POLYURETHANE COMPOSITES WITH THE ADDITION OF GRAPHITE WITH DIFFERENT DEGREES OF EXPANSION

K. Pietrzak[1*], J. Ryszkowska[2]

[1]*Faculty of Materials Science and Engineering, Warsaw University of Technology, Woloska 141, 02-507 Warsaw, Poland*
[2]*Faculty of Materials Science and Engineering, Warsaw University of Technology, Woloska 141, 02-507 Warsaw, Poland*
*kpietrzak@inmat.pw.edu.pl

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Abstract
The aim of this work was to verify the influence of graphite on the flammability of ureaurethane elastomers (PURM). Expandable graphite (EG) fillers were added to PURM to improve its thermal stability and reduce its flammability. Three types of elastomers were compared: unmodified PURM and PURM with the addition of two types of expandable graphite with expansions of 50 and 250. Flammability tests using a cone calorimeter (CC) were performed to assess the flammability of these materials. The thermal properties were measured using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Mechanical and physical tests revealed the changes in the properties of the composites. Infrared spectroscopy (FT-IR) analysis indicated that only small changes occurred in the chemical structure with the addition of the fillers.

1 Introduction

Polyurethanes (PUR) are widely used in many fields of technology and industry, such as transportation, engineering, and biomedicine. The reasons for the great interest in these polymers are their excellent properties, including high tensile strength, high abrasion resistance and high resistance to oil, grease and atmospheric conditions. Polyurethanes can be created to satisfy a wide range of desired properties and adapted to specific applications. The structure of these polyurethanes has a significant impact on their properties, and this structure depends on the chemical structure of the substrates used in the synthesis of the diisocyanates, polyols and chain and/or crosslinking agents [1-3]. As a result of these properties, polyurethanes can be produced as foams, elastomers, plastics, adhesives, coatings, fibres and leather-like materials. They are used in the automotive, construction, mining, and medical industries, among others [4]. The research described in this article concerns the use of ureaurethanes for wheels in mining.

Mining transport devices, including those of a suspended type, are operated under high loads and are exposed to significant levels of dust and variable temperatures ranging from -40°C to 50°C. Their elastomeric tire wheels are also subjected to complex stress fields. These factors cause a safety hazard during technical operation following rapid wear of the basic structural elements, namely the wheels. Tyres constitute significant elements of the wheels. Currently manufactured wheels composed of polyurethane can only be used for a short time, making it difficult to work in the mines. The wheels are subjected to considerable strain and high temperatures at the start the vehicles. For this reason, the manufacture of wheels composed of

ureaurethane polyurethanes was proposed. Because materials used in mining need to have a higher thermal resistance, expandable graphite (EG) was added to the PURM. Because of its properties, EG is used in an increasing number of fire-retardant applications as a blowing agent and as a smoke suppressor [5]. Its effectiveness in polyurethanes is presented in the literature [6-7].

The purpose of this study was to investigate the effect of expandable graphite on the flame retardancy and others properties of PURM elastomers.

2 Materials and testing methods

2.1 Samples and execution

Ureaurethane and composites were synthesised using one-shot polymerisation of the hard segment formed by 4.4'diphenylmethane diisocyanate (MDI, Aldrich) and dicyandiamide DYDI - Omnicure 5 (Emerald Performance Materials). The soft segment consisted of polydiol, which was formed from poly(ethylene adipate) (PEA) with a molecular weight of 2000 g/mol (Alfaster T620, Alfa Systems).

Ureaurethane (PURM) synthesis was performed at a molar composition of 2 mol PAE, 5 mol MDI and 3 mol DCDA, resulting in a content of approximately 28% of hard segments. Expandable graphite products from Sinograf with particle sizes of approximately 0.18 mm and 0.15 mm and degrees of expansion of 50 and 250, respectively, were added to attain a concentration of 5 wt.%.

PEA with DYDI was dried in a vacuum reactor for 0.5 h at 170°C ± 5°C and then for 1 h at 150°C ± 5°C under a pressure of 2-6 hPa with intense stirring. The anhydrous mixture was cooled to approximately 60 ± 3°C, and MDI was added. The product was cured for 8 h at 150 ± 5°C. The samples were then cooled to room temperature and conditioned for 2 weeks.

2.2 Measurements and characterisation

2.2.1 Scanning electron microscopy (SEM)

SEM observation was performed on a Hitachi TM3000 microscope. SEM was used to observe the structure of the fillers used in this study. The samples were coated with gold to increase their conductivity. A series of images at different magnifications was acquired.

2.2.2 Fourier transform infrared spectroscopy (FT-IR)

FT-IR was performed on a Nicolet FT-IR 6700 (using 64 counts) to investigate the chemical structure of PURM. The analyses were performed using Omnic software, and a baseline correction using CO_2 and H_2O was performed to eliminate the impact of residues of these compounds from the analysis.

2.2.3 Thermogravimetric analysis (TGA)

TGA was performed on a TA Instruments TGA Q500 device to verify the thermal stability of the elastomers examined in this study. The analysis was conducted on a sample weighing approximately 10 mg in a N_2 atmosphere, with a heating rate of 10°C/min from room temperature to 600°C.

2.2.4 Differential scanning calorimetry (DSC)

DSC was performed using a TA Instruments DSC Q1000. Samples weighing approximately 10 mg were subjected to heat in the temperature range of -90°C–260°C to determine their characteristic temperatures.

2.2.5 Dynamic mechanical analysis (DMA)
DMA was performed using a TA Instruments DMA Q800. The study was conducted on rectangular samples using the two-point bending method in the temperature range of -100°C–100°C.

2.2.6 Cone calorimeter (CC)
A CC test was performed to investigate the ureaurethanes' resistance to fire. The samples were 100 mm x 100 mm in size, and the thermal radiation flux density was 50 kW/m^2. The CC test was performed in accordance with ISO 5660.

2.2.7 Static tensile test
A static tensile test was performed using an Instron 1115 universal testing machine according to PN-EN ISO 527. The paddle-shaped samples were stretched at a constant speed of 500 mm/min.

2.2.8 Physical and mechanical measurement
The density (ρ) test was conducted using hydrostatic weighing, in accordance with ISO 2781. The hardness (H) test was conducted using a Shore A durometer, according to ASTM D2240-75. Wear resistance (ΔV) was determined according to ISO 4649.

3 Results and discussion
3.1 Scanning electron microscopy (SEM)
The structures of the fillers used in this study are presented in Fig. 1. The magnification of the images is 100x. EG50 was observed to take the form of particles of different shapes with sizes of approximately 20-100 µm. EG250 has the form of discs with a size of approximately 100-300 µm.
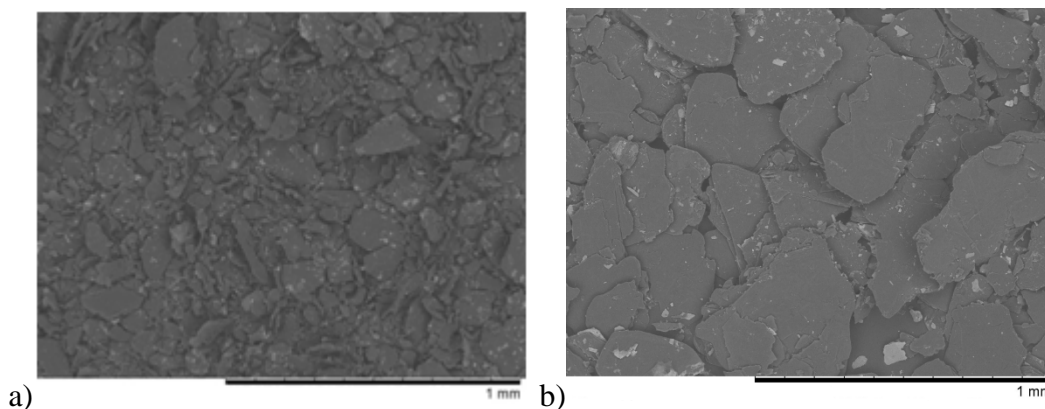

Figure 1. SEM images of fillers: a) EG50, 100x magnification, b) EG250, 100x magnification

3.2 Fourier transform infrared spectroscopy (FT-IR)
To study the effect of the addition of fillers on the chemical structure of PURM, Fourier transform infrared spectroscopy (FT-IR) was performed [8]. The FT-IR spectra of the investigated materials are plotted in Fig. 2. The addition of graphite with different expansion did not significantly affect the chemical structure of the ureaurethanes.
At 3339 cm-1, stretching N-H bonds are present, which are involved in the formation of hydrogen bonds. At 2960 cm^{-1} and 2880 cm^{-1}, symmetric and asymmetric CH$_2$ stretching vibrations are present, which are assigned to flexible segments. The C=O stretching at 1727 cm^{-1} corresponds to the C-O bond stretching vibrations of the ester group. At 1522 cm^{-1} and 1217 cm^{-1}, the amide II and amide III bands appear. The bands at 1163 cm^{-1} and 1078 cm^{-1}

correspond to the stretching vibrations of the C-O-C ester group. In addition, in ureaurethanes, there is a urea group that is associated with the amide I band at 1645 cm^{-1}, the amide II band at 1515–1560 cm^{-1} and the asymmetric bond stretching vibration associated with the N-C-N bond at 1300–1360 cm^{-1}. An important result of FT-IR spectroscopy is the lack of bandwidth from N=C=O groups, which indicates the complete reaction of other functional groups.
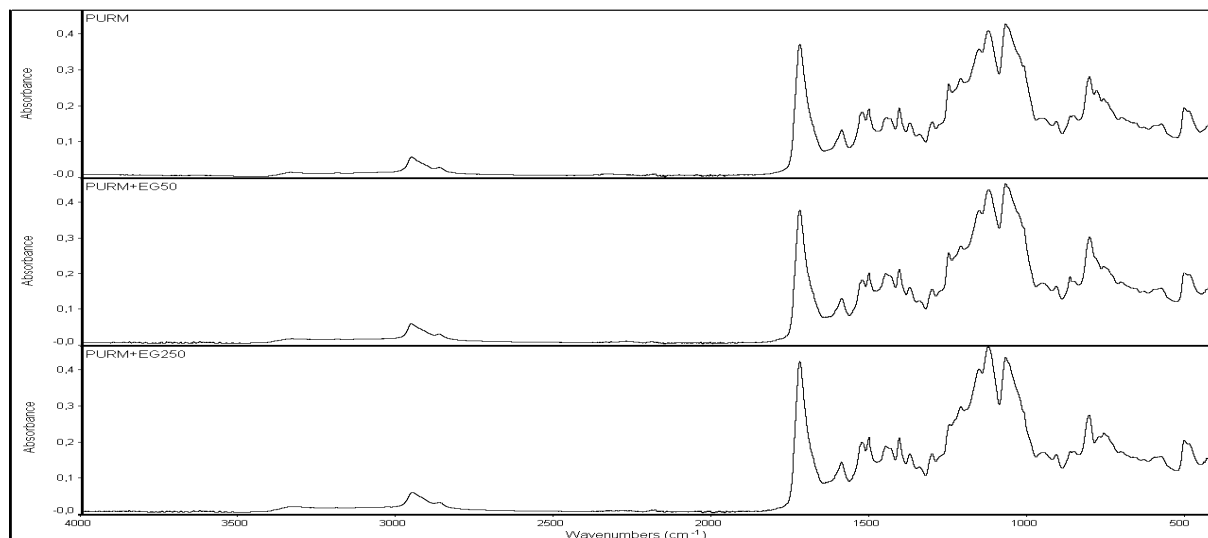
Figure 2. FT-IR spectra of tested ureaurethanes.

3.3 Thermogravimetric analysis (TGA)

The PURM thermal stability was determined using TGA. The DTG curves are plotted in Fig. 3. In the process of PURM degradation, two stages of degradation were observed. The first step of the degradation is correlated with the maximum rate of degradation of the hard segments (T_{max1}), and the second step is correlated with the maximum rate of degradation of the soft segments (T_{max2}). The T_{max1} and T_{max2} results are presented in Table 1. Upon the addition of EG, T_{max2} increased with an increase in the expansion of graphite. The temperature at 5% weight loss was also determined from the TG curve and is included in Table 1. The temperature corresponding to 5% of the smothering weight is considered to be the beginning of the decomposition temperature range of the material [9]. Adding EG250 causes an increase of the 5% mass loss temperature, which indicates an increase in the thermal resistance of the composite. This temperature is associated with the degradation of short-chain oligomers, which may have been produced during the ureaurethane polymerisation reaction.
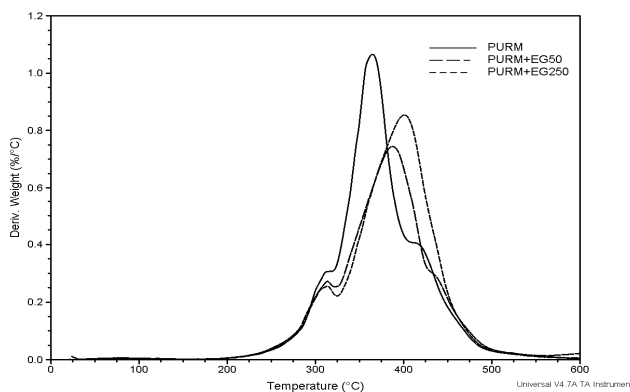
Figure 3. DTG curves of tested ureaurethanes.

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Material	T$_{5\%}$ [°C]	T$_{max1}$ [°C]	T$_{max2}$ [°C]
PURM	293.41 ± 0.23	311.00 ± 0.25	365.11 ± 0.52
PURM+EG50	292.69 ± 0.18	312.86 ± 0.31	386.89 ± 0.45
PURM+EG250	294.04 ± 0.31	313.22 ± 0.16	400.88 ± 0.28

Table 1. Results obtained from TG and DTG curves.

3.4 Differential scanning calorimetry (DSC)
DSC analysis was performed to obtain information about the glass transition temperature. The DSC curves are plotted in Fig. 4. The DSC thermal analysis revealed the presence of two glass transition temperatures for the soft segments (Tg$_{SS}$) and the rigid segments (Tg$_{SH}$) (Table 2). The glass transition temperature of the soft segments (Tg$_{SS}$) decreases in the composites containing EG. The lowest temperature occurred for PURM+EG50. The glass transition temperature of the hard segments (Tg$_{SH}$) decreased with the addition of filler. This decrease may be related to the deployment of hard segments in the distant vicinity of the filler, which increases their mobility. The decrease in the glass transition temperature of the rigid segments of the composites may also result from an increase of their dispersion size [1].

Material	Tg$_{SS}$ [°C]	Tg$_{SH}$ [°C]
PURM	-33.83 ± 0.18	243.06 ± 0.54
PURM+EG50	-38.84 ± 0.35	238.66 ± 0.75
PURM+EG250	-34.52 ± 0.26	239.51 ± 1.01

Table 2. Results obtained from the DSC curves.

3.5 Dynamic mechanical analysis (DMA)
To evaluate the mechanical properties over a wide temperature range, dynamic-mechanical thermal analysis was used. Table 3 presents the values of the elastic modulus set at temperatures of -30, 20 and 60°C and at the glass transition temperature. The curves in Fig. 4 exhibit a sudden reduction of the modulus (E') in the narrow transition temperature range in which the elastomers are in a highly fragile state. Below the glass transition temperature of the soft segments, the value of E' depends mainly on the amount of EG introduced. Above this temperature, the value of E' is also dependent on the mobility of the macromolecules [10]. The introduction of EG resulted in an increase in the glass transition temperature of the amorphous areas of the flexible segments (Tg), which were determined from the local maxima of the dissipation factor (Table 3). This factor is associated with a shift in the composite glass transition towards higher temperatures.
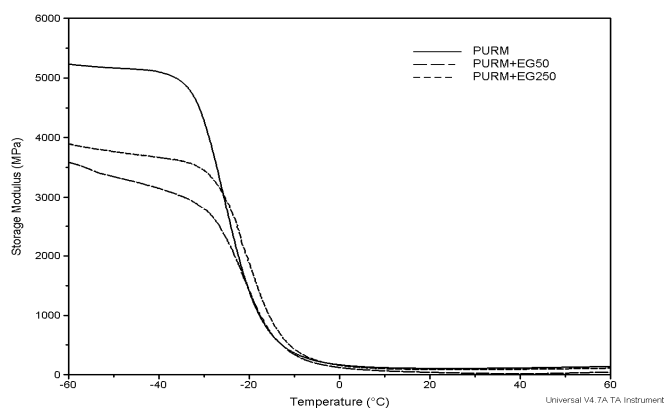
**Figure 4.** Storage modulus curves obtained from DMA analysis.

Material	E'$_{-30}$ [MPa]	E'$_{20}$ [MPa]	E'$_{60}$ [MPa]	Tg [°C]
PURM	4277 ± 0.56	107 ± 0.24	139 ± 0.32	-24.85 ± 0.15
PURM+EG50	2797 ± 0.78	41 ± 0.19	45 ± 0.41	-20.71 ± 0.18
PURM+EG250	3454 ± 0.89	87 ± 0.23	110 ± 0.25	-20.29 ± 0.22

Table 3. Results of elastic modulus and glass transition temperature obtained from the DMA curves.

3.6 Cone calorimeter (CC)

Improved thermal stability should correspond to increased stability of the polymeric materials under fire conditions [11]. The results of the CC measurements are presented in Fig. 5. The initial sections of the curves correspond to the heating periods of the tested materials, the evaporation of volatile products and the creation of flammable gases. After the ignition point, we observe a sudden increase in heat. Comparison of the curves in Fig. 5 clearly reveals a significant difference in the amount of heat released from the polyurethanes modified with EG particles compared with pure PURM. The peaks in the diagrams (Fig. 5) indicate the combustion of the pyrolysis products with the evolution of considerable heat (HRR$_{max}$). In PURM, one large peak represents this large amount of heat, and another smaller peak is also observed. In the composite with added EG, two significantly smaller peaks are observed, which indicates a change in the combustion mechanism. The lowest rate of heat release (HRR$_{max}$) was observed for PURM+EG50, which may be related to the fact that the expandable graphite is known as a filler that absorbs heat, leading to the reduction of the HRR$_{max}$ value. Another important parameter identified by the cone calorimeter is the time to ignition (tig) (Table 4). The times to the ignition points of the composites are shorter than those observed for pure PURM. This phenomenon may be a result of the previous decomposition of the organic parts present on the surface of the filler, which are not chemically bound to PURM.

Values for HRR$_{max}$ and tig were obtained and used to calculate the "fireproof protective impact indicator" (HRR$_{max}$/tig) (FPI), which is used to evaluate the effectiveness of flame retardant compounds. The calculated values are provided in Table 4. These data indicate that the FPI is reduced by 35% by the modification of ureaurethanes with EG50, which indicates improved performance of the composites [10].
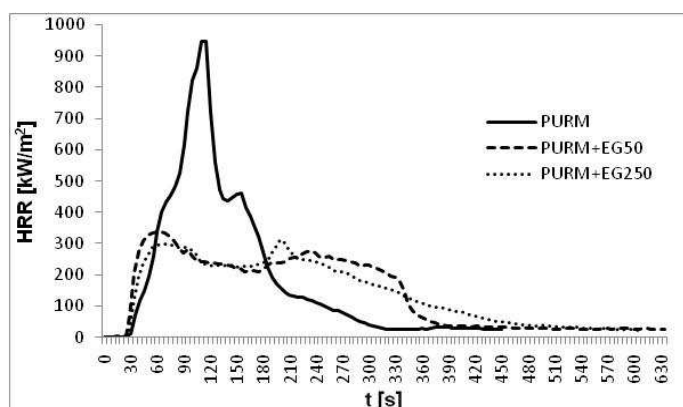
Figure 5. Heat release rate curves of urearethanes with different additives from CC tests.

Material	HRR$_{max}$ [kW/m^2]	tig [s]	FPI [kW/sm^2]
PURM	945.66 ± 5.23	22 ± 1	42.98 ± 0.24
PURM+EG50	337.99 ± 3.56	22 ± 1	15.36 ± 0.35
PURM+EG250	311.42 ± 3.78	23 ± 1	13.54 ± 0.18

Table 4. Characteristic parameters of the tested PURM obtained from CC tests.

3.7 Static tensile test

The results obtained in the static tensile tests are provided in Table 5. The lower value of the tensile strength (Rm) after the addition of EG may be a result of the weak interaction at the matrix-filler interface. The permanent elongation at break is lowest for PURM+EG50, which may indicate that this composite experienced the least dispersion of the filler into the matrix. The behaviour of the Young's modulus indicates that the addition of EG to the PURM increases the stiffness of the composite obtained. The PURM+EG50 composite has the highest stiffness, possibly because it contains the highest hard segment content.

Material	Tensile strength [MPa]	Elongation at break [%]	Young's modulus [MPa]
PURM	30.9 ± 4.15	114.5 ± 0.8	28.4 ± 0.04
PURM+EG50	22.4 ± 1.54	110.5 ± 0.6	37.0 ± 0.28
PURM+EG250	20.1 ± 3.03	116.5 ± 0.5	33.8 ± 0.21

Table 5. Results of the mechanical measurements obtained from the static tensile tests.

3.8 Physical and mechanical measurements

The results of the physical and mechanical properties are provided in Table 6. The highest density and hardness are recorded for the PURM+EG50 composite, implying that it contains many hard segments. Simultaneously, this composite has the worst wear resistance. The addition of EG caused a significant decrease in the wear resistance, which is an unfavourable characteristic for the desired application. This wear resistance is the result of poor dispersion of the filler in the matrix.

Material	Hardness [°ShA]	Density [g/cm^3]	Abrasive wear [mm^3]
PURM	87.5 ± 0.71	1.2525 ± 0.0017	29.9 ± 0.6
PURM+EG50	91.5 ± 0.69	1.2775 ± 0.0021	73.6 ± 0.5
PURM+EG250	90.2 ± 0.81	1.2729 ± 0.0018	56.3 ± 0.2

Table 6. Results of the physical and mechanical measurements.

4 Conclusions

The introduction of EG to ureaurethanes causes changes in their chemical structure and, consequently, in the properties of the produced materials. Modifying the expanded graphite content leads to changes in the course of thermal decomposition. The introduction of 5 wt.% EG leads to a significant increase in the decomposition temperature of the soft segments and a small increase in the decomposition temperature of the hard segments. The results obtained during TGA are confirmed by CC tests, in which the PURM+EG250 ureaurethane proved to be the most heat-resistant composite. Unfortunately, this material had compromised mechanical properties and wear resistance, which may be results of the incomplete connection of the filler with the matrix. Further research is required to determine the optimal composition and synthesis conditions to produce materials with optimal properties.

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