

Polyurethane foams obtained from residues of PET manufacturing and modified with carbon nanotubes

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Abstract. In this work we report the preparation of rigid microcellular polyurethane/carbon nanotube nanocomposites with different CNT loadings (0.09-0.46%) and various isocyanate indexes (110-260). Water was used as a blowing agent for samples. Density of all obtained samples – $200 \pm 10 \text{ kg/m}^3$. Electrical properties, as well as heat conductivity, cellular structure and mechanical properties of these nanocomposites were investigated.

1. Introduction

Polyurethanes (PUs) are segmented copolymers consisting of soft and hard segments. The first provide elastomeric properties, while second - dimensional stability. Neat PU foams were used as lightweight construction and isolating materials for various applications. To obtain materials with whole new set of properties, PU matrix can be modified by adding different reinforcing agents (organic or inorganic nanoparticles, nanofibers, nanoplatelets, etc.) [1, 2]. Carbon nanotubes (CNTs) have recently attracted a great deal of interest due to their high aspect ratio and surface area. If van der Waals forces between nanotubes are overpassed, they can be dispersed in polymer composites, CNTs can form conductive paths and the final composite presents improved electric, thermal and mechanical properties [1-5]. In order to enhance the electrical properties of polymer nanocomposite, it can be foamed – in this case nanoparticles (or nanotubes) are better distributed due to the use of a physical blowing agent [6]. The studies show that nano/microcellular polypropylene/multi walled CNT composites exhibits higher electrical conductivity, lower electrical percolation, higher dielectric permittivity and lower dielectric loss [6]. Carbon particles introduced into rigid PU foams can enhance material thermal insulating properties – cell walls and edges absorb increased amount of infrared radiation. Such additives also can act as fire retardants [3].

At relatively low CNTs concentrations and under specific conditions, a three-dimensional electrically conductive network may be formed in the polymer nanocomposite. It is achieved thanks to a physical contact between the dispersed conductive nanoparticles. This dramatically increased electrical conductivity is known as the electrical percolation threshold [4, 7]. Electrically conductive thermosetting nanocomposites have been obtained with extremely low CNT percolation thresholds ($\sim 0.0025 \text{ wt\% CNT}$) and electrical conductivities as high as 2 S/m for CNT contents as low as 1 wt\% [8].



In this work rigid PU/CNT composite foams were obtained. The influence on final composites of the CNT amount together with NCO index was determined. Mechanical properties, piezoresistivity as well as heat and electrical conductivity were investigated. The potential of the application of such composites in pressure sensors in automotive engineering were investigated.

2. Materials and methods

2.1. Materials

For preparation of PU foams as a main ingredient the polyether polyol Neopolyol[®] produced by Neo Group (hydroxyl number 370÷380 mg KOH/g, viscosity 3000÷4000 mPa·s, acid number <1 mg KOH/g, water content ≤0.1 %) was used. It is obtained in the transesterification of PET by diethylene glycol in the presence of functional additives [9]. Lupranol[®]3422 (hydroxyl number 490 mg KOH/g, viscosity 22750 mPa·s, water content ≤ 0.1 %) in the mixture was used as a functional polyol, Quadrol[®] (hydroxyl number 770 mg KOH/g, viscosity 52000 mPa·s, water content ≤0.1 %) - as cross-linking agent. Both are commercially available polyols from BASF. Distilled water was added as chemical blowing agent, while potassium acetate as trimerization catalyst and, tris(chloropropyl)phosphate as flame retardant. Surfactant Niaux silicone L-6915 LV was purchased from Momentive and catalyst PC CAT[®]NP 10 from Air Products. Polyisocyanate PMDI was obtained from BASF. In order to improve PU matrix conductivity, multi walled CNTs NC7000 by NanocylTM were used (diameter 9.5 nm, length 1.5 μm, volume resistivity 10⁻⁴ Ω·m).

2.2. Samples preparation

First CNTs in different amounts (0.09 to 0.46 wt%) were incorporated and dispersed in polyol using high shear mixer (Silverson L5M-A) with a square hole high shear screen. The mixture was stirred for 30 minutes at 10000 rpm. In order to avoid undesirable reactions, which can happen because of friction forces and associated heating-up, the suspension was cooled in water bath (the temperature of 100°C was never exceeded).

After the catalyst (potassium acetate), blowing agent and surfactant were mixed with polyol and CNT blend, isocyanate in 4 various proportions was added. The suspension was stirred for approximately 10 seconds and poured in a preheated closed stainless steel form with dimensions 150 x 150 x 50 mm. Afterwards the mould was closed and placed into the oven at 50 °C for at least 2 hours to cure. The precise formulation in parts by weight is summarized in Table 1 [10].

Table 1. The base formulation of PU foams.

Component	Parts by weight
<i>Neopolyol 380</i>	78.0
<i>Lupranol[®] 3422</i>	18.0
<i>Quadrol[®]</i>	4.0
TCPP	20.0
H ₂ O	1.0
<i>PC CAT[®] NP 10</i>	1.9
<i>Niaux silicone L 6915 LV</i>	2.0
Potassium acetate	1.6
<i>NC7000</i>	0.0 – 1.2
PMDI	130-307

2.3 Characterization

The density of samples was determined using samples intended for mechanical tests. The morphology of foam samples were characterized using SEM Tescan TS 5136 MM with secondary electron detector and VEGA TC computer software. Before taking SEM images, foam samples were cut into pieces of approximately 10 x 10 x 2 mm using scalpel blade and glued on aluminium specimen tables. To provide better electron conductivity, samples were coated with gold by

sputtering using sputter coater Emitech K550X. In order to determine the average size of the foam cells, foam cell size distribution and anisotropy, cell diameters in both axial and transverse directions were measured.

To determine strength and modulus of the elasticity, compression tests were performed. In this aim, Zwick/Roell Z100 testing equipment was used. Samples for compression tests were cut parallel to the foam growth direction. The results are the average of the measurements made on 5 various foam samples. It was done accordingly to the standard EN ISO 844:2009.

Heat conductivity was determined with Linseis HFM 200 thermal analyser. The size of samples 195 x 195 x 50 mm. Temperature of the top plate was 20°C, temperature of the bottom plate was 0°C.

Volume resistivity measurements and necessary calculations were carried out on the basis of the standard ASTM D257. Picoammeter Keithley Model 6487 together with Resistivity Test Fixture Model 8009 was used.

Piezoresistivity was measured using test equipment consisting of Zwick/Roell Z2.5 compression force tester and Agilent 34970A Data Logger 3. The samples were 20.0 ± 0.5 mm in diameter and 10 ± 1 mm thick. To ensure a good contact with the electrodes, specimens were coated with silver paste and dried at room temperature for 24 hours. Samples were compressed to 0.1 MPa with speed 0.005 MPa/s and then relaxed for 50 s.

3. Results and discussion

In order to control the crosslinking density and the morphology of the final nanocomposite material, various NCO and OH group (NCO/OH) ratios and various concentrations of CNTs were used. The density of all PU foams was controlled by the foaming in a closed mould (200 ± 10 kg/m³).

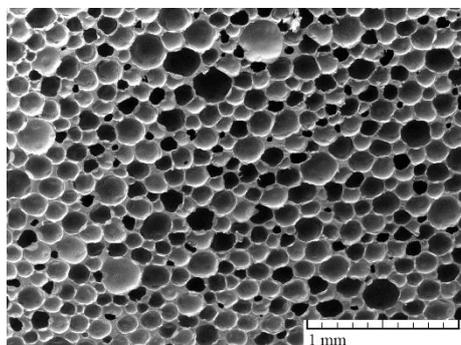


Figure 1. SEM micrographs of rigid PU foams with NCO index 160 unfilled (no CNTs present).

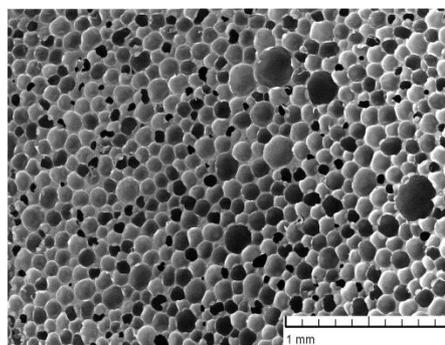


Figure 2. SEM micrographs of rigid PU foams with NCO index 160 filled with 0.12 wt% CNTs.

The morphology of rigid PU/CNT foams is observed by SEM. Figure 1 shows the microstructure of unfilled PU foam (no CNTs) and Figure 2 - PU foam filled with CNTs (0.12 wt%) (NCO/OH ratio - 160). The results show that with the increasing the amount of CNTs, the average size of foam cells decreases. It indicates that in small amounts of CNTs, they act as nucleation centres and produces finer cell structure and higher cell density. Overreaching 0.15 wt% of CNTs, the cell size increases in both axial and transverse directions (figure 3).

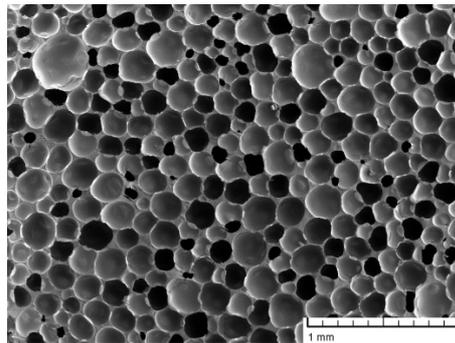


Figure 3. SEM micrographs of rigid PU foams with NCO index 160, filled with 0.21 wt% of CNTs.

Although the concentration of CNTs is, for example, 0.18 wt% in the final product, in polyol, in which additives were dispersed, CNTs constitute 1 wt%. Therefore the viscosity is high, dispersion difficult and foaming uneven. When increasing NCO/OH ratio, the foam cell size also increases. The main reason for such a result is that the same amount of surfactant is added in all cases, in order to provide a closed foam structure. All foam samples have an isotropic structure, which means that cells are close to an ideal circle.

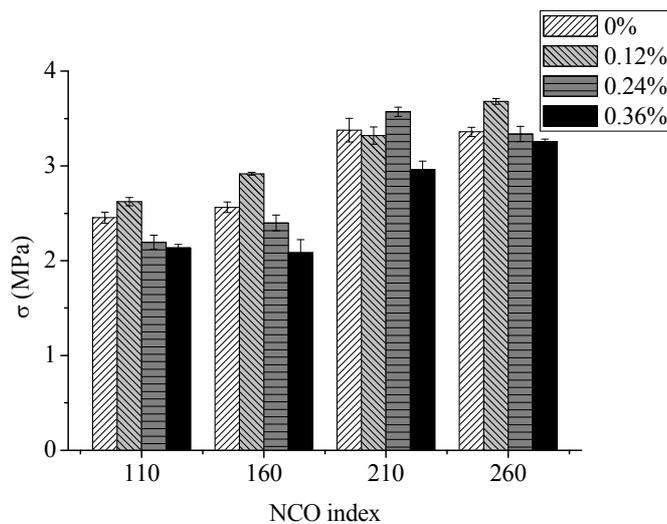


Figure 4. Compression strength of rigid PU foams with various NCO indexes and content of CNTs.

The obtained modulus and strength of PU foams from compression and tensile tests were normalized according to [11]. The results are given in Figure 4. It can be seen that when adding a small amount of CNTs, the compression strength becomes higher when compared to an unfilled sample. The same relation applies to the modulus of elasticity. If the CNTs content overreaches 0.15 wt%, both stiffness and strength decreases and these results correlate with the average foam cell sizes. With increasing NCO/OH ratio, the compressive strength increases.

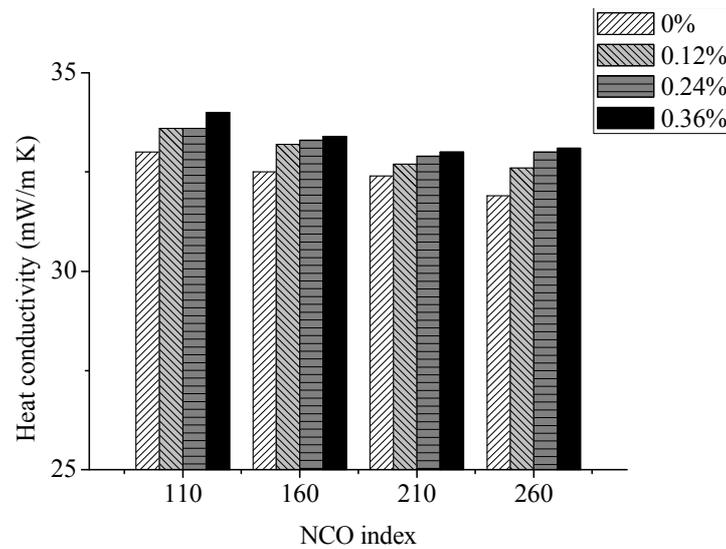


Figure 5. Heat conductivity of rigid PU foams with various NCO indexes and content of CNTs.

Heat conductivity of prepared composites is not dramatically affected neither by NCO index, neither by the concentration of dispersed CNTs (figure 5). However the trend is clear: when NCO index is increased, the thermal conductivity of the foams slightly decreases (33 to 31 mW/m·K).

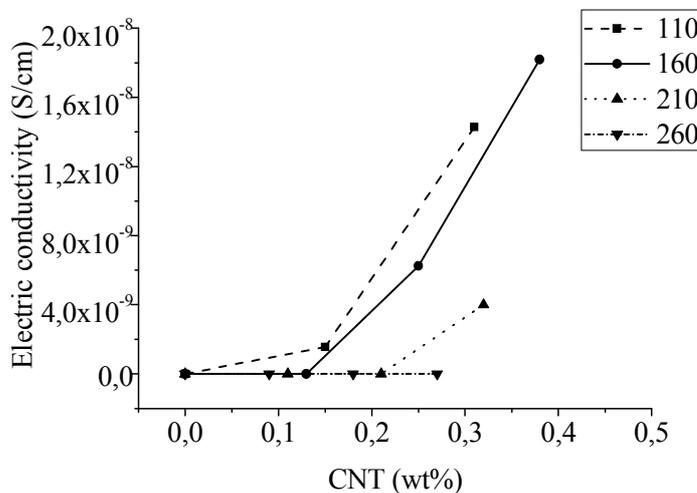


Figure 6. Volume electric conductivity of rigid PU foams.

From the Figure 6 it can be noticed that the volume electric conductivity for PU foams increases significantly, even if very small content of CNTs is added. In case of the NCO index of 110, adding only 0.3 wt% of CNTs, the conductivity improves by 5 to 6 orders of magnitude. CNTs and increased NCO index influence the electrical properties of PU foam in a negative manner – the conductivity decreases. The electric conductivity of foams with different NCO indexes and without additives remains the same (around 0 S/cm).

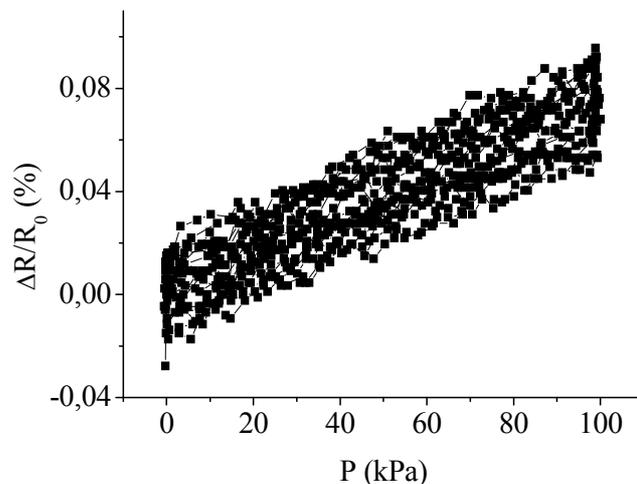


Figure 6. Piezoresistive sensitivity of rigid PU/CNT composite with 0.15 wt% of CNTs and the isocyanate index of 110.

All tested samples display positive pressure coefficient of resistance – by increasing the compressive force, the resistivity of composites increases (figure 5). The electrical resistance after several compressive loading cycles increases and does not return to its initial value. Thus it can be concluded that CNTs introduced in the nanocomposite under pressure do not form conductive networks – when the compressive force is applied, the distance between nanotubes grows.

4. Conclusions

The PU/CNT nanocomposite foams were obtained and their piezoelectric characteristics were tested. To produce PU foams, residues of PET manufacturing were used and CNTs were dispersed in liquid polyol using high shear mixer. Electrical conductivity for PU/CNT foams increases – with an increasing concentration of CNTs, but it is very difficult to effectively introduce more than 0.15 wt% of CNTs because of the viscosity of PU foams forming polyols. The most significant result is that electrical resistivity reduction can be reached if the NCO index is low. PU/CNT foam composites demonstrate the pressure sensitivity, therefore the obtained nanocomposite materials can find a potential application in automotive engineering, but additional studies should be performed in order to prove it.

5. References

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Acknowledgements

The financial support of Latvian National Research Programme IMIS2 and the FP7 project EVOLUTION under grant agreement No.314744 are greatly acknowledged.