

Elastic polyurethane foams containing graphene nanoplatelets

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Abstract

Elastic polyurethane foams were produced from two-component polyurethane systems (SPECFLEX NE 113 izocyjanian/NR 816 polioliol system—SPC and Elastic MBMarket company system POLYOL ET MB 500/ISO ET MB 800—ET) by using a one-step method. The foams were a graphene nanoplatelets (GNP) in the amount ranging from 1 to 2 wt.%. The effect of the nanofiller on polyurethane matrix was determined by analyzing the chemical structure, static and dynamic mechanical properties, and thermal stability of reinforced foams. The application of the carbon nanofiller resulted in increased density and hardness of the obtained composites. The addition of the nanofiller caused a shift in glass transition temperature toward lower temperature values, and an increase in the Young's modulus, but did not significantly affected the thermal stability of the obtained composites. The research results showed that graphene nanoplatelets nanofiller can be successfully used as a modifier of mechanical and thermal properties in elastic polyurethane foams.

KEYWORDS

foams, nanocomposites, polyurethanes, thermal properties

1 | INTRODUCTION

In recent years, nanotechnology has become a very dynamic branch of science because of the potential of nanoscale matter. The discovery of graphene in 2004 is of particular importance because of its excellent electrical and mechanical properties that cannot be observed in macroscopic scale.^[1,2] Novel engineering materials based on graphene have been investigated, including the methods of their production. Considering engineering materials, particular attention was paid to graphene as a component of composites, which can be dispersed in polyurethane matrix to mimic the exclusive graphene properties in the final material.^[3]

Polyurethane structure depends inter alia on the ingredients used, the reaction stoichiometry, and phase separated during the reaction forming a supermolecular structure.^[4] Formation of phases or hard segments (HS) and a soft (SS) caused by the variation in the effects of cohesion forces between the chemical bonds.^[5] Depending on the ratio of HS/SS we can obtain materials with different properties.

Because of the wide range of properties, polyurethanes (PU) are one of the most versatile and used polymeric

materials. They have several specific applications, such as flexible foam in upholstered furniture, rigid foam insulation in construction, PU thermoplastics used in medical equipment, footwear, coatings, adhesives, sealants, flooring and car interiors, among others.^[6] Their mechanical, thermal, and chemical properties can be tailored by the application of a wide range of polyols, isocyanates, and nanofillers.^[7]

Graphene is recognized as an allotropic form of elemental carbon,^[8,9] the biggest polycyclic aromatic compound derived from benzene,^[10] or as carbon polymer.^[11] Until now, scientists discovered three allotropes of carbon, consisting of sp^2 carbon atoms that have been classified as nanomaterials. The sequence of these discoveries is as follows: fullerenes,^[12] carbon nanotubes (CNT),^[13] and graphene.^[14] Graphene has extraordinary electrical properties that cannot be found in most of the materials used in the production of electronic systems.^[15] The electrical conductance of graphene is possible thanks to the conjugated π bonds that allow for the transfer of electrical charge. Graphene is characterized by the ambipolar conductance because of the presence of electrons and electron holes, while the conductance switching is possible via the value and direction of voltage applied.^[16,17] Graphene

also displays good mechanical properties. A graphene crystal is characterized by isotropy regarding its mechanical features. It is a rigid material in the planar dimension, being elastic in the third dimension. The nanoindentation study, performed with the use of atomic force microscope, allowed the determination of graphene's mechanical parameters. The elastic modulus (Young's modulus) and tensile strength of graphene are 1 TPa and 130 GPa, respectively.^[18] The aforementioned parameter values make graphene one of the strongest mechanically analyzed materials ever.

Applying numerous methods can produce graphene. Based on the review of scientific literature, two developmental trends in the methodology of graphene production can be distinguished. The methods using macroscopic graphite as an initial substrate are considered the top-down methodologies.^[19,20] Graphite characterized by layered structure can be expanded (exfoliated) even to single layers. The second types of methods are the so-called bottom-up procedures where graphene is obtained from non-graphite substrates.^[21,22] In this case, we deal with building the graphene structure from scratch by using precursors containing elemental carbon.

Graphene and other 2D nanoparticles with high aspect ratios display high affinity for polymer matrix.^[23] The particles of nanofiller dispersed in the matrix interact with it at the interphase boundary whose thickness depends on, *inter alia*, matrix type and the nanocomposite production method.^[24] The primary difference between conventional fillers and nanofillers is the ratio of surface area to a given mass. The surface area of nanofillers is about three orders of magnitude higher compared with conventional nanofillers.^[25,26] These characteristics alters the type of interactions between the nanoparticles and polymer chains. A relatively large surface area of nanofillers allows for increasing the area of interactions among nanofiller particles at the interphase boundary. This is the main feature of nanofillers that influences drastic changes in the polymer matrix properties at a relatively low level of nanofiller content. Another important parameter affecting the interphase interactions in nanocomposites is the nanofiller activity.^[27] The main measure of nanofiller activity in relation to matrix can be defined as the energy necessary for overcoming the interactions to separate the particles so no physical interactions among them are present. In the case of PUR nanocomposites containing graphenoid, the exemplary interaction is a hydrogen bond between the carboxyl groups of exfoliated graphene oxide (MEGO) and the urethane groups present in rigid segments.^[28] The nanofiller effect depends on the nanofiller production method. Frequently, this effect is related to the arrangement of nanofiller inside the polymer matrix. Generally, polymer nanocomposites are usually obtained via one of the three following methods: the solvent mixing,^[3] in situ polymerization,^[29] and the melt mixing.^[30]

Adding to the polyurethane matrix flakes of graphene contributes to the creation of new materials for a wider

spectrum of industrial applications. Increased interaction between the reinforcing factor and polymeric matrix may result in additional advantageous features of the material. Composites obtained from graphene and polyurethane may exhibit significant improvements in e.g., improving mechanical and thermal properties^[31] and conductivity.^[32]

This study was designed toward the development of new polyurethane nanocomposite using the two types of flexible polyurethane foams (SPC, ET), which are used in the shoe industry. The aim of the study was the determination of the influence of the graphene nanoplatelets (GNP) on the typical properties of the flexible polyurethane foams. The selection of the optimal product was based on the optimization of the amount of GNP and the application properties to develop new nanocomposite materials.

2 | EXPERIMENTAL

2.1 | Materials

Elastic polyurethane foams were obtained by employing commercially available systems produced by M.B. Market LTD (Poland). One system (System no. 1, SPECFLEX—SPC) consisted of polyol No. 816 (polyether with additives; viscosity 700 mPa·s) and isocyanate No. 113 (a mix of diphenylmethane-4,4'-diisocyanate, diphenylmethane-2,4'-diisocyanate, diisocyanate diphenylmethane; viscosity 125 mPa·s). The other system (System no. 2, ETMB—ET) was composed of ETMB 500 polyol (polyether resin with additives; viscosity 700–900 mPa·s) and ETMB 800 isocyanate (prepolymer containing MDI; viscosity 750–850 mPa·s). GNP (graphene nanoplatelets) manufactured by the American company ACS Material (bulk density 0.076 g/cm³, flake thickness 20 nm) were used as nanofiller (see Figure 1 to view the Transmission Electron Microscopy (TEM) micrograph of GNP used).

2.2 | Preparation of polyurethane nanocomposites

Elastic polyurethane foams were produced from a two-component system (A and B) at the ISO/POL mass ratios of 47/100 (SPECFLEX) and 97/100 (ET MB) by using a one-step method. Component A was a polyol mixture SPECFLEX No. 816, or ET MB 500. GNP nanofiller was added to component B (i.e., SPECFLEX NE 113 isocyanate, or ET MB 800 isocyanate) in the amount of 1 or 2 wt.% and this mixture was sonicated for 10 min and then homogenized at 6,000 rpm for 45 min. The components A and B were mixed at a specified mass ratio in a polypropylene container (rotating mixer 1,800 rpm, mixing time 10 s) and then poured into a preheated mold (40°C). The foam was demolded after 10 min. The obtained foam samples were heated in a dryer at 60°C for 24 hr and then seasoned at room temperature for 24 hr.

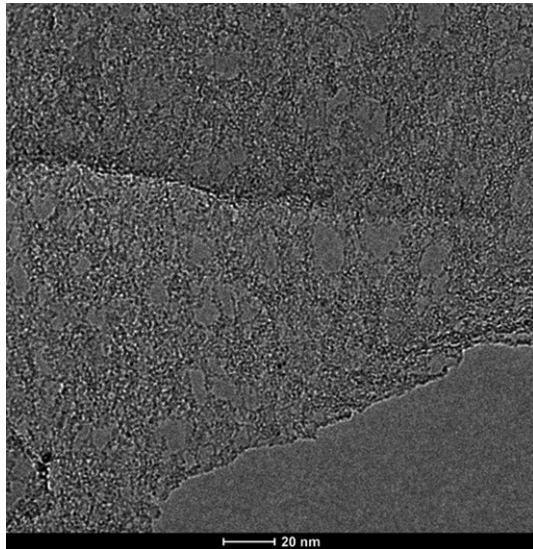


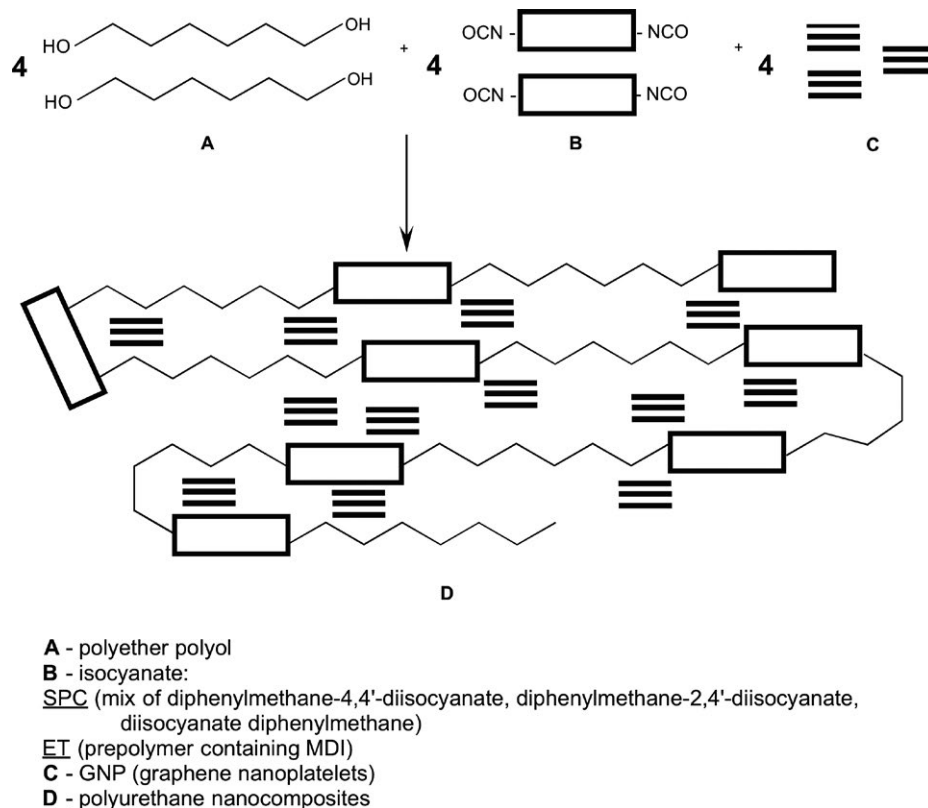
FIGURE 1 Transmission Electron Microscopy (TEM) micrograph of graphene nanoplatelets (GNP)

Electron Microscope FEI Europe, Tecnai F20 X-Twin coupled with EDX Spectrometer (samples were cut in cryo-mode using ultramicrotome).

Raman spectra were obtained on Renishaw in Via Spectroscopy with 514 nm laser at a power of 10 mV. Grating was set to $1,800\text{ cm}^{-1}$, while the acquisition time was 2 accumulations 10 s each in ambient atmosphere. The used objective had short focal distance and $100\times$ magnification. Scanning range was set between 100 and $3,400\text{ cm}^{-1}$.

The X-ray patterns of nanocomposite polyurethane foams were recorded by using an X'Pert Philips diffractometer (source radiation: $\text{CuK}_{\alpha 1}$ $\lambda = 0.1546\text{ nm}$, 40 kV, 30 mA) in the 5° – 50° (2θ range) and at a scanning rate of $0.25^\circ/\text{s}$.

The apparent density of polyurethane foams was determined in accordance with the PN—EN ISO 845:2000 standard. The Cubes with a volume of 8 cm^3 each were cut and then measured with a caliper (precision 0.1 mm) and weighted on an analytical balance (precision 0.0001 g).



SCHEME 1 Polyurethane nanocomposite foams preparation diagram

The modification process of polyurethane foams is presented in the Scheme 1.

2.3 | Measurements

Transmission Electron Microscopy analysis was performed by means of STEM-EDX technique using Transmission

Hardness was measured according to the PN-EN ISO 868:2005 standard. The samples were placed on a flat surface, and ten measurements were taken per sample by applying a Shore A durometer for 3 s.

Rebound resilience was determined by means of a Rebound Tester in accordance with the ISO 4662:2009 standard.



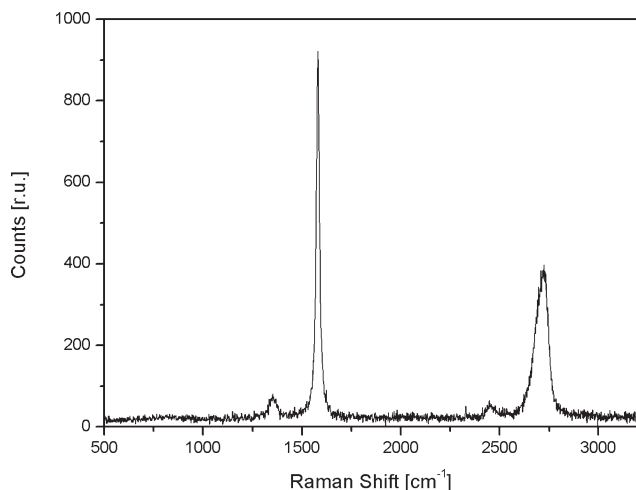


FIGURE 2 Raman spectrum of nanofiller, i.e., graphene nanoplatelets, graphene nanoplatelets (GNP)

Rebound resilience was measured by dropping a free-falling pendulum hammer from a given height, which impacted the sample. The amount of energy was shown on a pendulum scale. Ten measurements were recorded per each sample.

The tensile strength (TSb) and elongation at break (Eb) were measured under static load by using a Zwick Z020 tensile-testing machine, in accordance with the DIN EN ISO 527-1:1996-04 and DIN EN ISO 527-2:2012-06 standards. The dumbbell-shaped samples of standard dimensions were also tested at a rate of 50 mm/min. The measurements were performed at room temperature.

Dynamic mechanical analysis of the nanocomposite foams was performed using a DMA Q800 Analyzer (TA Instruments) in bending mode (single cantilever), under nitrogen atmosphere. The measurements were performed at a temperature range from -100 to 150°C , at an operating frequency of 1 Hz, with a heating rate of $3^{\circ}\text{C}/\text{min}$. The values of storage modulus, loss modulus and glass transition temperature were calculated.

Thermogravimetric analysis (TGA) was performed on a NETZSCH TG 209 apparatus using 15-mg samples at a temperature range 40 – 600°C , at a heating rate of $20^{\circ}\text{C}/\text{min}$, and under argon atmosphere.

3 | RESULTS AND DISCUSSION

3.1 | Structure analysis

The chemical structure of elastic polyurethane foams filled with GNP was determined by means of Raman spectroscopy. The spectrum of GNP, a nanofiller, is presented in Figure 2. The Raman spectra of polyurethane foams obtained from polyether matrix (ET), and the foams containing 1 and 2 wt.% of GNP are shown in Figure 3. The spectra of the reference foam and foams filled with 1 and 2 wt.% of GNP, obtained from polyether system (SPC), are also presented in Figure 4.

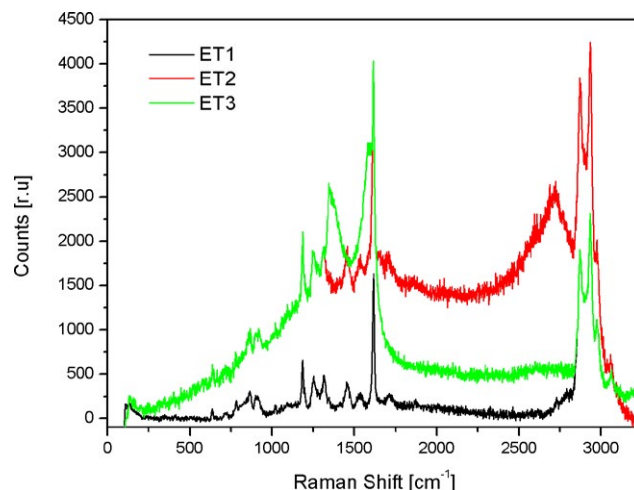


FIGURE 3 Raman spectra of polyurethane foams obtained from polyether system: matrix (ET), foam containing 1 wt.% of graphene nanoplatelets (GNP) ($\text{ET}_{1\%}$), and foam containing 2 wt.% of GNP ($\text{ET}_{2\%}$)

The reference spectrum of GNP displays bands at $3,250\text{ cm}^{-1}$, which are attributable to small amounts of H–O characterized by stretching vibrations (ν). Next, there is a strong stretching 2D-band at $2,650$ – $2,700\text{ cm}^{-1}$ as a result of the presence of the COOH and CHO groups. The CHO group manifests itself as a doublet of similar size, however, the second peak is too small which indicates that a different peak composition is possible. The small peak may not be connected to the larger one, which suggests the presence of triple $\text{C}\equiv\text{C}$ bond vibrations. Next, a strong G-band, attributable to the in-plane breathing vibration of $\text{C}=\text{C}$ rings in the aromatic honeycombs of graphene ($1,600\text{ cm}^{-1}$ ν), and the D-band at $1,380\text{ cm}^{-1}$ originating from the deformation (δ) of the same

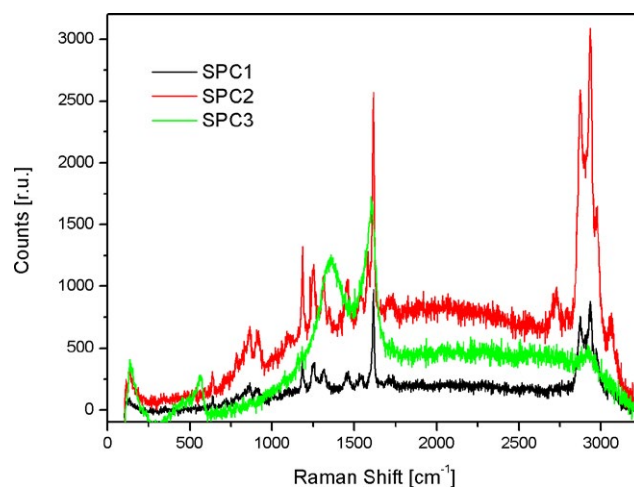


FIGURE 4 Raman spectra of polyurethane foams obtained from polyether system: matrix (SPC), foam containing 1 wt.% of graphene nanoplatelets (GNP) ($\text{SPC}_{1\%}$), and foam containing 2 wt.% of GNP ($\text{SPC}_{2\%}$)

groups as the ones registered within the D-band region, are visible. It is noticeable that the aforementioned spectra differ after GNP inclusion in the polymer matrix, as expected when the changes in bond structure and surface interactions are considered.

All the obtained spectra display the same polymer matrix as the main component, with the peaks located at the approximate Raman shift position, i.e., at the wavenumber expressed in the units of $[\text{cm}^{-1}]$. The ET samples seem to have more integrated matrix because the D-, G- and 2D-bands attributable to carbon nanofiller (1,380, 1,580, 2,700–2,850 cm^{-1}) occur concurrently with the bands originating from the matrix (good dispersion within the measuring range). The main bands attributable to the matrix are asymmetric valence (stretching) vibrations (ν_{as}) and symmetric valence vibrations (ν_{s}) originating from aliphatic CH_2 chains, accompanied by the C–H vibrations in the aromatic carbon rings (2,850, 2,900 and 3,060 cm^{-1}). Below, there are in-plane deformations (δ_{s}) attributable to the N–H and CH_2 groups at 1,600 cm^{-1} , and a number of peaks in the region downward from 1,450 cm^{-1} . In the region between 1,350 and 1,150 cm^{-1} , the peaks of valence vibrations (ν_{as} and ν_{s}) attributable to the C(=O)–O–C and C–N bonds of urethane groups are present. For the lower wavenumbers (500–1,000 cm^{-1}), there are only complex fluctuations of deformation vibrations (ω, τ) originating from aliphatic and aromatic C–H groups. The samples of ET foams seem to have lower resolution and signal quality because of the addition of graphene and the subsequent increase in fluorescence. The matrix is apparently becoming progressively amorphous.^[33–35]

For the identical measurement range, the samples obtained from the polyether system (SPC) do not display the same level of homogeneity as those produced from the polyether system (ET). The spectrum of SPC sample resembles the spectrum of pure polymer matrix (see the description for ET series) without strong fluorescence, however, also displaying very small peaks. The SPC_{0.5%} sample is of much better quality; its intensity is much higher and even weak signals are better visible. The fluorescence also increased, as manifested by a bulge in the registered spectrum, however, not as much as the signal quality. It is possible that the measurement was made on the surface with better topography. Sample SPC_{1%} produced the spectrum attributable to carbon nanofiller that can be noticed in the pores of the foam. The spectra of GNP in the produced foams differ from the pure GNP spectrum (see Figure 2) most likely because the foams have lost their primary ordered structure as a result of processing and the integration with matrix.

The analysis of structural measurements performed on the samples of produced polyurethane foams was aimed at determining the structure type of the obtained composites. Polyurethane materials based on both ET and SPC systems are characterized by the high degree of amorphism of their

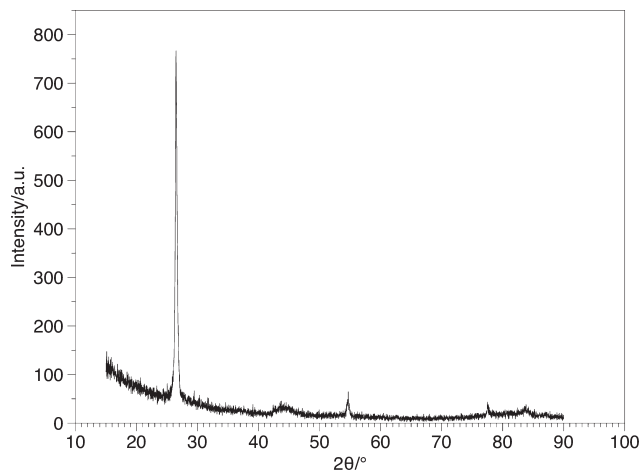


FIGURE 5 Diffractogram registered for graphene nanoplatelets (GNP)

polyurethane matrices. This causes that in the pertinent diffractograms only broad diffraction maxima of low intensity are visible for 8° – 30° 2θ are observed for amorphous phase of SPC and ET matrices. The amorphism of the composites has been confirmed by the DSC results, i.e., the melting/crystallization peaks are not present on the thermograms. Moreover, the diffraction analysis was conducted on the samples of commercially available GNP filler, which is characterized by the presence of graphene nanolayers (Figure 5). The incorporation of such system into polyurethane matrix results in diffractograms with the low-intensity diffraction maxima for ca. $2\theta = 27^\circ$, which correspond to the interlayer distances of ca. 0.33 nm that are characteristic of graphite structures. For GNP 1% and 2% wt., the intensity is changed (with increasing amount of nanofiller) and is characteristic for the neat nanofiller GNP (Figure 6).

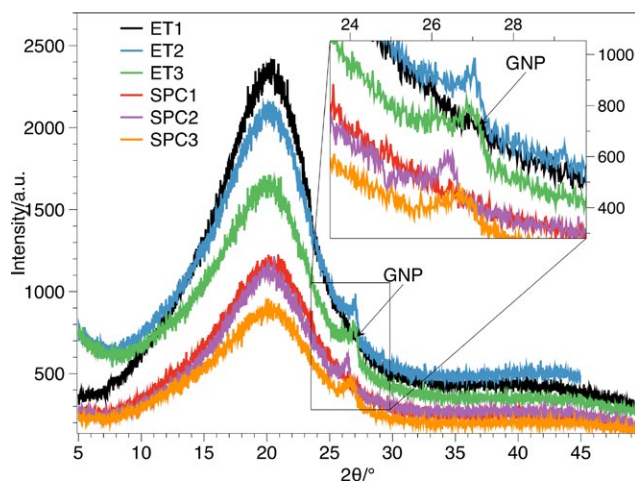


FIGURE 6 Diffractograms registered by using X-ray diffraction (XRD) for the ET and SPC systems containing graphene nanoplatelets (GNP)



TABLE 1 Mechanical properties of nanocomposite polyurethane foams.

Properties	Sample					
	SPC 1	SPC 2	SPC 3	ET 1	ET 2	ET 3
Density (kg/m ³)	388 ± 2.9	450.5 ± 3.6	586.6 ± 18.1	433 ± 14.2	467 ± 7	507.9 ± 9.6
TS _B (MPa)	250 ± 12	288 ± 20	238 ± 12	129 ± 5	141 ± 10	180 ± 11
Eb (%)	108 ± 7	96 ± 8	94 ± 6	228 ± 9	153 ± 3	210 ± 10
Hardness (°ShA)	38.3 ± 3.8	51.4 ± 2.3	46.1 ± 1.9	21.8 ± 0.5	27.2 ± 2.9	29.5 ± 1.5
Elasticity (%)	18.9 ± 0.8	18.6 ± 0.9	19.0 ± 1.0	30.7 ± 1.0	33.4 ± 0.9	33.8 ± 0.8

3.2 | Evaluation of mechanical properties

The results of apparent density, tensile strength (TS_B), elongation at break (Eb), hardness and elasticity of nanocomposite polyurethane foams are presented in Table 1.

The nanocomposite polyurethane foams were characterized by higher apparent density than that of the reference materials. The apparent density for pure SPC systems was 388 kg/m³ and for ET systems—433 kg/m³. The filling of nanocomposites with 1 wt.% of GNP resulted in the average density increase by 62 kg/m³ (SPC) and 34 kg/m³ for ET systems and for nanocomposites containing 2 wt.% graphene nanoplatelets, density increase to 586 kg/m³ and to 507 kg/m³ for SPC and ET systems, respectively.

The apparent density of filled systems possibly increase as a result of composite viscosity increase during the foaming step.^[36]

High viscosity created a barrier against the formed gas bubbles which, in turn, influenced the foaming process.

The incorporation of GNP caused strengthening of the obtained material, which has been demonstrated by the results of tensile testing. It was found that the TS_B values for the composites containing 1 and 2 wt.% of GNP were higher or equal to that of the reference material. The observed increase in tensile strength also caused the phase separation between the hard and soft segments of the matrix,^[37] which is stimulated by the presence of nanofiller.

The increased nanofiller content resulted in increased rigidity of the composites, which was reflected in the values of elongation at break. For the pure foams, the Eb values were 108% and 228%. For the GNP content of only 1 wt.%, the value of Eb decreased by 12% for SPC composites and 75% (ET composites) relative to the reference material. The increasing amount of GNP, dispersed in the flexible polyurethane foams, caused a significant decrease in the elongation at break compared with that of the matrix. This can be explained by the higher frequency of contact between graphene nanoplatelets and the stretching material, which results in the physical and chemical damage to the composite matrix.

The hardness values of the obtained flexible polyurethane foams nanocomposites containing GNP are presented also in Table 1. The hardness of these materials changed in

dependence on the nanofiller content. In the case of ET composites, it was found that a larger amount of carbon nanofiller has a smaller positive effect on the composite hardness in comparison with the SPC composites. Based on the resilience measurements, it was determined that the addition of carbon nanofiller did not significantly change this parameter. GNP added to the SPC matrix did not significantly change the elasticity of the modified material because the obtained elasticity value of ca. 19% was close to the corresponding value measured in the sample of reference foam. In the case of ET composites, the nanofiller addition resulted in a ca. 3% increase in the value of elasticity.

3.3 | Dynamic mechanical analysis

The results of dynamic thermomechanical analysis of flexible polyurethane foams containing 1 and 2 wt.% of GNP are shown in Figure 7 and Table 2.

Table 2 contains the values of storage modulus (E') measured at temperatures ranging from -60 to 0°C, and the temperatures of glass transition. The addition of GNP to polyurethane matrix resulted in an increased storage modulus (E') compared with that of pure polyurethane. At -10°C, all GNP-reinforced samples were characterized by the higher values of storage modulus (E') compared with the reference sample. The observed increase in the elastic modulus (Figure 7) is in good agreement with the known effect of carbon nanofiller on polymer matrices.^[38] An increase in the modulus of nanocomposites because of the nanofiller addition is reasonably well-understood. The underlying causes involve a hydrodynamic effect, adsorption of polymer chains onto the filler surfaces, and an increase in the crosslink density via polymer/filler interaction.

Glass transition temperature was determined as a maximum peak of the tan δ versus temperature curve (Figure 7). The obtained glass transition temperatures for the SPC samples (made with SPECFLEX System) had lower values than those of flexible foam prepared with the use of ET Systems.

The observed difference results from the different structure of polymer matrix because the SPC composite had been made from the mixture of diisocyanates (mix of MDI and pMDI). In all cases, the incorporation of GNP caused a slight



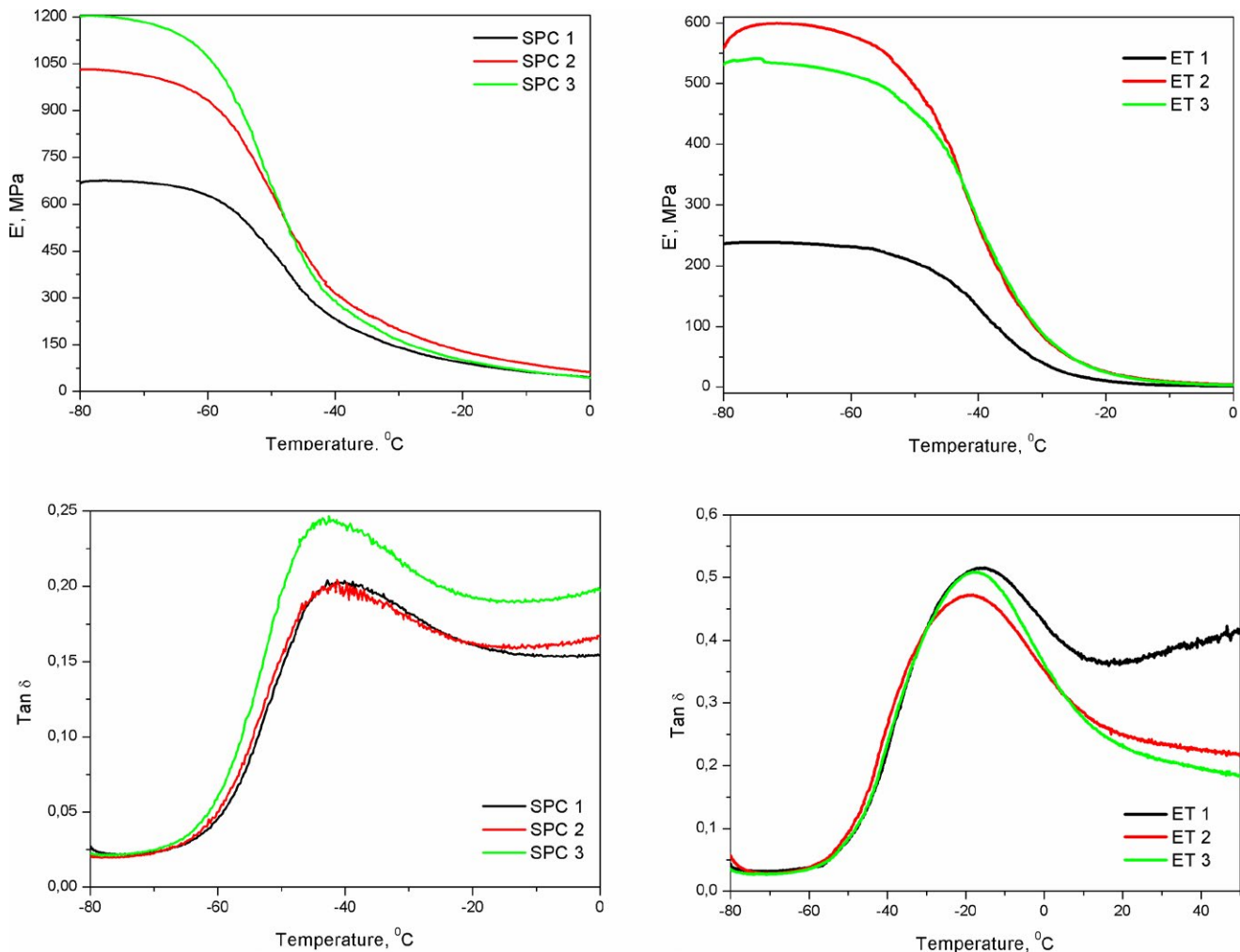


FIGURE 7 Storage modulus and $\tan\delta$ curves of flexible nanocomposite polyurethane foams

TABLE 2 The values of glass transition temperature and storage modulus of pure and nanocomposite foams.

Sample	T_g (°C)	Storage modulus (MPa)						
		-60	-50	-40	-30	-20	-10	0
SPC 1	-40	628	452	235	143	92	64	50
SPC 2	-41	939	642	323	203	129	92	64
SPC 3	-42	1073	670	291	166	101	69	50
ET 1	-15	227	209	135	42	9	4	4
ET 2	-17	578	507	270	90	25	6	4
ET 3	-18	516	461	286	90	25	9	4

downward shift of glass transition temperature. The observed temperature shift can be explained by the reduced chain mobility of soft segments as a result of good dispersion of carbon nanofiller in polyurethane matrix.^[39]

3.4 | Thermogravimetric analysis

The effects of the GNP addition on thermal stability of the resulting foams were assessed by the TG and derivative

thermogravimetric analysis. The outcome of the analysis of flexible nanocomposite polyurethane foams, performed under nitrogen atmosphere, are presented in Figures 8 and 9. The temperatures of 2%, 5%, 10%, and 50% mass loss (T_2 , T_5 , T_{10} and T_{50} , respectively), and the temperature of maximum rate of decomposition (T_{max}) for the nanocomposite foams are summarized in Table 3.

Polyurethanes degrade via a two-step process, i.e., the first step is associated with the degradation of hard segments,



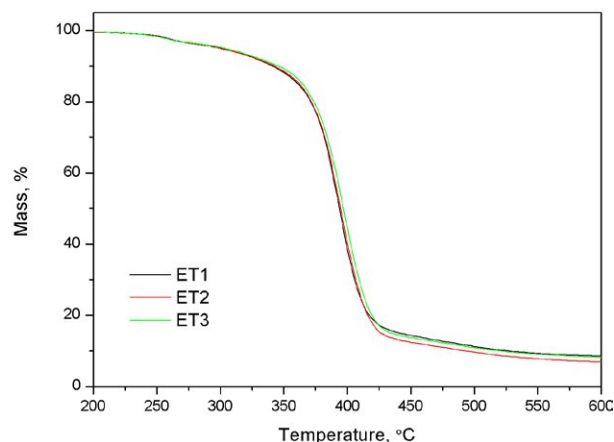
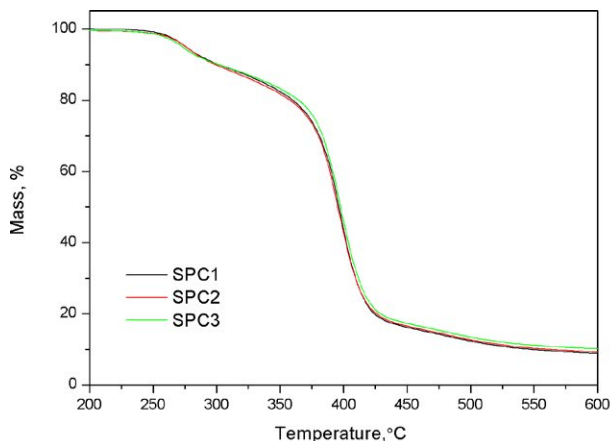


FIGURE 8 Mass loss curve as a function of temperature for pure foam and nanocomposite foams

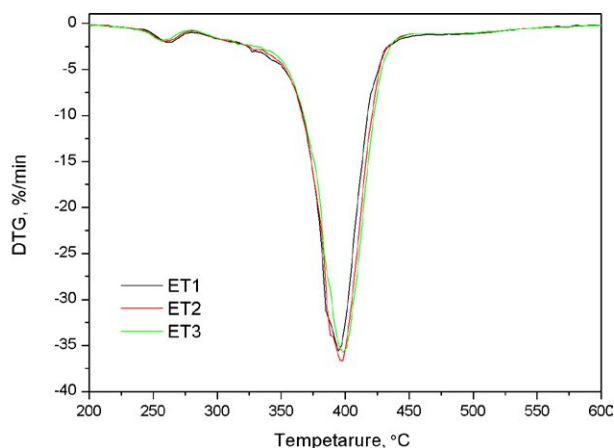
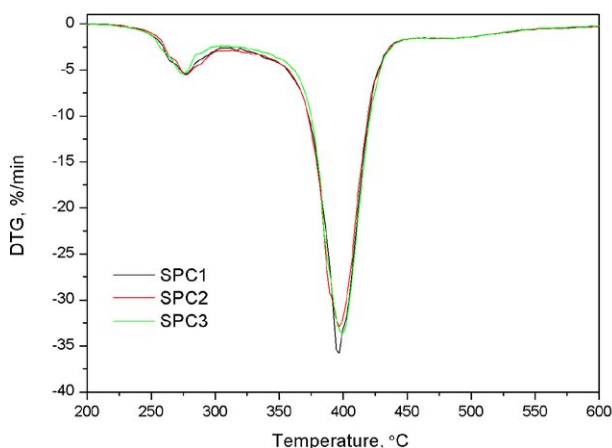


FIGURE 9 Differential thermogravimetric curve as a function of temperature for pure foam and nanocomposite foams

which depolymerize into the main monomers, while the second step is the result of the decomposition of soft segments.^[40] The first degradation step occurs at a temperature range from 275 to 320°C, while the second step takes place between 380 and 480°C.

The incorporation of GNP did not cause a large change in the temperature at which the nanocomposite decomposition starts. Moreover, with progressing decomposition at elevated temperatures, the obtained curves overlap for the entire temperature range (Figure 9). The noticeable changes were found in the case of DTG curve where the effect of GNP addition on the decomposition rate of the obtained nanocomposites was apparent in comparison with the non-modified matrix. The effect occurred at temperatures characteristic for the rigid segment decomposition (250–280°C) as well as for the degradation of residues in the second decomposition stage (370–430°C). The incorporation of 1.0 wt.% of GNP resulted in the upward shift of $T_{\max I}$ by 2°C, and of $T_{\max II}$ by 6°C compared with the reference sample. It was

TABLE 3 Temperatures of 2%, 5%, and 10% mass loss and the maximum decomposition rate (T_{\max}) for different foam samples.

Sample	Temperature (°C)					
	T_2	T_5	T_{10}	T_{50}	$T_{\max I}$	$T_{\max II}$
SPC1	262	276	302	396	277	396
SPC2	261	276	299	396	278	397
SPC3	258	273	302	398	279	400
ET1	257	300	341	394	263	395
ET2	256	301	343	395	260	397
ET3	255	303	346	397	257	398

also noticed that the amount of ash slightly increased, which may indicate that only matrix had decomposed. The amount of residue, which increases with the increasing content of nanofiller, to a large extent consisted of the nanofiller that had not undergone decomposition at the highest temperature applied.

4 | CONCLUSIONS

The structure of the obtained nanocomposites was analyzed by Raman spectroscopy and X-ray diffraction technique. It has been shown that the spectra of the produced foams are different from the pure GNP spectrum most likely because the foams have lost their primary ordered structure because of the processing and the integration with matrix. X-ray diffraction demonstrated that the flexible polyurethane foams based on both systems are characterized by the high degree of amorphism of their polyurethane matrices which was confirmed by the DSC results. The presented results indicate that the addition of carbon nanofiller in the form of graphene platelets, in the amount of 1 and 2 wt.%, to polyurethane matrix results in the improvement of mechanical parameters of the produced composites, i.e., higher apparent density (SPC3—51%; ET3—17%), higher hardness (SPC2—34%; ET3—38%), better tensile strength (SPC2—15%; ET3—40%) and higher storage modulus at low temperature (−50°C, SPC3—48%; ET3—142%) were archived, in comparison with the non-modified materials (SPC1 and ET1). Based on the results of static and dynamic testing, it was observed that the hardness of the obtained materials increased with increasing content of carbon nanofiller. This phenomenon is connected to lowered mobility of polymer chains. In this study, we demonstrated that the GNP addition does not significantly influence the thermal stability of the produced composites. These new reinforced polyurethane materials can be used as elastic shoe inserts or for example, in automotive industry, in car seats application.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this paper.

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