

# Mechanical behavior of particle-reinforced polyurethane composites for load-bearing drives

Anna Porąbka<sup>a</sup>, Vasiliki-Maria Archodoulaki<sup>b</sup>, Jadwiga Laska<sup>a,\*</sup>

<sup>a</sup> AGH University of Science and Technology, Faculty of Materials Science and Ceramics, al. Mickiewicza 30, 30-059 Krakow, Poland

<sup>b</sup> Vienna University of Technology, Institute of Materials Science and –Technology, Favoritenstraße 9 11/E308, A-1040 Vienna, Austria

## Article history:

Received 7 September 2019

Received in revised form

28 September 2019

Accepted 29 September 2019

Available online 30 September 2019

## Abstract

Two series of polyurethane composites were prepared using NDI- and MDI-based prepolymers and common polyol. NDI-based polyurethane is generally resistant to mechanical wear and rebound-resilient whereas MDI-based PU has cushioning and vibration damping features, and both types can be used as a matrix for load-bearing composites. The objective of this study was to compare the mechanical properties of composites containing 5% vol. of ceramic particles prepared with the use of the mentioned PU systems, and unmodified commercial materials. The effect of various ceramic particles on physical and mechanical properties was studied. The results showed that the mechanical properties changed in comparison to reference materials:  $E'$  improved, and impact strength performed favorably in certain materials. Both the tensile strengths and the elongations at break of the composites were found to decrease with the content of ceramic particles; however, the hardness increased gradually. Since ceramic particles offer better stiffness and hardness, the selected composites could be a viable alternative to the pure commercial PUs available in the industry.

**Keywords:** Polyurethanes, composites, mechanical properties

## Introduction

Polyurethane (PU) elastomers are widely used in the industry and consumer products, particularly in the areas where heavy pressure, load, impact and wear occur because they possess excellent comprehensive properties such as high wear-, oil- and corrosion resistance, high elasticity and damping, good adhesion to other materials and so on [1, 2]. They are characterized by excellent tensile strength, high resilience and wear resistance, high abrasion resistance, tear strength and excellent shock absorption [3–6] as well as high flexibility even at low temperatures [7]. The polyurethanes are an important and very versatile class of polymer materials with desirable properties. For example, PUs are being used as materials to replace traditional metallic materials in the mineral and mechanical industries [1, 8–10]. They are usually used as adhesives, coatings, foams, and different kinds of plastics and elastomers, but also as matrix resins for composites. The attractiveness of polyurethanes stems from their hydrophobicity, excellent thermal, oxidative and weather stability. Polyurethanes have the advantage of having low viscosity, excellent bonding with the ground and fast reaction time<sup>[3]</sup>. The polyurethane systems together with proper

fillers can produce composites that can compete in many aspects with the traditional materials.

Therefore, PU elastomer applications are becoming more and more popular within material and other corresponding areas of use. However, there are some shortcomings for PUs used as materials for coatings such as their poor heat resistances, high costs, etc. In general, the temperature window of conditions within which PUs can be used as coating materials ranges from the glass-rubber transition (–50 to 25°C) to tens of degrees below the melting or decomposition temperature (~120°C).

Polyurethane cast resins are two-component systems consisting of a resin (based on polyol, in case of composites, equipped with fillers and additives) and a hardener components (made up of the isocyanate substance class). In the most simple way of casting, manual potting, both components are weighed according to the required ratio and mixed [11]. Almost all data presented in the literature [12] concerning the effect of diol chain extenders on mechanical properties, revealed that 1,4-butanediol offers the best tensile properties, as a result of the specific crystalline structure and conformation of the hard segment. Also, the structure of diisocyanates has a strong effect on the domain morphology and the mechanical resistance of polyurethane materials. So, the symmetric isocyanates form crystallizing hard segments with good packing ability, produce materials with high mechanical resistance [13].

\*Corresponding author: jlaska@agh.edu.pl

For correct processing and good properties of the material all components must be mixed homogeneously. No air bubbles are allowed in the reaction paste. In addition, the isocyanate group is able to react with water. If this reaction occurs, gaseous  $\text{CO}_2$  is formed in the mixture. This reaction is totally undesired for casted materials because they will be more or less filled with voids. This results in a loss of mechanical properties. Because of this reaction, the mixture can be enhanced with water absorbing materials, mostly zeolites containing aluminosilicates. Suitable zeolites exhibit high affinity towards water, and due to this, one of the most relevant fillers can be e.g. fly ash. They bind or remove free water from the mixture, allowing for a secure reaction of polyol and isocyanate forming polyurethane. If the basic guidelines are considered during the processing, reproducible results with high quality modern PUs can be achieved [11].

The composites technology, in which particulate fillers are added into the polymers, may provide a good method for PU to solve even more problems. For example, it is common for many producers to add fillers such as powders or fibers, etc. into various PUs to increase stiffness and modulus, and to reduce thermal expansion coefficients and product costs [2, 14, 15]. However, when the fillers are all fine and lacking hardness they may not improve the toughness and impact strength. There are few, if any, publications exploring the effect of hard ceramic particles (such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{SiC}$ , etc.) on the mechanical strength of PU matrix composites [1].

The use of particle reinforced composite materials as an alternative to pure polyurethane coatings in transport mining units could become widespread thanks to their main technological advantages, i.e. low weight, high specific strength, proper stiffness, environmental resistance and long life. Compared to metals, composite parts can be easily made with a relatively low tooling cost. The mining industry is an interesting area for new types of rapidly manufactured composites because they use prolonged high temperature conditioning processes for fabrication of composite parts, which is justified when high performance materials or high exploitation temperatures are required[3] such as in drive couplings.

One of the most popular form of composites used in structural applications is a polymer matrix reinforced with ceramic particles. Particle reinforced composites of polyurethane offer many advantages in terms of manipulative requirements, including dimensional stability, good conformability, strength and toughness.

In this paper, the matrix resins under study included NDI- and MDI-based polyurethanes, which are compared with two other commercially available ones. The objective of this study was however to show the feasibility of utilizing NDI- and MDI-based polyurethane matrix resins for ceramic particle reinforced composites and examine the effects of the type and size of the filler on their mechanical properties. The mechanical properties of all types of composites were measured and described. The

effect of the matrix prepolymer and filler on hardness, tensile strength, impact strength and modulus were studied. Dynamic-mechanical analysis was mainly employed to determine the elastic behavior of polyurethane composites. This paper helps to understand the variation rule of the mechanical properties of ceramic particles reinforced elastomer composites [3].

## Materials and Methods

### Description of materials

Two types of polyurethane resin were synthesized in this study: based on NDI and MDI, and common polyol – 1,4-butanediol (supplied by Gasket, Poland). The polyurethanes were marked in the text as 3.1.1B and 5.1.1, respectively. Moreover, the tests were performed also on other commercial PU supplied by Gasket, Poland, and three types of Vulkollan (Bayer, Germany): V18, V27 and V30 based on Desmodur 15 (1,5-naphthalenediisocyanate and 1,4-butanediol).

In order to modify polyurethane systems, the following ceramic additives were used: basalt powder (Krzeniów, Poland, 0–200  $\mu\text{m}$ ), finely ground sand (0–20  $\mu\text{m}$  and 20–50  $\mu\text{m}$ ), silicon carbide (0–10  $\mu\text{m}$ ), nanosilica (Aerosil OX 50, Evonik, Germany, 0–90 nm), and fly ash (FA) microspheres (Połaniec, Poland) divided into fractions of grain sizes: <15  $\mu\text{m}$ , 15–30  $\mu\text{m}$  and 30–45  $\mu\text{m}$  respectively.

### Fabrication of composites

To remove absorbed moisture, and prevent void formation, all ceramic powders were being dried at 105°C for 2 hours before the use. The polymeric components were molten at the temperature of 70°C and stirred. Appropriate amounts of polyol and prepolymer were weighed (0.433:1 weight ratio) as well as the amount of fillers corresponding to 5% vol. Then, they were placed in a polypropylene form tightly inserted into a glass reactor, and heated to 70°C. Polyol was thoroughly mixed mechanically with ceramic powder. Only then could the prepolymer be added to the system and the reactor tightly closed and thoroughly degassed. The mixture was being stirred well for 1–2 min until gelation began, and removed from the reactor. Then, the composite was being conditioned for two 12 h cycles at 120°C. The plates were being conditioned for three months in order to ensure finishing of all chemical reactions and acquiring the optimal properties by the materials. After this fabrication procedure one could cut several specimens for each series of tests.

### Methods

The mechanical properties of the composites were tested on the specimens cut from each plate. The thickness of each specimen was measured at three sections to verify its regularity. Tensile strength and elongation at break were tested according to ISO 37 standard in ambient conditions using strength testing machine Cometech QC-508B1-204 and Zwick 1435. The dynamic-me-

chanical tests were carried out using Dynamic Mechanical Analyzer 2980, TA Instruments to evaluate properties of 10×5×50 mm polished bar samples in the temperature range of -100°C and +110°C at a programmed heating rate of 2°C/min, amplitude 70 μm and force 0.05 N. The sample preparations were critical for data reproducibility. According to the rigidity and dimensions of the test specimens, a three-point bending mode was used to mount the sample in the DMA measurement device. The sample was clamped inside an environmental chamber and cooled to an initial temperature. Samples were being equilibrated at initial temperature -100°C for 10 min before measurements were made. Liquid nitrogen was used to achieve the subambient temperature. Under constant force control, the sample is subjected to an oscillation deformation, and the oscillating stress is measured [16]. The response of the materials is monitored at a constant frequency and a constant amplitude of deformation, and data are recorded at defined time intervals. Data was collected at an oscillation frequency of 1 Hz [16]. The measurements were performed following ASTM E1640-99 standard. Results were evaluated using Universal Analysis v.4.5 software. Impact experiments with PU composites were performed with Instron Ceast 9050 in four points: -78°C, -40°C, -30°C and 23°C on the 80×10×4 mm-sized notched samples. The impact velocity was about 3–4 m/s and the distance between supports was 62 mm. The characterization of composites included determination of composites hardness as well. Durometer RX-1700-A was applied to measure Shore A hardness.

## Results and discussion

DMA is a powerful tool in testing the mechanical properties of polymers and composites. It provides information on the ability of viscoelastic materials to store and dissipate mechanical energy upon deformation [16]. When reading a DMA plot, the storage modulus ( $E'$ ) and the loss modulus ( $E''$ ) reflect the elastic and viscous character of the sample, respectively [16].  $E'$  is the measure of material stiffness [17]. Higher content of hard segment results in higher modulus values in the viscoelastic state above the glass transition [18] (Table 1). These two moduli may be combined to generate a unified  $\tan \delta$ :  $\tan \delta = E''/E'$  [16]. The temperature associated with the peak magnitude of  $\tan \delta$  is defined as the glass transition temperature  $T_g$ , but for the purpose of this study it was more reasonable to consider the  $T_g$  reading from the peak values in  $E''$  plot [18, 19] or by a drop in storage modulus resulting in the peak on the storage modulus-temperature curve [3].

DMA is very sensitive to glass transition because the mechanical properties (such as modulus and damping) measured by DMA depend strongly on the material's relaxation time, which undergoes large changes during the glass transition. It provides the most credible information on changes that occur during glass transition and therefore is well suited to measuring  $T_g$ . The DMA

traces are frequency dependent but yield unambiguous peaks for  $T_g$  [20]. The registered range of  $T_g$  temperatures varies from -53°C (commercial PU) to -25°C (5.1.1). Addition of the filler in all composites decreased the  $T_g$  compared to corresponding pure PU.

Thus, qualitatively speaking, on the lower temperature side of  $\tan \delta$  maximum, the material will be glassy and rigid with a high modulus and low elongation. In the glass transition region, the material is expected to be leathery with large changes in the modulus and  $\tan \delta$  values. Above the glass transition region, the material becomes rubbery and capable of great elongation and possesses a low modulus [16]. In general, the  $T_g$  is affected by a number of chemical and molecular structures (such as the effect of cross-links, molecular weight, bulkiness of the side groups attached to the backbone, molecular polarity, etc.) or physical modification and the relative amount of components present [16]. The sharper  $\tan \delta$  transitions suggest more uniform cross-links, e.g. pure PUs with hardness below 93°ShA. The broadest  $\tan \delta$  transition suggests the great degree of heterogeneity of cross-links (e.g. Commercial PU) [17]. The lower values of tensile (Young's) modulus (softer materials) result from lower crosslinking density and the presence of side dangling chains. These differences in modulus are present at higher temperatures, also, as observed by DMA (Table 1) [3].

### Tensile strength and elongation at break

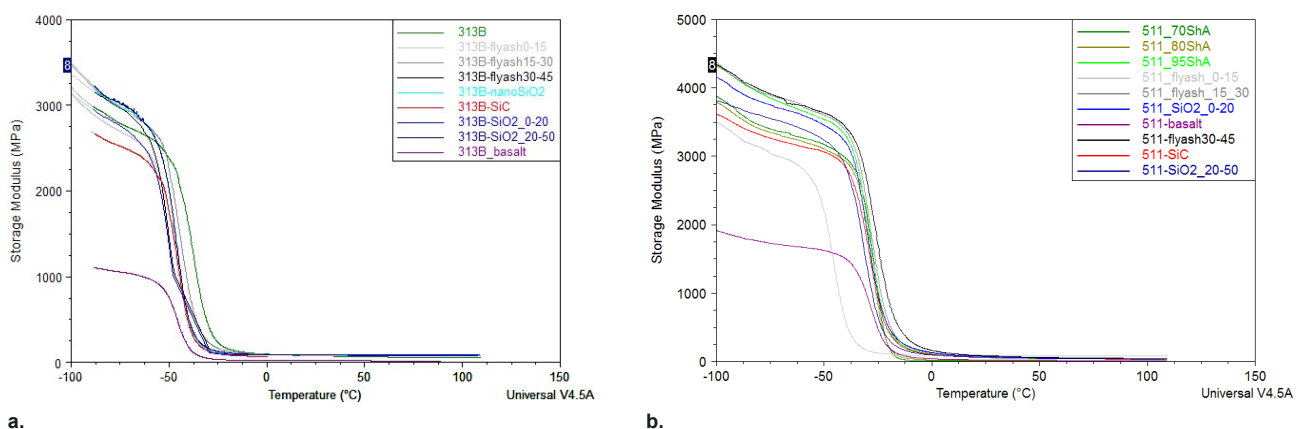
Table 1 presents the values obtained in various mechanical tests. Data deduced from static tensile strength indicate that the  $R_m$  and  $\epsilon_{max}$  parameters decreased compared to pure reference materials. For example, tensile strength of the 3.1.3B composites decreased about 50%, and  $R_m$  of 5.1.1 composites analogously. The highest  $R_m$  was registered for pure 3.1.3B 95°ShA material (43.55±5.89 MPa), and the lowest for 3.1.3B+basalt (5.95±0.45 MPa). The elongation at break decreased in all 5.1.1 composites but in 3.1.3B composites containing FA 30–45 μm and nano-SiO<sub>2</sub> slightly increased.

### Storage modulus

Obtained plots (Figure 1) show evolution of the storage moduli  $E'$  of the elastomers with and without fillers with the temperature increase and illustrate the typical dynamic mechanical behavior of the samples. The greater rigidity of most of the composites at room temperature is partly attributed to the composition of the polyurethane composites that contained 5% vol. of ceramic (nano)particles. Comparing the storage modulus of pure PUs to the composites' one also in 78°C, the two types of materials were characterized by similar tendency as in ambient temperature; so their elastic properties were quite comparable with each other. Any differences between the tested materials might be due to density, chemical composition, properties or formation. The overall elastic properties (stiffness) of the specimens appear to be weighed combination of the individual properties of components present. The relative contribution of each component to

**Table 1.** Summary of the data obtained in the mechanical tests: hardness, tensile strength ( $R_m$ ), elongation at break ( $\epsilon_{max}$ ), storage modulus  $E'$  and loss modulus  $E''$

	Material	Hardness [°ShA]	$R_m$ [MPa]	$\epsilon_{max}$ [%]	Modulus (25°C)		Modulus (-78°C)
					$E'$ [MPa]	$E''$ [MPa]	$E'$ [MPa]
313B	pure	70	11.84±3.50	856.02±116.31	6.54	0.12	2458
	pure	80	9.93±3.47	614.86±142.14	18.01	0.90	2872
	pure	95	43.55±5.89	496.27±34.58	77.32	6.88	2831
	basalt	82	5.95±0.45	239.16±44.44	20.41	1.04	1066
	FA 0–15 $\mu$ m	94	15.16±2.91	366.95±82.09	82.95	5.41	2741
	FA 15–30 $\mu$ m	97	25.71±4.28	423.72±41.81	87.63	2.82	3011
	FA 30–45 $\mu$ m	95	21.19±2.08	407.63±43.85	89.96	3.88	3022
	nanoSiO <sub>2</sub> $\mu$ m	98	25.39±2.14	473.66±30.18	85.63	3.25	3023
	SiO <sub>2</sub> 0–20 $\mu$ m	93	17.69±0.75	174.09±30.96	86.12	5.09	2807
	SiO <sub>2</sub> 20–50 $\mu$ m	97	22.8±1.13	397.83±28.13	87.29	3.59	3074
	SiC	95	21.07±5.43	306.46±86.86	63.95	3.13	2554
511	pure	70	15.25±2.05	995.71±30.86	7.69	0.35	3430
	pure	80	12.41±0.87	760.55±82.62	16.33	1.24	3381
	pure	95	40.92±3.70	512.69±20.86	60.42	8.19	3892
	basalt	84	13.46±0.87	284.57±22.47	24.81	3.46	1747
	FA 0–15 $\mu$ m	96	16.94±2.62	303.49±72.12	93.09	4.52	3114
	FA 15–30 $\mu$ m	96	21.19±2.88	354.37±51.94	70.17	8.70	3929
	FA 30–45 $\mu$ m	93	21.19±2.08	407.63±43.85	86.26	12.11	3947
	SiO <sub>2</sub> 0–20 $\mu$ m	95	19.42±3.44	299.10±86.68	76.86	8.94	3784
	SiO <sub>2</sub> 20–50 $\mu$ m	93	26.07±2.27	444.31±41.52	61.49	7.60	3583
	SiC	94	26.67±4.20	306.65±41.10	62.47	8.12	3300
	Commercial PU	95	28.18±2.36	613.17±28.57	92.36	12.10	2534
Vulkollan 18	82	16.58±1.91	754.16±42.09	1.90	0.18	258	
Vulkollan 27	93	13.46±1.12	455.85±98.49	91.19	5.22	4038	
Vulkollan 30	94	9.92±1.56	101.71±13.65	105.70	6.75	4225	



**Figure 1.** Storage modulus vs. temperature plots registered for a) 3.1.3B. b) 5.1.1 composites with reference to unmodified PUs

the storage modulus of the samples would be proportional to its relative fractional amount [16].

Table 1 summarizes the storage modulus data in function of temperature. In the glassy solid state at  $-78^{\circ}\text{C}$  most of 3.1.3B composites have shown reinforcement effect up to about 16%, except 3.1.3B+SiC and 3.1.3B+basalt, whose modulus decreased by 17% and 74% respectively. Most likely the introduction of 5% of ceramic particles cause the increase of the entropy in those mixtures and caused the reduction of composite matrix cohesion through loss in total hydrogen bonding and decrease of crystallinity degree [21]. The 5.1.1 composites of this kind behaved similarly.

Among 3.1.3B-based materials, the 3.1.3B+FA 30–45  $\mu\text{m}$  composite is characterized by the highest value of  $E'$ : 89.96 MPa at room temperature ( $25^{\circ}\text{C}$ ) compared to the pure 3.1.3B material, that is, 77.32 MPa. And among 5.1.1-based materials, the 5.1.1+FA 0–15  $\mu\text{m}$  one is distinguished by  $E'$  equal to 93.09 MPa while pure 5.1.1 has 60.42 MPa. Storage moduli of the remaining composites containing FA and  $\text{SiO}_2$  are also high: they range from 82.95 to 87.63 MPa (Table 1). Pure PUGAs 3.1.3B and 5.1.1 had lower storage moduli than the Vulkollans 27 and 30, although harder ones. Whereas all softer materials ( $\sim 70$ – $80^{\circ}\text{ShA}$ ) had lower  $E'$  than the hard ones ( $\sim 93$ – $95^{\circ}\text{ShA}$ ). So it was interesting that the Vulkollan 18 was characterized by lower storage modulus (1.9 MPa) than PUGA materials (about 18 and 16 MPa respectively), which was inappropriate to their hardness  $\sim 80^{\circ}\text{ShA}$ . The Commercial PU performed very well having  $E'$  equal to 92.36 MPa at room temperature. The highest  $E'$  value amongst all belonged to Vulkollan 30, that is, 105.7 MPa. The storage moduli  $E'$  of the used 5.1.1-based materials were generally slightly lower than those of 3.1.3B-based materials at ambient temperature. However in the  $-78^{\circ}\text{C}$  region  $E'$  was characterised by an abrupt increase, especially when the temperature reached the glass transition region. This relation inverted as determined by DMA.

All materials and polyurethanes are characterized by the glassy region, the glass transition (noticed by a sudden decrease in storage modulus) and the rubbery plateau, except Commercial PU, whose slope falls directly without plateau in the plot. In the glassy region the storage modulus does not vary with increase in temperature, because of the lack of movement of the polymer chains below the glass transition. And the addition of some fillers or their grain fractions decreases the storage modulus due to the lack of miscibility between the particles and the polymer matrix. After glass transition is reached, the storage modulus decreases in the filled polyurethanes as well as in pure ones to the same extent.

### Tan $\delta$

The values of the glass transition temperature and degree of crosslinking in the filled polyurethanes can be analysed from the curves of  $\tan \delta$  vs. temperature (Figure 2). The addition of the fillers moves the glass transition at lower temperature due

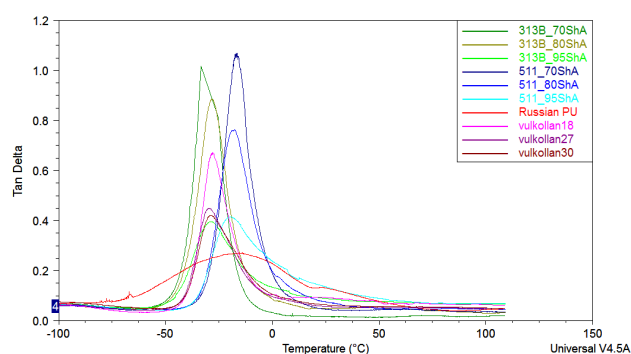
to their influence on the degree of phase separation between soft and hard segments in the polyurethane matrix. Furthermore, only the addition of FA 30–45  $\mu\text{m}$  and  $\text{SiO}_2$  0–20  $\mu\text{m}$  to 3.1.3B and FA 0–15  $\mu\text{m}$  to 5.1.1 strongly decreases the glass transition temperature of the polyurethane. Whereas the addition of the other fillers does not significantly change the glass transition temperature value of the polyurethane. On the other hand, the addition of nanosilica to 3.1.3B decreases the degree of crosslinking of the polyurethane, because of an increase in the maximum value of the  $\tan \delta$  curve is noticed. This is in agreement with the lack of miscibility of the nanosilica particles in the polyurethane matrix [22]. There are no appreciable differences in  $\tan \delta$  of the materials based on the selected PUGA hard system e.g. on 3.1.3B 95 $^{\circ}\text{ShA}$  [16].  $\tan \delta$  values are placed in a very similar range. But the differences occur only in the values obtained for the soft materials of all origins – higher, narrower (sharper) peaks. The exception is that the  $\tan \delta$  curve of 3.1.3B+nanosilica appeared with the highest  $\tan \delta$  peak value among all other composite materials through the whole scanning temperature range, because the nanosilica increased the viscous property (loss modulus) of this sample [16, 22].

Increased slope and narrowing of the  $\tan \delta$  transition peak (i.e. a better resolved transition peak) indicate slightly better phase separation [16]. However, due to the existence of hydrogen bonds in all of the PU networks under study as mentioned earlier, the occurrence of phase separation was inevitable and the transition could be related to the  $T_g$  of a soft-segment phase caused by a weak phase separation. The weakness of the degree of the phase separation is also evidenced by  $T_g$  measurement, which detected only one  $T_g$ .

The  $T_g$  values of crosslinked PUs are affected by several factors, including the relative amounts of the soft and hard segments, the crosslinking density and the amount of hydrogen bonding. The  $T_g$  values for the 5.1.1-based materials were lower than those for the 3.1.3B samples. This is probably due to a smaller amount of hydrogen bonding in 5.1.1 compared to 3.1.3B and the presence of a large amount of dangling chains in 5.1.1 networks resulting from the hydroxyl groups being located in the middle of the chains [20]. As expected, higher content of hard segment results in higher modulus values in the viscoelastic state above the glass transition, but in the glassy state the previously 'soft' segments changed to rigid structures, therefore enhancing the modulus of 5.1.1 over the modulus of 3.1.3B. The peak maxima in the 5.1.1 composites, which would be taken as the glass transition temperatures are almost the same, indicating the same level of phase separation, excluding 5.1.1+FA 0–15  $\mu\text{m}$  [18]. Compared to the original polyurethane, the  $\tan \delta$  temperature of the composites decreased with the addition of the dispersed particles, indicating a stronger interaction of particles with the hard domain of the PU and consequential increase in the segregation of the flexible segment domain. This specific interaction between the particles and the hard segment domain

could also be observed in the behavior of the storage modulus  $E'$  and loss modulus  $E''$  curves [21].

The most important similarity between the 3.1.3B- and 5.1.1-based composites was that the  $\tan \delta$  peaks are shifted to lower temperature, especially 5.1.1+FA 0–15  $\mu\text{m}$ .  $\tan \delta$  peaks of the 5.1.1 composites are not shifted, except 5.1.1+FA 0–15  $\mu\text{m}$ . Almost all of the peaks of the composites are similar to the peaks of pure PU.  $\tan \delta$  peaks of the soft PUs (70 and 80°ShA) are noticeably higher than those of hard PUGAs. Among the composites, the 3.1.3B+nanosilica and 3.1.3B+SiC ones are characterized by notably high  $\tan \delta$  peaks as well as 5.1.1 with the addition of SiO<sub>2</sub> 20–50  $\mu\text{m}$  and all FA fractions. These sharper  $\tan \delta$  transitions observed for the softer PUGA systems suggest more uniform cross-links compared to Vulkollan materials and especially to Commercial PU. Commercial PU is characterized by the broadest  $\tan \delta$  transition of all PU systems, suggesting the greatest degree of heterogeneity of cross-links [17].

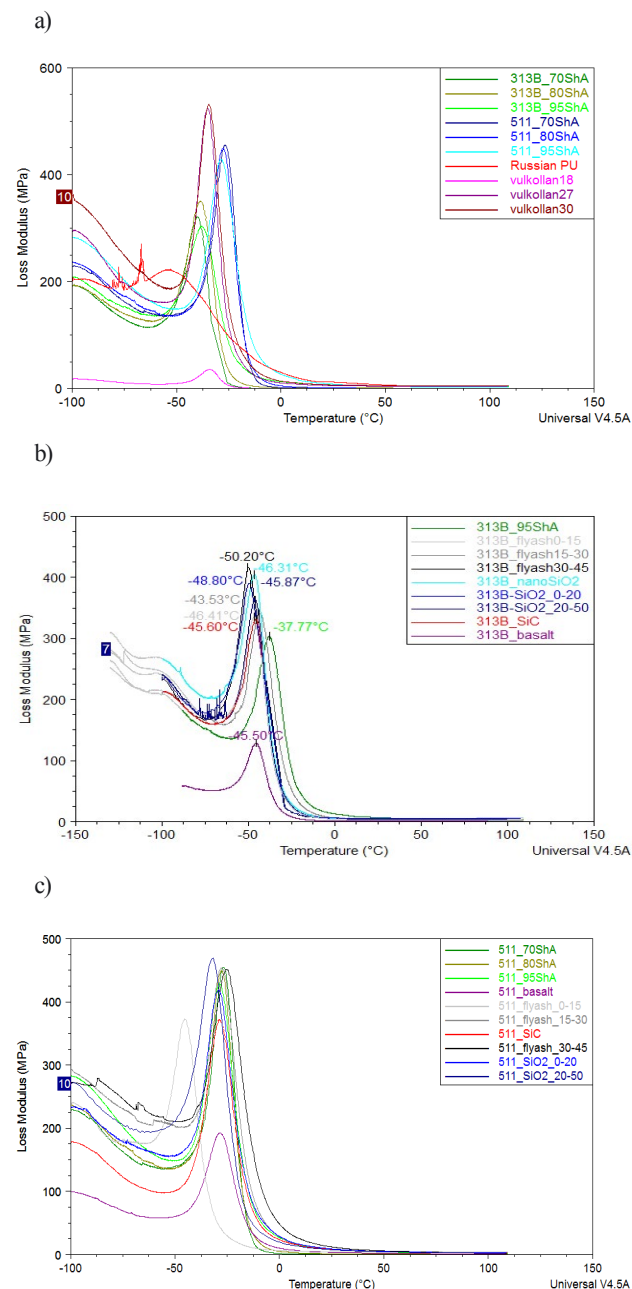


**Figure 2.**  $\tan \delta$  vs. temperature plots of unmodified PU materials of different hardness: 3.1.3B 70, 80, 95°ShA, 5.1.1 70, 80, 95°ShA, Commercial PU 95°ShA and Vulkollan 81.93 and 94°ShA

### Loss modulus

The peak maxima of the loss moduli  $E''$  diagrams (Figure 3) are similar in shape and temperature range. An increase in damping was observed in PUs with 5% particles content compared to pure 3.1.3B and then no significant change was observed for 5.1.1, even if a reduction of the relative concentration of polyurethane took place. The observed damping of the 3.1.3B composites was similar to the original PU 3.1.3B ones. The greater damping observed was attributed to an increase in the interphase volume of the flexible segment formed by hard segments bonded stronger to the particles and also to the heat dissipation due to the molecular motion into the particle surface [21]. The biggest damping (over 12 MPa) was observed at room temperature in 5.1.1+FA 30–45  $\mu\text{m}$  and Commercial PU which is characterised by a very broad  $E''$  transition that ranges over a broad temperature range (75°C to +25°C). High values of  $E''$  suggest greater mobility of the polymer chains associated with the dissipation of energy when the polymer is subjected to deformation. Thus the composites having a high and broad  $E''$  transition can have the ability to absorb energy associated with impact (compare

Table 1, e.g., 3.1.3B+SiO<sub>2</sub> 0–20  $\mu\text{m}$ ) [17]. On the other hand, the highest loss modulus peak is exhibited by 3.1.3B+FA 30–45  $\mu\text{m}$ . And among 5.1.1 composites it is 5.1.1+SiO<sub>2</sub> 0–20  $\mu\text{m}$ . Therefore, DMA helps to explain the superior impact resistance of the composites containing fly ash and silica (nanosilica) compared to the pure materials or composites containing SiC or basalt.



**Figure 3.** Loss modulus vs. temperature plots of a) pure PUs, b) 3.1.3B composites, c) 5.1.1 composites

### Impact response

The impact measurement and the DMA data suggest that all the materials that are characterised by respectively high and broad  $E''$  peaks endured also the impact: 3.1.3B+FA 0–15  $\mu\text{m}$ , 3.1.3B+SiO<sub>2</sub> 0–20  $\mu\text{m}$  and Commercial PU. The DMA data suggest that

while broad loss transitions indicate superior mechanical properties such as impact resistance, sharper loss transitions, such as those characterized by pure materials, appear to be related to the superior chemical agent resistance [16, 17]. The ability of elastomeric materials to absorb energy of impact stands behind a wide variety of applications in the industry and transportation [23]. The impact response of the PU composites was addressed in this study. When products made of polymers are utilized in industrial practice, impact loading often occurs in addition to static loading. Examples of this include stone impact on frontal surfaces of automotive, railway rolling stock. etc. Impact loading results in increased strain rate significantly altering the strength and break behavior of most plastics. In addition to increased strain rate, factors contributing to brittle fracture include low temperatures and multiaxial stress states together with residual stresses. Stress concentrations at notches contribute especially to the formation of brittle fracture, therefore tests are often performed on notched specimens. The tests mostly used for evaluating the toughness of plastics under impact loading include the *Charpy* or notched *Charpy* impact test. the uniaxial impact or notched impact test and the biaxial free-falling dart test owing to their relatively simple applicability. On specimens with rectangular cross-sections, plastic sheets and films, conventional toughness values are acquired that generally decrease with increasing strain rate. i.e. the occurrence of macroscopic brittle fracture phenomena is promoted. The *Charpy* impact test in various arrangements has gained the greatest importance in the quality control of plastics because of its methodological simplicity, short testing time and relatively low consumption of materials. Although, its use in quality assurance is undisputed, its applicability is limited in the area of material development and optimization. The specimen lies with its notched side centrally between two supports (*Charpy* configuration). The *Charpy* im-

pact test was performed on notched specimens with three-point support and serves to evaluate the toughness behavior of plastics under impact loading. It is standardized in ISO 179. Notched *Charpy* impact strength  $a_{cN}$  is calculated from the absorbed energy  $W_c$ , related to the smallest initial cross-section of the specimen at notch base [24]:

$$a_{cN} = \frac{W_c}{b_N \cdot h}$$

$b_N$  remaining specimen width at notch base.

Figure 4 presents the impact strength values of selected modified and unmodified materials depending on the temperature of measurement.

Noteworthy is the lack of fracture of the 3.1.3B-based materials in low temperatures (-30°C and 40°C), due to their flexibility and resilient behavior. The value of impact resistance, further improved with incorporation of SiO<sub>2</sub> 0–20 μm to the 3.1.3B matrix, which is difficult to evaluate, because the sample did not break. Remarkable impact strength is presented by 3.1.3B+FA 0–15 μm and commercial PU although both were broken: 12.4 kJ/m<sup>2</sup> and 21.4 kJ/m<sup>2</sup> respectively. Once again, one can also observe the resilient and stress dissipating capability of 3.1.3B+FA 0–15 μm and Commercial PU. At -78°C the impact strength of 3.1.3B and 5.1.1 generally increased after incorporation of the SiO<sub>2</sub> and FA particles.

With regard to the energy, it was comparable: the higher the value of impact strength, the higher the energy absorbed. The notably high energy absorbed was registered for the following samples, depending on the temperature of measurement: at 23°C for the 5.1.1-based materials (1.4–1.5 J) and Commercial PU (1.53 J). At -30°C pure 5.1.1 absorbed the most energy. At -40°C it was 3.1.3B and at -78°C – the composite 3.1.3B+SiO<sub>2</sub> 0–20 μm which survived the impacts well.

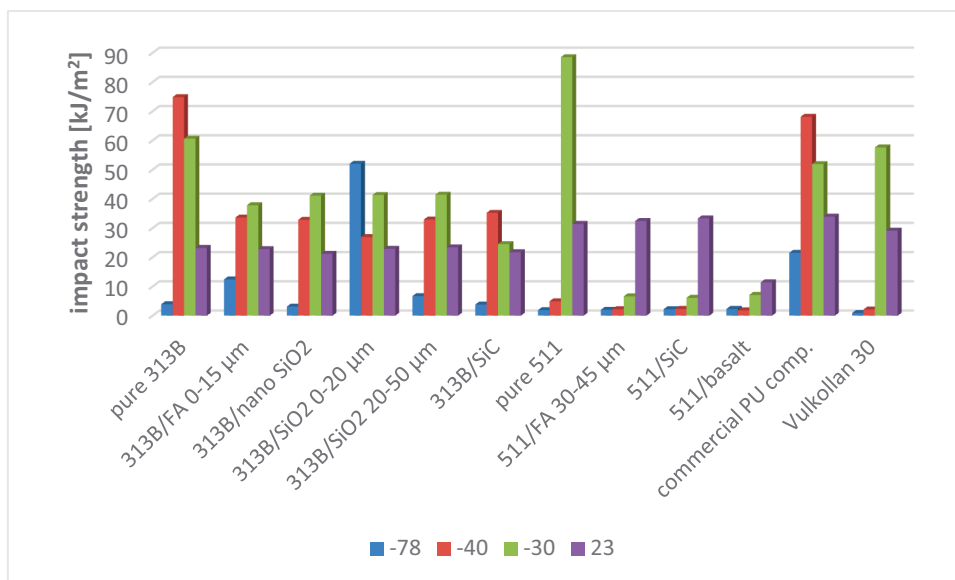


Figure 4. Comparison of impact strength values at different temperatures. i.e., -78°C, -40°C, -30°C, and 23°C

## Conclusions

Ceramic particle reinforced polyurethane matrix composites were successfully fabricated. The assumed research plan was carried out and revealed favorable influence of the FA and SiO<sub>2</sub> fillers on E', E'', tan δ, hardness and impact strength. DMA provided clear indications of mechanical property changes with temperature increase and use. The characteristics of the pure and modified PU materials concluded that Vulkollan 30, commercial PU and composites containing FA were characterized by a higher storage modulus than the pure 3.1.3b and 5.1.1 systems at room temperature, indicating that they were more rigid than the other materials. Comparing the storage modulus of pure PUs to the composites also at -78°C, the two types of materials were characterized by similar tendency in elastic behavior as in ambient temperature. In the glassy solid state at -78°C, most of the 3.1.3B composites showed reinforcement effect, except of 3.1.3B+SiC and 3.1.3B+basalt. Most likely the introduction of 5% of those ceramic particles caused the reduction of the composite matrix cohesion. The 5.1.1 composites behaved similarly. So, in the DMA, the composites of PUGA 3.1.3B and 5.1.1 showed generally higher storage moduli and lower loss moduli than commercial Pus, but suggested that PUGA 3.1.3B had better particle/polymeric matrix interface (according to E'' values).

Dynamic-mechanical tests are appropriate up to 110°C because over this temperature the soft segments are already in a molten state. Moreover, the 3.1.3B composites had lower T<sub>g</sub>, useful in more requiring conditions than the 5.1.1 composites most likely due to intermolecular secondary (hydrogen) bonding, creating a well-defined three-dimensional network. Although, the composites were heterogeneous materials, only one pronounced glass transition was seen. The precise T<sub>g</sub> value was dependent on the relative amounts of all components present at a given time. Mechanical modification could have shifted the T<sub>g</sub> as well. The values of the glass transition temperature (T<sub>g</sub>) of the filled polyurethanes were analysed from the peaks of tan delta and loss modulus vs temperature (not presented). The addition of the fillers moves the glass transition to lower temperature due to their influence on the degree of phase separation between soft and hard segments in the polyurethane matrix. Furthermore, only the addition of FA 30–45 μm and SiO<sub>2</sub> 0–20 μm to 3.1.3.B and FA 0–15 μm to 5.1.1 strongly decreases T<sub>g</sub> of PU. On the other hand, the addition of nanosilica to 3.1.3B decreases the degree of crosslinking of PU, because of an increase in the maximum value of the tan delta curve is noticed. This is in agreement with the lack of miscibility of the nanosilica particles in the polyurethane matrix. The nanosilica increased the viscous property (E'') of this sample.

The additives on the other hand did not improve R<sub>m</sub> and ε – these properties did not show most reasonable trend of improvement, but the hardness increased. However, the authors succeeded in producing and testing elastomeric materials withstanding

high mechanical load in the transportation industry. It seems that the fabricated and tested materials are most likely to be used for a load-bearing coating prototype in mining transport units. The composites containing FA and SiO<sub>2</sub> of the fine grain fractions are promising as fillers for PU modification. Basalt and SiC did not perform satisfactory. Fillers other than FA and SiO<sub>2</sub> created bubbles and cracks on the filled polyurethanes, so the viscoelastic properties were inferior to those of unfilled PUs.

Future works could focus on examining the friction behavior as well, in addition to the already examined mechanical properties. In order to obtain the PU-composites with better mechanical properties, it is suggested to insert only the promising fillers and examine the friction behavior as well.

## Acknowledgments

The study was financially supported by the Faculty of Materials Science and Ceramics AGH UST in Kraków.

## References

1. Akindoyo JO, Beg MDH, Ghazali S, Islam MR, Nitthiyah Jeyaratnam Yuvaraj AR. Polyurethane types, synthesis and applications – a review. *RSC Advances*. 2017; 6: 114453–114482.
2. Atiqah A, Mastura MT, Ahmed Ali BA, Jawaid M, Sapuan SM, A Review on Polyurethane and its Polymer Composites: *Current Organic Synthesis*. 2017; 4: 233–248.
3. Shiferaw EW, Lule Z, Kim J. Thermal Conductivity and Mechanical Properties of Thermoplastic Polyurethane-/Silane-Modified Al<sub>2</sub>O<sub>3</sub> Composite Fabricated via Melt Compounding. *Polymers*. 2019; 11(7):1103.
4. Su K-H, Su C-Y, Cho C-T, Lin C-H, Jhou G-F, Chang C-C. Effect of crosslinking on thermal and mechanical properties of polyurethanes. *Scientific Reports*. 2019; 9:14397.
5. Sair S, Oushabi A, Kammouni A, Tanane O, Abboud Y, El Bouari A. Mechanical and thermal conductivity properties of hempfiber reinforced polyurethane composites. *Case Studies in Construction Materials*. 2018; 8:203-212.
6. Xiong J, Zheng Z, Qin X, Li M, Li H, Wang X. The thermal and mechanical properties of a polyurethane/multi-walled carbon nanotube composite. *Carbon*. 2006; 44(13):2701–2707.
7. Junrui Z, Weiping T, Zilin D. Synthesis and characterization of transparent and high impact resistance polyurethane coatings based on polyester polyols and isocyanate trimers. *Progress in Organic Coatings*. 2012; 75:579– 583.
8. Sare IR, Mardel JI, Hill AJ. Wear-resistant metallic and elastomeric materials in the mining and mineral processing industries – an overview. *Wear*. 2001; 250:1–10.
9. Garrison TF, Kessler MR. *Bio-Based Plant Oil Polymers and Composites*. Oxford UK, Wolfram USA; Elsevier 2016.



10. Ryszkowska J, Auguścik M, Zieleniewska M, Szczepkowski L, Kurańska M, Bąk S, Antos-Bielska M, Prociak A, Semi-rigid polyurethane foams with rapeseed polyol of different viscosity, *Polimery*. 2018; 63(1):10–17.
11. Ed.: Thomas S, Datta J, Haponiuk JT, Reghunadhan A. *Polyurethanes Polymers. Blends and Interpenetrating Polymer Networks*. Amsterdam, Oxford, Cambridge; Elsevier 2017.
12. Zhang F, Javni I, Bili O, Bili N, Zoran S. Petrovic, Jan Ilavsky. *Eur. Polymer J*. 2015; 64(11):1607–1616.
13. Fernández-d'Arlas B, Baumann RP, Pöseltd E, Müller AJ. Influence of composition on the isothermal crystallisation of segmented thermoplastic polyurethanes. *Cryst. Eng. Com*. 2017; 19: 4720–4733.
14. Zhou SX, Wu LM, Sun J, Shen WD. The change of the properties of acrylic-based polyurethane via addition of nano-silica. *Progress in Organic Coatings*. 2002; 45:33–42.
15. Baral D, De PP, Nando GB. Thermal characterization of mica-filled thermoplastic polyurethane composites. *Polymer Degradation and Stability*. 1999; 65:47–51.
16. Lu H, Obeng Y, Richardson KA. Applicability of dynamic mechanical analysis for CMP polyurethane pad studies. *Materials Characterization*. 2003; 49:177–186.
17. Crawford DM, Escarsega JA. Dynamic mechanical analysis of novel polyurethane coating for military applications. *Thermochimica Acta*. 2000; 357-358:161–168.
18. Datta J, Rohn M. Thermal properties of polyurethanes synthesized using waste polyurethane foam glycolysates. *Journal of Thermal Analysis and Calorimetry*. 2007; 88(2):437–440.
19. [www.perkinelmer.com](http://www.perkinelmer.com) accessed 16.08.2019
20. Narine SS, Kong X, Bouzidi L, Sporns P. Physical properties of polyurethanes produced from polyols from seed oils: I. Elastomers. *Journal of American Oil Chemists' Society*. 2007; 84:55–63.
21. Mothe CG, Araujo CR. Properties of polyurethane elastomers and composites by thermal analysis. *Thermochimica Acta*. 2000; 357-358:321–325.
22. Bahattab MA, Donate-Robles J, Garcia-Pacios V, Martin-Martinez JM. Characterization of polyurethane adhesives containing nanosilicas of different particle size. *International Journal of Adhesion & Adhesives*. 2011; 31:97–103.
23. Zaretsky E, Asaf Z, Ran Aizik EF. Impact response of high density flexible polyurethane foam. *International Journal of Impact Engineering*. 2012; 39(1):1–7.
24. Grellmann W, Seidler S. *Polymer testing*. Cincinnati, Ohio; Hanser Gardner Publications 2007.