

POLYURETHANE COMPOSITES WITH IMPROVED MECHANICAL PROPERTIES

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Abstract: *This work presents results of investigation of composite materials based on polyurethane (PUR) and hydrophilic fillers: A200 (nanosilica). The effect of the filler content on the mechanical properties of the final composite material are determined. The introduction of nanosilica (5 wt.-%) to foams gives the best mechanical properties (highest compressive strength). The obtained results are discussed in terms of effects of content of filler particles on density and thermal properties of the polymer composites. These results correlate well with the results of microscope analysis. Increasing filler percentage reduced the PUR foam density and size of pores.*

Keywords: Polymer Composite, Silica, Mechanical Properties, Polyurethane, Foams.

1. Introduction

In recent years much attention has been focused on development of new inorganic-organic composite materials of prospective use in many areas (Hajji et al., 1999). Polymers have been modified by incorporating various inorganic fillers to achieve special (exciting bulk, mechanical, functional, electrical, surface etc.) properties (Sadej et al., 2016, 2014, M. Sadej-Bajerlain et al., 2011, Ziobrowski et al., 2014). From among the inorganic substances, silicon dioxide has become of greatest importance as an active filler of polymers because of its good resistance to heat and electricity, mechanical stability, relatively low costs, hardness, high specific surface area (Rotzoll et al., 2008, Kuo et al., 2000). Silica has been widely applied in various industries, besides common plastics and rubber reinforcement, many other potential and practical applications of polymer/silica nanocomposites have been reported: coatings, flame-retardant materials, optical devices, electronics photoluminescent conducting film, ultrapermeable reverse-selective membranes, proton exchange membranes, grouting materials, sensors, etc. (Zou et al., 2004).

Many investigations have been made by the researchers on the potential of the nanosilica as reinforcements for polymers composites. Yern Chee Ching et al. (Ching et al. 2013) studied effect of nanosilica filled polyurethane composite coating on polypropylene substrate. The macroscopic properties of composites are affected by the polymer-nanofiller molecular architecture. Fan et al. (Fan et al. 2012) studied the physical properties of soybean oil-based rigid PU foams modified with glass microspheres and nanoclay. Foams with fillers displayed roughly the same thermal conductivity as soy-polyol based foams without fillers. Banik and Sain (Banik et al. 2009) enhanced the foam loading property by incorporating cellulosic materials such as fibers, but the effect was limited due to the tendency to aggregate for cellulosic materials. The presence of cellulosic materials was observed to have a notable influence on the density of the foams.

Polyurethane foams are a special type of engineering plastic with excellent physical properties (including toughness, and resistance to abrasion and temperature), used in the automotive industry, thermal insulation, packaging material and in commercial applications. However, little is known, about the influence of unmodified silica on the pores network, and the resulting material-specific properties. The main objective of the study was to obtain a polyurethane composites containing filler (unmodified silica A200) and to determine its effect on the physical properties of polymer composites.

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2. Methods

Polyurethane (PU) foam with various amounts of nanosilica contents were prepared. The isocyanate, used in this study was a polymeric diphenylmethane diisocyanate (MDI), with functionality 2.7 and isocyanate equivalent weight 134. Dimethylcyclohexylamine and pentamethyldiethylenetriamine were used as catalysts. The average primary particle size of Aerosil A 200 was 7 nm in average diameter with the specific surface area of 200 m²/g. The fillers were dried at 110 °C for 2 h before use. For preparation of the PUR foam with silica, the necessary silica content (0-5 wt.-%) was added to the siloxane polyol (Sigma Aldrich) and mixed with the other ingredients according to the standard procedure. The expansion time was 600s (the form prior to pouring of the foam was heated in an oven to a temperature of 40 °C).

Compressive strength

Compression tests were performed on prismatic bar specimens with dimension of 50 x 50 x 50 mm using a testing machine, Zwick Material Testing ZW TN1P 2.5. Tests were performed according to the ASTM C365-00 at a speed of 10 mm/min.

Thermal conductivity

Thermal conductivity measures the ability of a material to transfer heat. The Heat Flow meter method, designed specifically for insulating materials, is defined by international standards ASTM C518, ISO 8301, and DIN EN 12667. The coefficient of thermal conductivity was measured (at 20 °C) using a Laser Comp Fox Heat Flow instrument 200. To perform the test, polymer composites were prepared with dimensions of 200 x 200 x 30 mm.

Density foams

The density of the foam material (50 x 50 x 50 mm) was determined from specific gravity measurements in accordance with ASTM D792. The specific gravity measurements were found by conducting buoyancy tests with water as the medium for immersion. The equipment consisted of analytical balance (accuracy 0.0001 g). Density was calculated from the formula:

$$\rho = m/V \text{ [kg / m}^3\text{]} \quad (1)$$

ρ - density [kg / m³]

m - mass of the sample [kg]

V -volume [m³]

Examination of the structure porous polymer composites

Examination of the porous structure of the polymer composites were made using a microscope Xi CAM BVMS 109C-28. During the study we used an approximation x300. Selected for the unfilled matrix polymer and polymer composites containing 5 % wt.-% (by weight silica relative to the weight of the polyol).

3. Results

Mechanical properties of the investigated polymer composites are shown in Fig. 1a. The compressive strength increases almost linearly with the filler content (to 3 wt.-%). This indicates that the addition of nanosilica has helped in improving mechanical properties in the polyurethane foam. Addition of only 3 wt. -% of silica into the PUR foam increases its compressive strength about 30 %.

Fig. 1b illustrates the thermal properties of PUR filled silica at different applied loads. Since 5 wt.-% of nano-SiO₂ filled PUR composite shows the lowest thermal conductivity. The results obtained indicate that the filler addition affect the thermal properties of the polymer matrix.

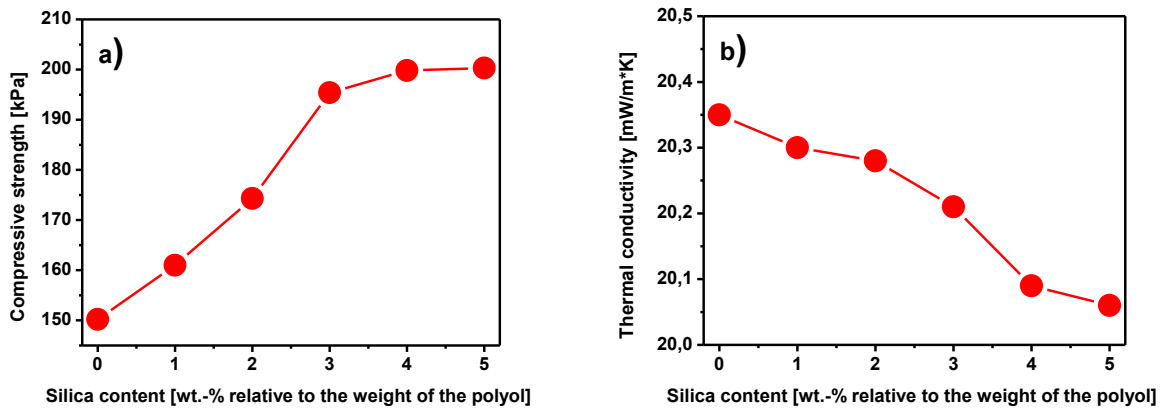


Fig. 1: The dependence of the: a) compressive strength; b) thermal conductivity on silica content in the system.

The compressive strength of foams increases with silica content and with foam density, this is shown in Fig. 2, which illustrates a decrease in compressive strength value with decreasing foam density.

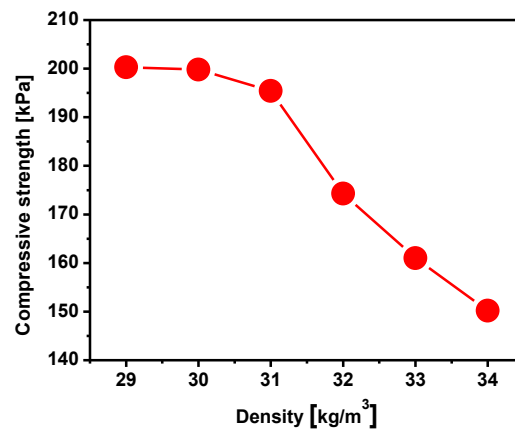


Fig. 2: The dependence of density foam on silica content in the system.

Microscope Xi CAM was used to investigate the dispersion of nano-SiO₂ particle and porous surface changes of the nano-SiO₂ filled PUR. The image in Fig. 3 reveals the dispersion condition of 0 wt.-% and 5 wt.-% of nano-SiO₂ contents in polyurethane foams. As can we see, introduction of the fillers causes changes in structure of foam. Foams reinforced with fillers had more cells and smaller cell size than foams without fillers.

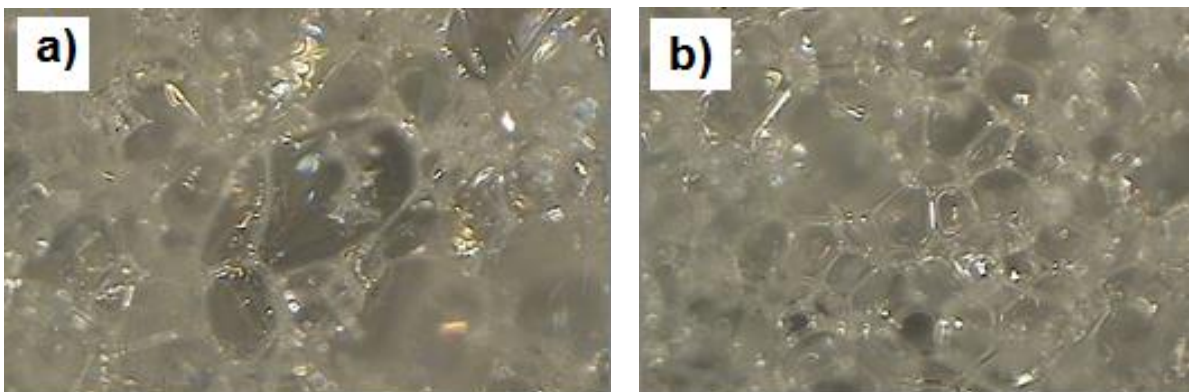


Fig. 3: Porous structure of the polymer composites: a) 0 wt.-% and b) 5 wt.-% of silica content in the system.

4. Conclusions

The effect of the PU/nano-SiO₂ composite on compressive strength and thermal behavior of polymer composite was investigated and compared. It can be concluded that the addition of small amounts of nano-SiO₂ (5 wt.-%) content can exhibit the improvement of compressive strength of the polyurethane matrix. Foams reinforced with fillers had more cells and smaller cell size than foams without fillers. These materials are interest because of their wide applications.

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References

- Ching, Y.C. and Syamimie, N. (2013) Effect of nanosilica filled polyurethane composite coating on polypropylene substrate, *J. Nanomat.* 8 pp.
- Banik, I. and Sain, M.M. (2009) Water-blown soy polyol based polyurethane foams modified by cellulosic materials obtained from different sources, *J. Appl. Polym. Sci.* 112: 1974–1987.
- Hajji, P., David, L., Gerard, J.F., Pascault, J.P. and Vigier, G. (1999) Synthesis, structure, and morphology of polymer–silica hybrid nanocomposites based on hydroxyethyl methacrylate, *J. Polym. Sci. Part B: Polym. Phys.* 37: 3172-3187.
- Fan, H., Tekeei, A., Suppes, G.J. and Hsieh, F.H. (2012) Properties of biobased rigid polyurethane foams reinforced with fillers: microspheres and nanoclay, *Intern. J. Polym. Sci.* Article ID 474803, pp. 8.
- Kuo, P.L., Chen, Ch.L. and Hou, S.S. (2000) Function and performance of silicone copolymers, 5. Syntheses and surface characterization of an acrylized silica monomer, *Macromol. Chem. Phys.* 201:1451-1457.
- Sadej, M., Andrzejewska, E., Kurc, B., Gojzewski, H. and Jesionowski T. (2014) Surface-dependent effect of functional silica fillers on photocuring kinetics of hydrogel materials, *J. Polym. Sci. Part A: Polym. Chem.* 52: 3472-3487.
- Sadej, M. and Andrzejewska, E. (2016) Silica/aluminum oxide hybrid as a filler for photocurable composites, *Prog. Org. Coat.* 94:1-8.
- Sadej, M., Gojzewski, H. and Andrzejewska E. (2016) Photocurable polymethacrylate-silica nanocomposites: correlation between dispersion stability, curing kinetics, morphology and properties, *J. Polym. Res.* 23: 116.
- Rotzoll, R. and Vana, P. (2008) Synthesis of poly(methyl acrylate) loops grafted onto silica nanoparticles via reversible addition-fragmentation chain transfer polymerization, *J. Appl. Polym. Sci.: Part A: Polym. Chem.* 45:7656-7666.
- Ziobrowski, P., Andrzejewska, E., Szybowicz, M., Nowicka, A., Sadej-Bajerlein, M., Gojzewski, H. and Drozdowski, M. (2014) Particle clustering in photocurable nanocomposites: dependence of curing kinetics and viscoelastic properties *J. Appl. Polym. Sci.*, 131:1-9.
- Zou, H., Wu, S. and Shen J. (2008) Polymer/silica nanocomposites: preparation, characterization, properties, and applications, *Chem. Rev.* 108:3893-3957.