256 cm<sup>-1</sup> (symmetric -CH<sub>3</sub> bending vibration), 1130 cm<sup>-1</sup> and 1077 cm<sup>-1</sup> (C-O-C stretching vibration). Changes in bands within the range 2850–2950 cm<sup>-1</sup> may be associated with a reordering in the PUUR soft phase while the changes within the band 1630–1740 cm<sup>-1</sup> have to do with the reordering in PUUR hard phase of polyurethanes. Within the bands 1452 cm<sup>-1</sup>, 1256 cm<sup>-1</sup>, 1130 cm<sup>-1</sup> and 1077 cm<sup>-1</sup>, their range coincides with that of the range of bands characteristic of the glass derived from groups Si-OH and/or Si-CH<sub>3</sub> (1405 cm<sup>-1</sup>), Si-O-Si (1100–1080 cm<sup>-1</sup>). In the FT-IR PUUR spectrum, 865 cm<sup>-1</sup> and 799 cm<sup>-1</sup> (symmetric Si-O-Si bending vibration), 501 cm<sup>-1</sup> (Si-O bending vibration) bands appeared, whose presence is associated with the use of silicone distribution means. After the introduction of FG, the intensity of the bands increases due to the overlapping of the glass-derived bands. On the spectrum there are no other additional peaks. That might suggest the presence of a coating on the surface of the FG and CF.

On the basis of multiplet band 1630–1750 cm<sup>-1</sup> corresponding to the stretching vibrations of the C=O group, the index of hydrogen bonding (*R*) and degree of phase separation (*DPS*) were indicated (Table 2).

The introduction of fillers reduces the possibility of the formation of hydrogen bonds (HB) in PUUR within the rigid segment area, which is indicated by the decrease in *R* and *DPS*. -OH groups of the FG surface may react with the -NCO groups of the substrate mixture in order to manufacture matrix composites [20]. Additional chemical bonds that may occur at the surface between the filler and the matrix can limit the mobility of matrix macromolecules, which hinders the formation of hydrogen bonds in the hard phase. The more FG inside the composite, the greater the reduction of *DPS*.

**Fig. 1.** FT-IR spectra of PUUR and composites

An important parameter that varies with the change of macromolecules density compression is density ( $\rho$ ). Increased polyurethane density indicates an increase in the compression density in either soft or hard phase. Therefore, in the materials analyzed, there were also examined the changes in their density. The differences in the density are the result of various fillers, but they may also occur due to the changes in the compression density of the macromolecules [21]. On the basis of the rule of mixture, the value of theoretical density was determined in accordance with formula (4) [22]. The calculation results are shown in Table 2.

$$\rho_T = V_{V_{\text{PUUR}}} \cdot \rho_{\text{PUUR}} + V_{V_{\text{CF}}} \cdot \rho_{\text{CF}} + V_{V_{\text{FG}}} \cdot \rho_{\text{FG}} \quad (4)$$

where: PUUR density equals  $\rho_{\text{PUUR}} = 1.2559$  g/cm<sup>3</sup>, FGs density –  $\rho_{\text{FG}} = 2.6$  g/cm<sup>3</sup> and CF density –  $\rho_{\text{CF}} = 1.8$  g/cm<sup>3</sup>;  $V_{V_{\text{PUUR}}}$ ,  $V_{V_{\text{FG}}}$ ,  $V_{V_{\text{CF}}}$  respective volume share of PUUR, FG and CF.

The theoretical density determined by the rule of mixtures is lower than the density determined during the

**Table 3.** Results of the DSC and TGA analysis of the obtained PUUR and composites

Sample	$T_{\text{gss}}$ °C	$T_{m1}$ °C	$\Delta H_{m1}$ J/g	$T_{m2}$ °C	$\Delta H_{m2}$ J/g	$T_1$ °C	$T_2$ °C
PUUR	-29.8	86	3.4	190	1.7	293	407
FG/CF-0/100	-30.5	77	1.9	200	1.1	299	386
FG/CF-25/75	-31.7	96	4.8	206	3.5	297	368
FG/CF-50/50	-32.8	111	1.7	202	1.4	300	363
FG/CF-75/25	-32.2	89	3.2	207	2.9	305	360
FG/CF-100/0	-32.7	76	4.3	209	3.3	302	352



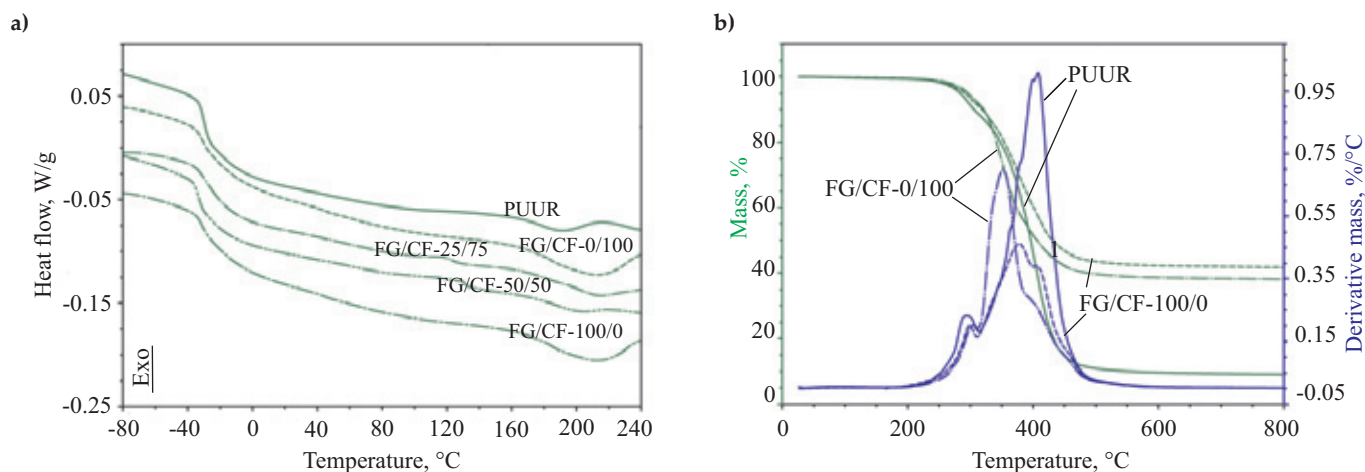


Fig. 2. Thermograms of: a) DSC, b) TGA and DTG

measurements taken. Probably the reason for this change is the reduced compressed density in the hard phase of the matrix, as can be concluded from the *DPS* reduction.

The results of DSC, TGA and DTG analysis were summarized in Fig. 2 and Table 3. On the DSC curves there is a soft phase glass transition ( $T_{gSS}$ ) and two endothermic peaks associated with the changes taking place in the hard phase, at a  $T_{m1}$  and  $T_{m2}$  temperature with enthalpy change of  $\Delta H_{m1}$  and  $\Delta H_{m2}$ . On the basis of DTG curves, it can be concluded that during the thermal composite degradation there are two stages of degradation, *T1* and *T2* respectively, associated with the degradation of the hard and soft phase.

As a result of the DSC analysis it can be concluded that the introduction of fillers reduces the glass transition temperature of the soft phase of matrix composites. This is probably due to the changes in the phase separation degree of the matrix composites. Another change may be seen in the temperature of both extremes associated with the dissociation of hydrogen bonds in the PUUR hard phase and the enthalpy of these changes. An analysis of DTG curves (a derivative of mass change with respect to temperature) allows to demonstrate that the maximum temperature of the degradation of the hard phase of the polyurethane matrix composites increases (*T1*). The maximum temperature degradation rate of the soft phase is significantly reduced than in PUUR (*T2*).

Also under analysis fell the changed properties of the obtained materials with the application of DMA. Figure 3 shows the changing curve of their storage modulus ( $E'$ )

and tangent delta ( $\tan \delta$ ). Based on the changes that took place in  $E'$ , behavioral patterns were established at different temperatures associated with the usage of PUUR (Table 4). On the  $\tan \delta$  curve, the so-called  $\alpha$  relaxation temperature, related to the glass transition temperature ( $T_g$ ), was determined. On some of the curves of  $\tan \delta$  of the tested materials it was observed that the second peak correlates with  $\beta$  transition, which is due to the initial mobility of molecular side chain segment.

The introduction of fillers results in an increase in the glass transition temperature. The greatest changes in  $T_g$  were observed when the carbon fiber or glass frit was introduced. The introduction of the FG, CF or a mixture containing 75 % of CF causes that the  $\beta$  ( $T_\beta$ ) transformation temperature becomes visible, which is due to initial mobility of molecular side chain segment and may assume as impact strength of PUUR at room temperature.

On the basis of  $\tan \delta$  curves, the ability of a material to absorb and accumulate energy can be evaluated. This ability may be assessed on the basis of the loss tangent ( $\tan \delta$ ), the value of which corresponds to the ratio of loss modulus ( $E''$ ) to the storage modulus ( $E'$ ) [23]. Materials with high vibration-absorption and energy accumulation capacity are considered to possess  $\tan \delta > 0.3$  across a wide temperature range [5, 23]. PUUR has the greatest vibration-absorption capacity but only within a range of temperatures below room temperature. After the introduction of fillers the ability of urethane-ureas to absorb vibrations decreases ( $\tan \gamma$  falls), and hence so does their

Table 4. Results of the DMTA curve analysis and static tensile strength of the obtained PUUR and composites

Sample	$T_{g'}^{\circ}\text{C}$	$\tan \gamma$	$T_{\beta'}^{\circ}\text{C}$	$\tan \beta$	$V_c$ mol·m <sup>-3</sup>	$\tan \delta > 0.3$ °C	$E'$ , MPa		
							-30 °C	20 °C	60 °C
PUUR	-8.9	0.56	-	-	2.4	-19.7–13.8	2494	22	52
FG/CF-0/100	-3.7	0.17	62.1	0.12	13.3	-	7353	1649	696
FG/CF-25/75	-7.9	0.37	80.8	0.11	8.2	-15.5–1.7	5642	195	74
FG/CF-50/50	-8.3	0.36	-	-	6.7	-15.1–0.3	6808	309	144
FG/CF-75/25	-5.6	0.26	-	-	4.8	-	8311	678	245
FG/CF-100/0	-4.4	0.30	67.9	0.19	2.3	-	4588	187	39

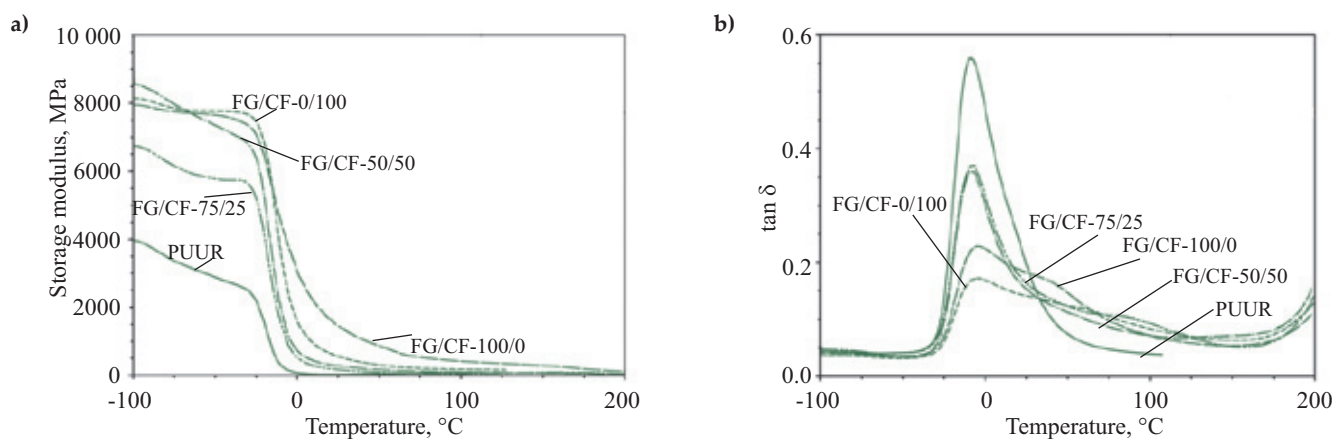


Fig. 3. Results of urethane and composites analysis with DMA: a) storage modulus  $E'$ , b)  $\tan \delta$

energy accumulation capacity. In the case of materials applied for road wheel tires, it is important that the ability to accumulate energy is the lowest. The higher the capacity to accumulate energy, the faster the period in which the tire material heats up, which may result in its degradation.

Based on DMA data a cross-linking degree was calculated ( $V_c$ ). Cross-linking of the analyzed materials may be the result of strong hydrogen bonding between the HS and weaker ones between the segments of the polyurethane matrix and fillers. Cross-linking may also result from the OH group reaction on the surface of FG and -NCO groups.

In PUUR strong HB connect the hard segments to form hard domains and their agglomerates.

In the analyzed materials, the introduction of fillers resulted in a reduction in the amount of HB connecting the rigid segment ( $R$  – Table 2). Connections resulting from the creation of HB in the hard phase make the cross-linking density of the matrix, determined on the basis of the DMTA, amount to  $V_c = 2.4 \text{ mol}\cdot\text{m}^{-3}$ . The introduction of a FG filler into this matrix resulted in only a slight reduction in  $V_c$ , which may be a result of limited mobility of the macromolecules with a formation of connections between the surface of FG and PUUR at the same time. The introduction of an increased amount of CF into the matrix leads to a systematic increase in the cross-linking density up to the value of  $V_c = 13.3 \text{ mol}\cdot\text{m}^{-3}$  for the composite containing only CF. This phenomenon may occur due to the formation of interaction between the flexible

segments of the matrix and carbon fiber. FT-IR spectra manifested significant changes in the structure of the soft phase composite matrix, which are indicated by a varied image of spectra within the  $2830\text{--}3000 \text{ cm}^{-1}$  range (Fig. 4). From this figure it can be concluded that the intensity of the bands derived from stretching vibration of symmetrical and asymmetrical CH groups bound and unbound hydrogen bonds is changing. The decomposition process was carried out with the method used for the band within the range of  $1640\text{--}1760 \text{ cm}^{-1}$ . The decomposition of multiplet bands was carried out within the range of  $2830\text{--}2980 \text{ cm}^{-1}$  and the result is summarized in Table 5.

From the result in Table 5 it can be concluded that the intensity of the bands derived from stretching vibration of symmetrical CH groups is higher in composites with higher content of FG, but the intensity of asymmetrical CH groups is lower.

The introduction of a greater amount of filler in the form of carbon fibers reduces the volume resistivity ( $VR$ ) of the polyurethane matrix which leads to better electrical conductivity (Table 6).  $VR$  is reduced to  $4.1\cdot 10^9$  for matrix material (PUUR),  $5.6\cdot 10^9$  for the 50 % FG composite (FG/CF-100/0) and to  $1.7\cdot 10^5$  for the 50 % CF material (FG/CF-0/100). Similar correlations were raised by Kowalczyk *et al.* [24]. They observed that better electrical conductivity took place after the introduction of larger amounts of carbon nanofillers into the polyurethane coating.

There were also analyzed the mechanical properties in rebound and hardness tests as well as during attempts

Table 5. Result of multiplet band decomposition within the range of  $2830\text{--}2980 \text{ cm}^{-1}$  composites spectra (C-part of area band in multiple band, %)

Sample	Band $\text{cm}^{-1}$	C %	Band $\text{cm}^{-1}$	C %	Band $\text{cm}^{-1}$	C %	Band $\text{cm}^{-1}$	C %	Band $\text{cm}^{-1}$	C %
	2960		2920		2900		2870		2850	
FG/CF-0/100	2961	41.6	2918	47.0	2906	2.9	2869	8.9	2850	0.0
FG/CF-25/75	2960	40.2	2924	41.1	2908	4.5	2867	9.5	2847	4.8
FG/CF-50/50	2962	41.5	2923	32.3	2904	7.9	2870	11.8	2846	6.5
FG/CF-75/25	2963	46.9	2923	28.4	2906	6.5	2870	6.2	2851	11.3
FG/CF-100/0	2962	44.1	2918	18.9	2898	5.3	2877	9.5	2848	22.1

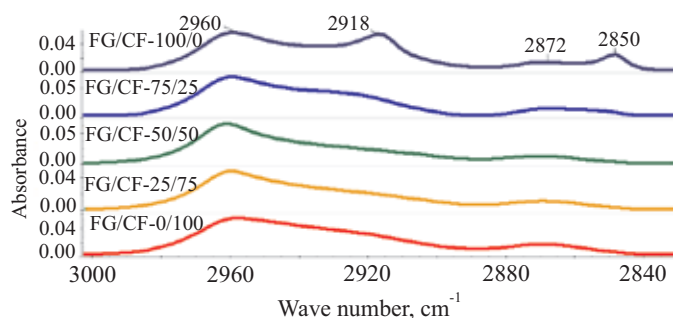


Fig 4. Part of FT-IR composite spectra within the range of 2840–3000  $\text{cm}^{-1}$  of the PUUR and composites

Table 6. Impact of fillers on the volume resistivity of polyurea-urethanes and composites

Sample	Volume resistivity $\Omega\cdot\text{m}$	Temperature $^{\circ}\text{C}$	Humidity %
PUUR	$4.1\cdot 10^9$	31	19
FG/CF-0/100	$1.7\cdot 10^5$	28	25
FG/CF-25/75	$3.5\cdot 10^6$	30	22
FG/CF-50/50	$1.4\cdot 10^7$	30	21
FG/CF-75/25	$1.6\cdot 10^7$	31	20
FG/CF-100/0	$5.6\cdot 10^9$	31	21

Table 7. Mechanical properties of the obtained PUUR and composites

Material	$\sigma_{100}$ , MPa	$R_m$ , MPa	$E$ , MPa	$\epsilon_r$ , %	$\epsilon_i$ , %	$\eta$ , %	$H$ , $^{\circ}\text{ShA}$	$V$ , $\text{cm}^3$	Wear mass, %
PUUR	$6.3 \pm 0.2$	$28.0 \pm 0.5$	$50.3 \pm 1.1$	$332 \pm 3$	$1.25 \pm 0.05$	$28.3 \pm 0.3$	$86.5 \pm 0.5$	$0.047 \pm 0.008$	-
FG/CF-0/100	$26.3 \pm 3.2$	$31.3 \pm 1.9$	$81.8 \pm 10.9$	$1.10 \pm 0.02$	$0.13 \pm 0.02$	$21.8 \pm 0.2$	$84.4 \pm 1.1$	$0.128 \pm 0.006$	0.31
FG/CF-25/75	$25.2 \pm 1.4$	$26.6 \pm 0.5$	$40.5 \pm 10.2$	$1.17 \pm 0.05$	$0.06 \pm 0.01$	$25.3 \pm 0.2$	$81.5 \pm 0.5$	$0.155 \pm 0.022$	0.57
FG/CF-50/50	$18.2 \pm 0.8$	$20.3 \pm 0.2$	$20.9 \pm 2.1$	$1.28 \pm 0.55$	$0.09 \pm 0.02$	$26.2 \pm 0.4$	$79.8 \pm 0.5$	$0.219 \pm 0.006$	0.75
FG/CF-75/25	$14.9 \pm 0.2$	$15.6 \pm 0.3$	$8.5 \pm 0.7$	$2.12 \pm 0.45$	$0.20 \pm 0.03$	$28.9 \pm 0.3$	$78.5 \pm 0.5$	$0.193 \pm 0.008$	0.27
FG/CF-100/0	$17.0 \pm 0.5$	$17.5 \pm 0.2$	$7.7 \pm 0.9$	$1.84 \pm 0.21$	$0.11 \pm 0.02$	$28.5 \pm 0.3$	$85.0 \pm 0.5$	$0.205 \pm 0.028$	0.30

of static stretching. The results of these tests are summarized in Table 7. The introduction of CF reduces resilience ( $\eta$ ) and FG reduced hardness ( $H$ ), when compared to PUUR, and boosts abrasive wear ( $V$ ) 3 to 4 times. Fillers lead to 3 to 4-fold increase in the stress at elongation of 100 % ( $\sigma_{100}$ ). Increasing FG in composites causes reduction in tensile strength ( $R_m$ ) and the modulus of elasticity ( $E$ ). The  $E$  modulus for the composite containing CF-50 (FG/CF-0/100) is much larger than for PUUR. Elongation at break ( $\epsilon_i$ ) of composites is significantly lower than it is the case with PUUR, but fillers have a positive influence on permanent deformations ( $\epsilon_r$ ), which for composites are approximately five to a dozen-or-so times smaller than for PUUR.

The reason behind such changes in properties may be an altered level of intermolecular interactions in the matrix of composites and bonds formed between the matrix and the FG and the change in the distribution of fillers within the matrix. Mishnaevsky and Dai [25] proved that in the hybrid composites containing carbon fiber and glass, strength resistance and elongation at break depend on the positioning of fibers within the matrix and on their quantity. Moreover, a significant cause of reduction in strength properties for some composites is their microporosity (Table 2) increasing with the amount of frit in the composites.

It is envisaged that one of the applications of polyurethane composites with CF and FG will be wheel tire. It is

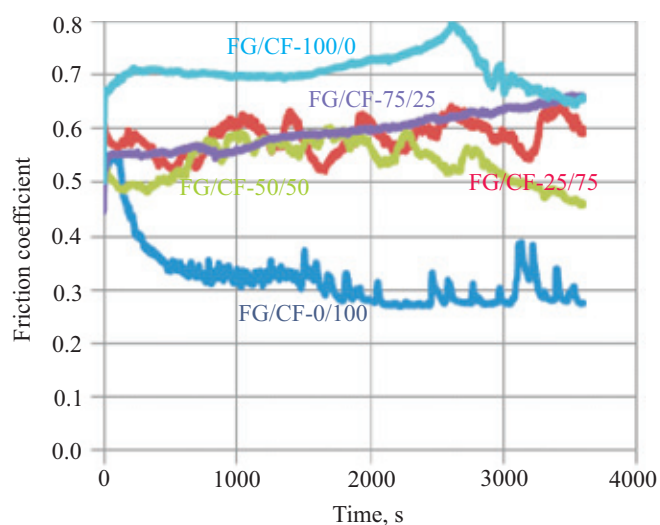


Fig. 5. Change in friction coefficient of the PUUR and composites during the test

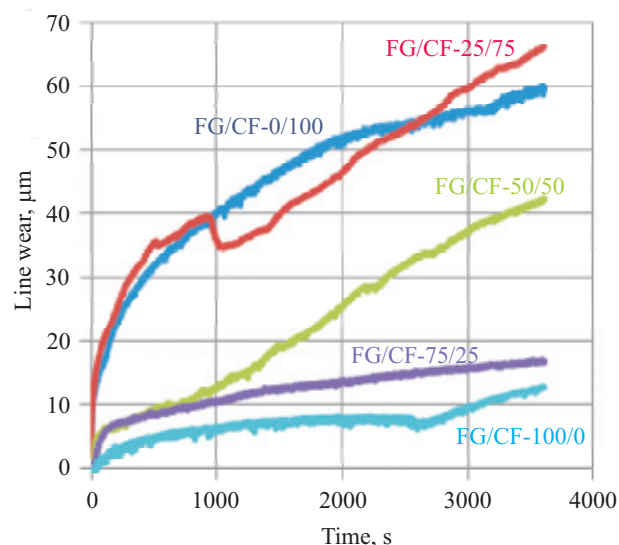


Fig. 6. Change in linear wear of the PUUR and composite samples during the test



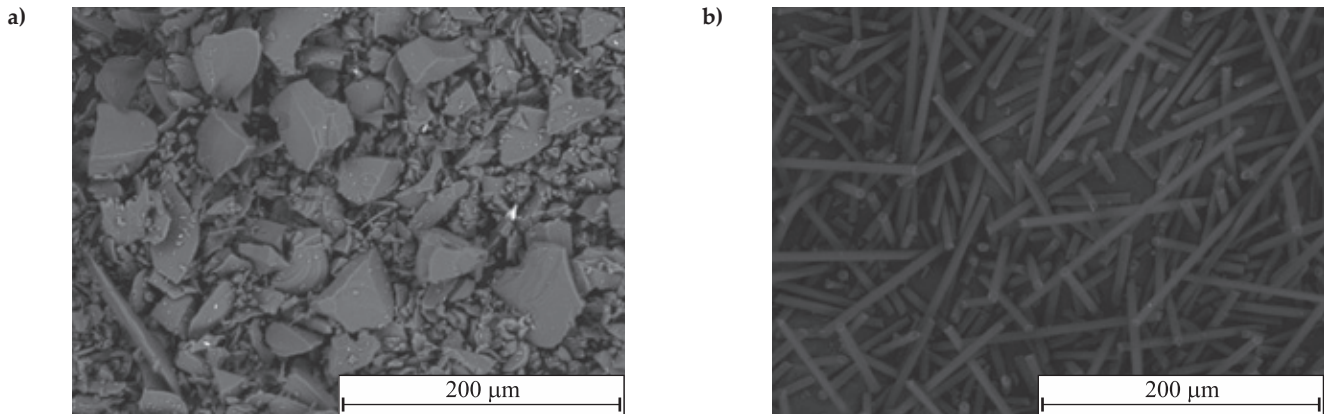


Fig. 7. SEM pictures of the particles of: a) glass frit, b) carbon fibers

important to comprehend their behavior in pair tribological tests, wherein the rod is made out of the composite and the shield out of steel. The analysis examined the coefficient of friction (Fig. 5), the amount of samples (Fig. 6) and composite mass (Table 5). The nature of changes in the coefficient of friction and linear wear for each sample indicates that during the test as the filler particles appeared on the surface, these parameters change. A sample containing the highest amount of CF is characterized by the lowest coefficient of friction of approximately 0.3 and as for the sample containing the highest amount of FG this figure stands approximately at 0.7. Changes in linear wear are also the smallest for a sample containing only FG and the highest for the sample containing only the mixture of 25 % CF and 75 % FG. The composite mass wear test set-

ties in within the range of 0.27–0.75 %. For polyurethane carbon in a 6-hour test, the same figure was between 0.01 and 0.4 % [17], and therefore for the composites it is much higher. The nature of changes in the mass wear of the composite samples is similar to that of abrasive wear (Table 5). Differences in mass and abrasive wear, just as the changes in tensile properties may be due to differences in the positioning of the filler in the matrix [25].

Since many of the composites' properties depend on the shape and arrangement of the filler in the matrix, the shape of the particles and their distribution in the polyurethane matrix was analyzed. Fig. 7 shows images of the filler structure, whose shape and size affect the properties of the composites. The glass particle size evaluated on the basis of measurements carried out with the ap-

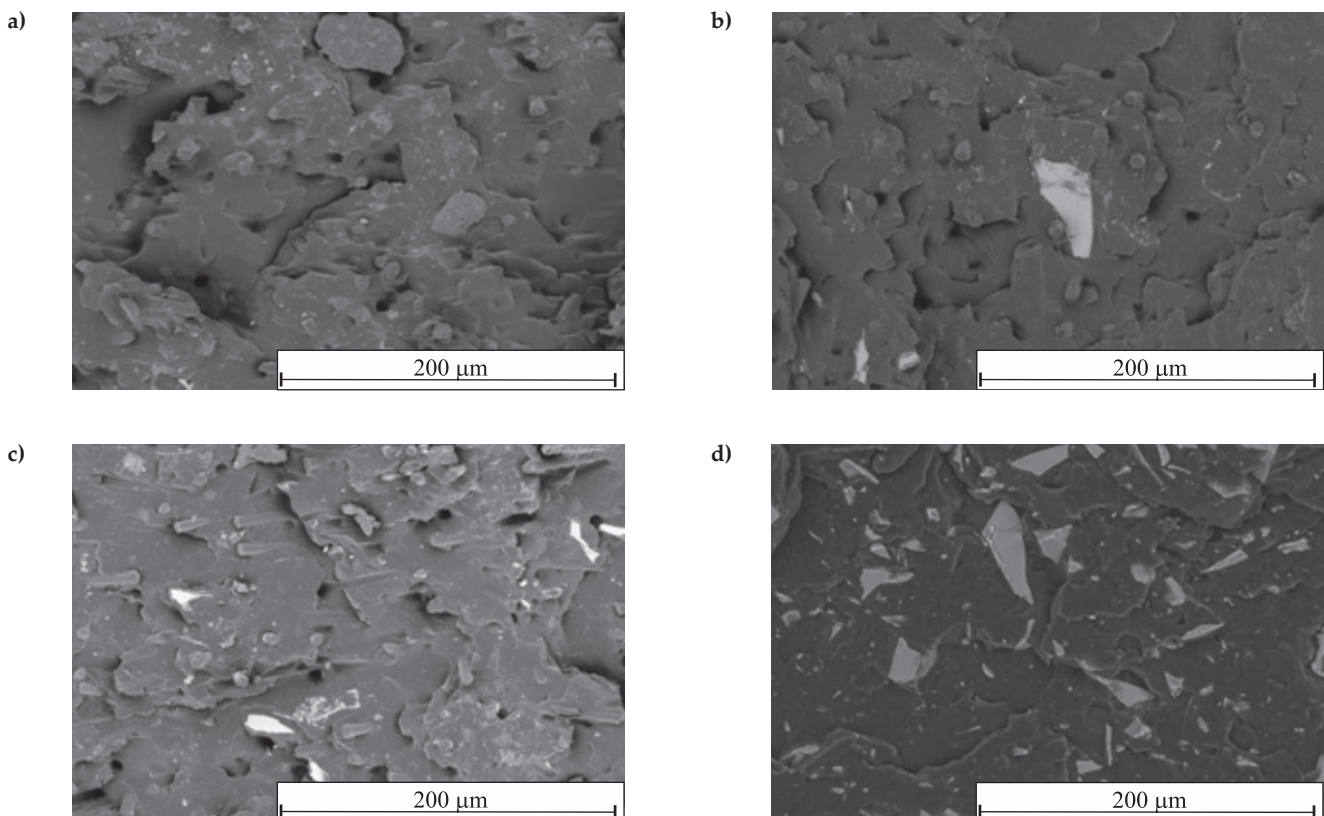


Fig. 8. SEM pictures of the composites: a) FG/CF-0/100, b) FG/CF-25/75, c) FG/CF-50/50, d) FG/CF-100/0



plication of SEM varied between 5 and 80  $\mu\text{m}$ . Carbon fibers have a diameter of approximately 6.5  $\mu\text{m}$ .

After the introduction of fillers a change in the course of brittle fracture of composites may be observed. The breaking point of composite with the glass particles (Fig. 8d) is significantly different from that of carbon fiber material (Fig. 8a) and composite with mixtures of fillers (Fig. 8b and 8c). These differences result from varied quantity, shape and characteristics of the fillers. On the composites break images one can observe micropores. The amount of micropores in the CF composites (Fig. 8a) is greater than that of FG composites (Fig. 8d). This result is consistent with the result of the analysis of density variations (Table 2). The consequence of these changes in the structure of composites can be seen in their changing properties.

### CONCLUSIONS

As a result of PUUR filler-induced mixture modification of glass frit particles and carbon fibers, the resistance properties of the composites obtained in comparison to the matrix have changed. After the introduction of fillers, only the CF composite increased its tensile strength and modulus of elasticity. The abrasive wear of this composite is the lowest among the analyzed materials, but higher than that of the matrix. Thermal characteristics of these materials change, while the ability of these materials to accumulate energy visibly decreases. This feature of the composite with only CF will contribute to a greater longevity of wheels with tires covered with this material. Particularly advantageous properties were observed for the PUUR carbon fiber. The introduction of the filler in the form of chopped carbon fibers increased the electrical conductivity of the composite. In the case of wheels, an important parameter was the permanent tire material deformation. All composites analyzed were characterized by a significantly lower permanent deformation when compared to PUUR matrix.

*The study has been financed within the framework of the project Nr PBS1/A5/3/2012, entitled: "Elastomer composite materials for applications in friction systems transmitting the drive in extreme load conditions used in transport machines and equipment".*

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