

Polyurethane composites with enhanced thermal conductivity containing boron nitrides

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Abstract: Boron nitride (BN) is very promising particulate fillers for production of polyurethane (PUR) composites dedicated to thermally conductive materials in electronic devices. Composites containing polyurethane-based matrices filled with BN were prepared. The effect of the filler content on the mechanical (the compressive strength), physical (process parameters, the density) and thermal properties (thermal conductivity) of the final composite material were determined. Foams obtained were characterized in terms of their process parameters such as: cream time, gel time and tack-free time. The mechanical properties of the composites were improved (compressive strength increased about 40% reached at very low filler content 3 wt % of BN), and the relative increase of thermal conductivity, as compared to the matrix, was about 8%. It was concluded that BN can be used as a filler to obtain rigid PUR foams having the characteristics of thermal conductive material.

Keywords: polyurethane foams, polymer composites, boron nitride, mechanical properties.

Kompozyty poliuretanowe o zwiększonym przewodnictwie cieplnym zawierające azotek boru

Streszczenie: Określono wpływ zawartości cząstek azotku boru (BN) w kompozytach poliuretanowych (PUR) na ich wytrzymałość na ściskanie, gęstość oraz właściwości termiczne. Wyznaczono parametry procesowe uzyskanych pianek PUR, takie jak: czas kremowania, czas żelowania i czas suchego lica. Właściwości mechaniczne kompozytów były o ok. 40% lepsze niż osnowy PUR, przy bardzo małej zawartości napełniacza – 3% mas., a względny wzrost przewodności cieplnej wynosił około 8%. Stwierdzono, że cząstki BN można stosować jako napełniacz w celu uzyskania termoprzewodzących sztywnych pianek PUR.

Słowa kluczowe: pianki poliuretanowe, kompozyty polimerowe, azotek boru, właściwości mechaniczne.

Thermally conductive and electrically insulating materials are of a great importance from the scientific point of view, as well as for many applications in industry, and engineering. High thermal conductivity and electrical insulation are rarely found in one material, especially in polymers [1]. The intrinsic thermal conductivity of polyurethane foam is very low (typically 0.02–0.03 W/mK), therefore it is necessary to enhance these properties for material used in special applications, e.g. in electronic packaging.

Boron nitride (BN) particles possess excellent properties, such as high thermal stability, electrical insulation and chemical resistance, and additionally have relatively

high thermal conductivity coefficient values [2–5]. BN is a high temperature ceramic, soft and lubricious material that can be compounded into polymer matrix with minimal impact on processing equipment. The most common structure of BN is the hexagonal form (hBN), a structure analog of graphene. As a consequence of the layered structure, the filler particles have anisotropic properties, this anisotropy is clearly seen in the thermal conductivity, value of the thermal conductivity in the plane is high (several hundred W/mK), whereas the through-plane conductivity is low (a few W/mK), which results from different conduction of phonons.

A number of articles have been devoted to polymer composite containing BN particles, but they focused on the preparation of thermally conductive composites polymer based mainly on silicone rubber [3], epoxy resin or epoxy-thiol system [4–6], polyimide [7] or (meth)acrylate matrix [8, 9]. Bulk-sized boron nitride nanotube and hexagonal boron nitride nanosheets have been used as fillers only in thermoplastic polyurethane elastomer [10–12].

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The improvements of mechanical and thermal properties in these composites have been achieved. The thermal conductivity had a various value and has been found to be correlated with the form of boron nitride, its content, size, surface modification and orientation of the filler in matrix. Owing to the effective surface modification of BN, it was possible to obtain improvement in thermal conductivity in polyurethane composite [11].

Polyurethane foams are a special type of engineering plastic, used in the automotive industry, packaging material and in commercial applications. This materials are typically formed by polyaddition reactions between polyfunctional alcohols (polyol polyether or polyol polyester) and polyisocyanate to form urethane linkages isocyanates with polyols. PUR foam have been reinforced with various types of fillers such as glass fiber or silica [13, 14], carbon nanotube [15, 16], nanoclay [17], lignin or cellulose nanofibrils [18–20] and the effects were analyzed in terms of cell forming kinetics, physical, mechanical and thermal properties. In our continuing investigations on preparation and properties of PUR foam [14] we undertook research concerning a filler – boron nitride. The effects of content and particle size of BN and Si_3N_4 filler on the thermal conductivity and mechanical property of methacrylate were studied in the previous studies [9]. It was found that addition of the fillers improves polymerization kinetics and mechanical properties of the polymer matrix. Despite the very low loading level a substantial improvement in thermal conductivity was obtained: 2.5-fold increase after addition of 0.5 wt % of BN [9]. Therefore, boron nitride represent promising polymer fillers, and have the potential to significantly improve properties of composites, especially their ability to transfer heat (because heat dissipation is a crucial point for the electronic devices).

EXPERIMENTAL PART

Materials

Polyurethane (PUR) foam with various amounts of boron nitride contents were prepared. The isocyanate, used in this study was a polymeric diphenylmethane diisocyanate (PMDI Lupranat M20S, Basf), with functionality 2.7 and isocyanate equivalent weight 134, polyol (Lupranol 3424, Basf), $MW = 560$ g/mol. Dimethylcyclohexylamine (Sigma-Aldrich) and pentamethyldiethylenetriamine (Sigma-Aldrich) were used as catalysts. The boron nitride was the HeBoFill® 641 (product from HENZE Nitride Products, Germany), it has hexagonal particles (12 μm median particle size) with a specific surface area 7 m^2/g .

Preparation of PUR foams with BN

The fillers were dried at 110 °C for 2 h before use. For preparation of the PUR foams with BN, the necessary fillers content (0–5 wt %) was added to the polyol and

mixed. Accurate homogenization was obtained by means of a mechanical stirrer (6000 rpm, mixing time 1200 s). Then, in the appropriate weight ratio, the isocyanate was mixed with the polyol component and catalysts, using a mechanical stirrer (6000 rpm, mixing time 10 s). The foaming process took place at 20 °C. The mixture was then poured into a closed mold where the foaming process took place. The foaming time was 600 s (the mold was heated in the oven to 40 °C before pouring the foam). The parameters of foaming process (cream time, gel time, tack-free time) were determined according to the generalized PUR reaction.

Methods of testing

– Compression tests were performed on prismatic bar specimens with dimension of 50 × 50 × 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 [14].

– 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 TA instruments. To perform the test, polymer composites were prepared with dimensions of 200 × 200 × 30 mm.

– Microscope Xi CAM (Bosch) was used to investigate the dispersion of BN particle and porous surface changes of the BN filled PUR.

– The density of the foam material (50 × 50 × 50 mm) was determined from specific gravity measurements in accordance with ASTM D792 [14].

RESULTS AND DISCUSSION

Mechanical properties of the investigated polymer composites are shown in Fig. 1a. The compressive strength increases with the filler content. This indicates that the addition of BN improve mechanical properties in the polyurethane foam, addition of only 3 wt % of BN into the PUR foam increases its compressive strength about 40%, demonstrating potential applications of particles BN for mechanical reinforcement of polyurethane matrix (the increase of compressive strength results from the presence of hard particles of boron nitride in foam).

Figure 1b shows thermal conductivity of the investigated composites as functions of BN content. Thermal conductivity of composite materials are of a complex nature, due to the presence of at least three phases, *i.e.*, matrix, filler, the matrix-filler interphase, and depends on a lot of parameters, *e.g.*, intrinsic conductivity of the filler and matrix, aspect ratio (diameter/thickness ratio) concentration of the filler, shape and size of the particles, density and homogeneity of materials [3]. As we can see, thermal

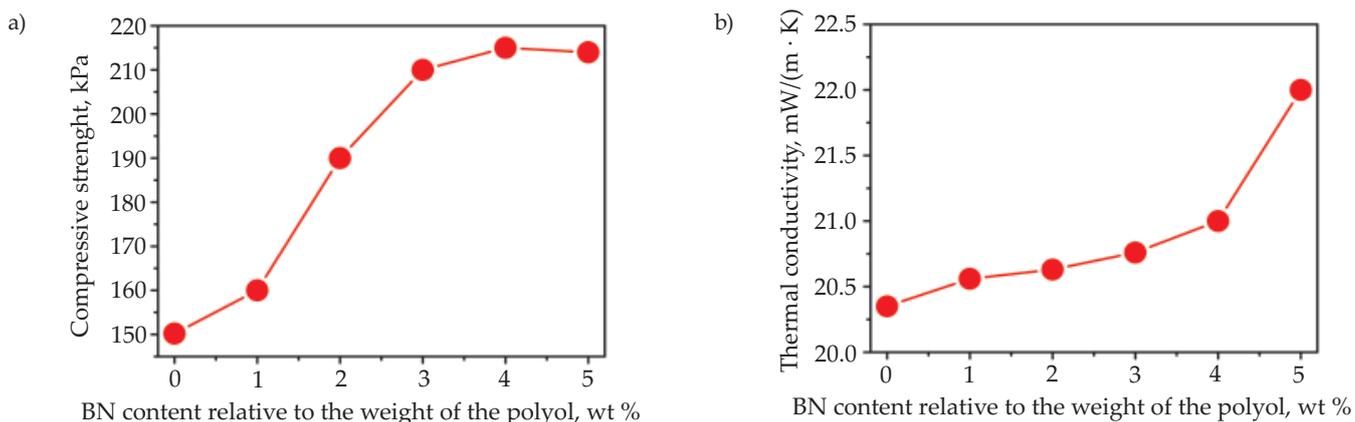


Fig. 1. The dependence of: a) the compressive strength, b) thermal conductivity on BN content (with the respect to the polyol weight); lines are drawn to guide the eye

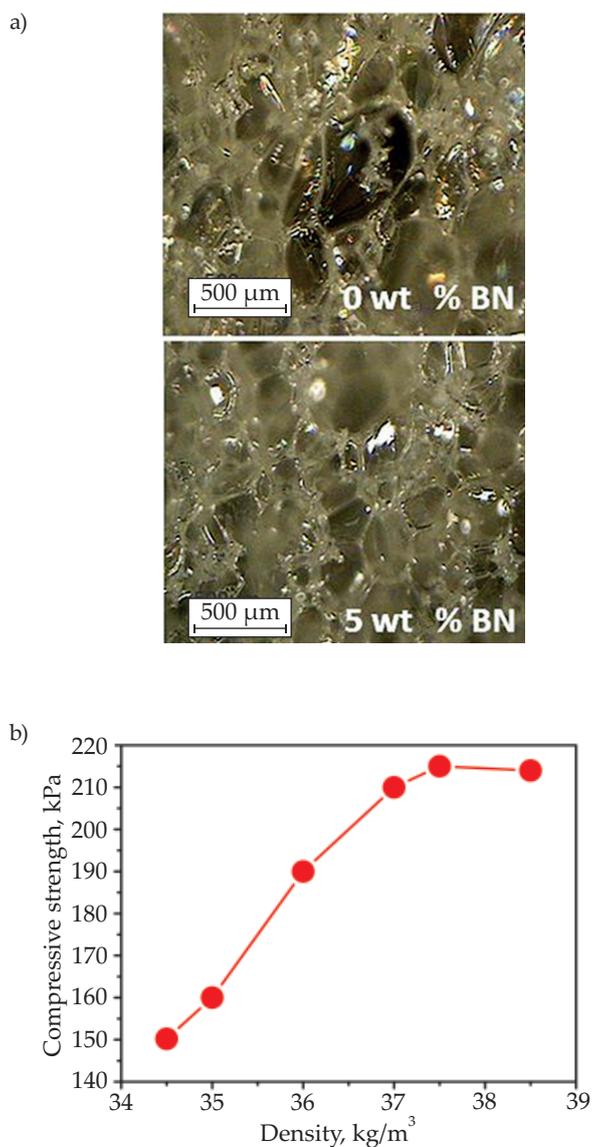


Fig. 2. a) Porous structure of the polymer composites containing 0 and 5 wt % of BN (with the respect to the polyol weight), b) the dependence of compressive strength on density foam; lines are drawn to guide the eye

conductivity of composite increase monotonically with the filler content in the whole range studied. The relative increase of thermal conductivity, as compared to the matrix, is quite high (increase about 8% reached at very low filler content), indicating improvement of thermal properties. This may suggest that at higher contents of the fillers, heat conduction can be even higher and filler will form conducting paths in the foam matrix. BN belongs to fillers with high aspect ratio values, polymer composites loaded with fillers having low aspect ratio usually exhibit a lower thermal conductivity, whereas high-aspect-ratio fillers enable to reach the percolation threshold at lower concentrations [21].

Polyurethane foam have insulating properties, the thermal conductivity of polyurethane foams is under effect of cell size, structure and cell gas. Good thermal conductivity can only be obtained for opened cells in the foam structure. Figure 2a show porous structure of the polymer composites containing: 0 wt % and 5 wt % of BN (with the respect to the polyol weight) in the system. As can we see, introduction of the fillers causes changes in structure of foam. Foams reinforced with fillers have more opened cells than foams without fillers, this is also reason of partial improvement thermal conductivity of this material. In turn, Fig. 2b illustrates dependence of the compressive strength on density of the foams. Apparent density is an important property of rigid PUR foams because it strongly affects other properties of foams such as dimensional stability, morphology, water uptake, thermostability, compressive strength and modulus [20]. The density of the unfilled foam is 34.5 kg/m³. Introducing inorganic fillers into the foam cause an increase in apparent density of polyurethane composites. Higher apparent density of foams has a positive effect on increasing their mechanical strength.

Polymerization reaction rate of PUR foam is a very important factor for final properties of composite. The rate of synthesis of PUR foam is measured as cream time (beginning of the foam reaction), gel time (the time when the foam has developed enough gel strength to be dimensionally stable), and tack free time (the time between

Table 1. Reaction profile of polyurethane foams with reaction time

Reaction time, s	Filler content, wt %					
	0	1.0	2.0	3.0	4.0	5.0
Cream time	9	10	10	9	10	10
Gel time	55	54	56	55	54	55
Tack-free time	82	83	80	81	82	80

the beginning of the foam pour and the point at which the outer skin of the foam loses its stickiness). The reaction profiles of PUR with and without BN particles are shown in Table 1.

From Table 1, it is observed that the reaction profiles for PUR foams with different content of BN and neat foam show similar cream, gel and tack free time with the reaction time. From this result, it is suggested that the additives used in this study did not affect the bubble growth of chemical reaction.

CONCLUSIONS

The main objective of the study was to obtain a polyurethane composites containing boron nitride and to determine its effect on the mechanical, physical and thermal properties of polymer composites. The results obtained indicate that the filler addition affect the thermal properties of the polymer matrix, despite the very low loading level (up to 5 wt %). The relative increase of thermal conductivity, as compared to the matrix, is moderate (increase about 8%). Mechanical testing showed that BN improves mechanical characteristics of the polyurethane matrix, compressive strength (at filler content 3 wt %) increase 40%. The reaction profiles for PUR foams with different content of BN and neat matrix show similar cream, gel, and tack free time with the reaction time, it is suggested that the filler used in this study did not affect the bubble growth of chemical reaction.

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