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The influence of ultrasonic exposure on polytetrafluoroethylene structure modified with boron nitride

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Abstract. The purpose of study is to state influence patterns of ultrasonic exposure on the density and porosity change of the synthesized polymer composite material based on polytetrafluoroethylene, modified with boron nitride. The density of 5 % boron nitride samples manufactured by ultrasonic pressing is 9% higher than the similar samples manufactured by cold pressing have and this confirms the structure defectiveness results received by electron microscopy. As the result of carried studies it was stated that polymer composite material pressing with ultrasonic vibration is an active technology increasing efficiency of matrix structure modification and affecting significantly the structure formation processes in it.

1. Introduction

Structural modification is the basis of different methods to increase polymer composite material (PCM) mechanical properties. The most widely used structural modification method is introducing different type fillers in polymer matrix: dispersed, fiber, ultradispersed [1–4].

The development of PCM obtaining technology in order to increase external energy deposition level allows one to get significant improvement of PCM properties.

One of the advanced active energy deposition methods is imposing ultrasonic vibrations (UV) on pressed powder mixture. This increases powder flow time, levelness of polymer particle lay-up, arched structures are destroyed, the development of powder particle viscous deformation is rather simplified, the porosity is decreased and the density of pressed material is increased. This has a positive influence on friction changing between particles and mould walls, enables one to form complex products with rather small efforts of pressing.

2. Statement of problem

The purpose of study is to state influence patterns of ultrasonic exposure on the density and porosity change of the synthesized polymer composite material based on polytetrafluoroethylene, modified with boron nitride.

To make research, the following concentrations of boron nitride in polytetrafluoroethylene were chosen: 1.0, 3.0, 5.0, and 10.0%.

To produce samples the special equipment based on the hydraulic press MT-50 was assembled [5]. Ultrasonic generator UZG 2-4M with 2.5 kW input operating at frequency from 17.5 to 23 kHz was used. The magnetostrictive transducer PMS 15-A-18 with 17.8 kHz resonance frequency was taken as the source of ultrasonic vibrations. The effort of pressing was 54 MPa and the range was 16 μm. After pressing the samples were subjected to baking at 360 °C.

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Composite material structure defectiveness was studied on the samples obtained with and without ultrasonic vibrations.

3. Theory

To clarify processes of polytetrafluoroethylene structural modification as the result of ultrasonic treatment, the polymer composite material (PCM) substructure was studied by electron-microscopic analysis.

To examine structure defectiveness, in this study JEM–6460 LV microscope was used (resolution is 3nm) and in order to make the conductive coating cleave on the surface, silver spraying in conditions of high vacuum was used.

The density of samples was studied by hydrostatic weighing on the 0.0001 g/cm^3 high-accuracy weighing machine VIBR-HTR.

4. Experiment Results

Microscopic studies found differences in composite morphology. Electron microscope data showed that modified composite obtained without ultrasonic treatment has non-uniform structure. It consisted of various shape nanoobjects. Besides, in the sample there can be noticed agglomerates of particles less than 2 nm covering lots of crystallites by dense layer.

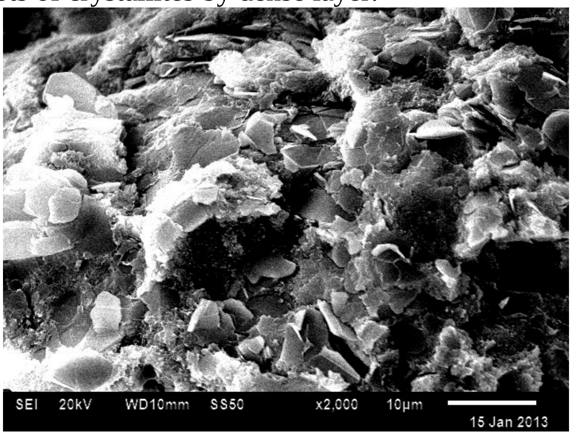

Figure 1. The micrograph of polytetrafluoroethylene modified with boron nitride and manufactured by static cold pressing.

In the modified composite obtained with ultrasonic treatment crystallites have specific morphology. They are characterized by complex structure-layer extended ones consisting of 50 nm blocks and 1–5 nm nanoparticles. In the PCM sample fracture nanoparticles are noticed to be denser than the others forming contaminations in crystallites.

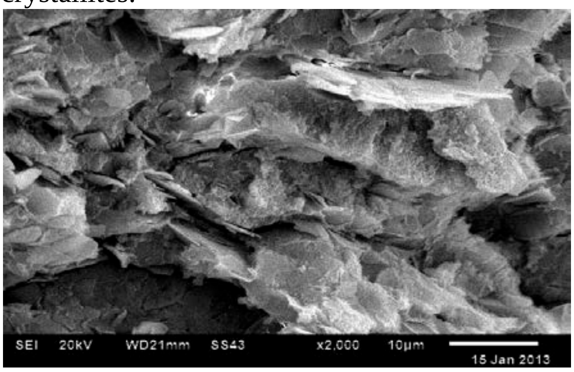

Figure 2. The micrograph of polytetrafluoroethylene modified with boron nitride and manufactured by ultrasonic pressing.

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The second type of objects observed in such composite is chain structures consisting of blocks with 50–100 nm width (Fig. 3). The chain structures, observed on this sample morphology study, are suggested to be parts of PTFE supramolecular structure formed as the result of ultrasonic treatment. These parts contain the abundance of carbons. In the PTFE molecular composition carbon is twice less than fluorine.

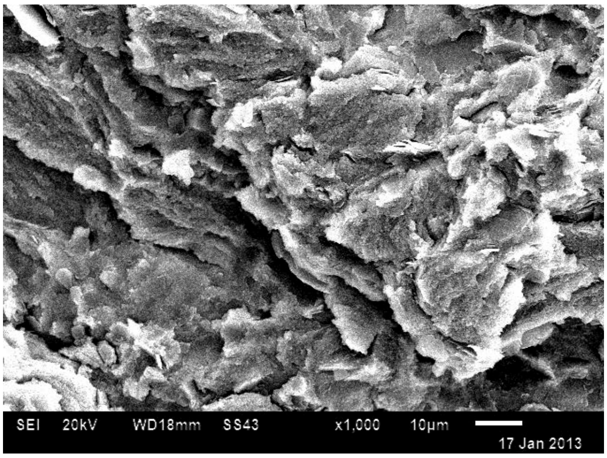

Figure 3. The micrograph of polytetrafluoroethylene modified with 5% boron nitride and manufactured by ultrasonic pressing.

Also it is important to state that sample surface of PCM obtained by static cold pressing is more spongy and porous; the defined boundaries of formations that can be identified as spherulites are not observed (Fig. 4). Crystalline formations near filler particle surfaces are not observed.

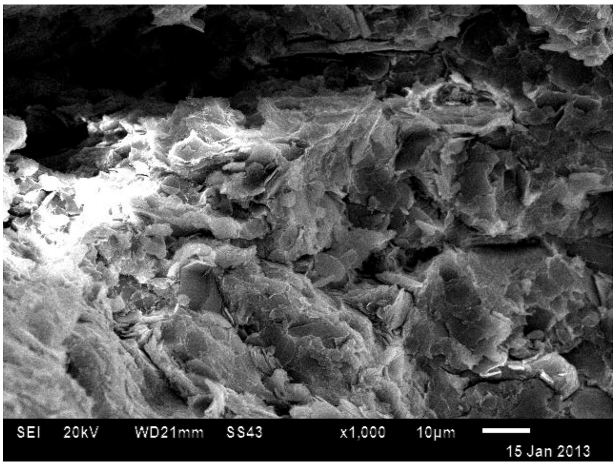

Figure 4. The surface of PCM manufactured by static cold pressing.

It should be said the increase of PCM wear resistance in result of ultrasonic treatment is defined by setting up spherulites of different shapes and sizes in the matrix.
In composite material obtained by ultrasonic pressing along with supramolecular formations similar to PTFE there can be found sites of polymer with structure not typical for pure PTFE, which can be identified as strong defective irregularly shaped spherulites (Fig. 5).
The boron nitride particles decrease polytetrafluoroethylene layer mobility that in its turn can result in wear resistance increase of synthesized composite material based on it. In composite material synthesized by ultrasonic pressing at optimum performance a high-volume contact between boron nitride particles can be observed and this defines the main way of obtaining indicated structure and its interference with physical and mechanical properties.

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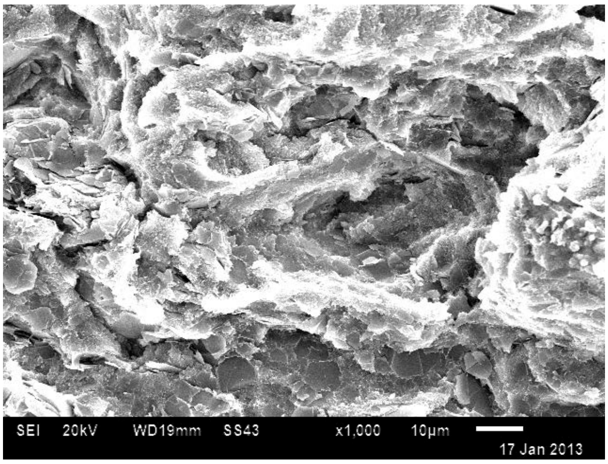

Figure 5. The cleave surface of polytetrafluoroethylene modified with boron nitride and manufactured by ultrasonic pressing.

When filler concentration is increased, the volume of polymer interreacting with boron nitride is decreasing. Therefore, the rate of more solid intermediate layer becomes higher up to polymer self-reinforcement effect followed by strengthening molecular interaction. As a result, the polymer acquires the structure similar to network polymer where strengthening phase acts as crosslinks preventing polymer chains from moving (Fig. 6).

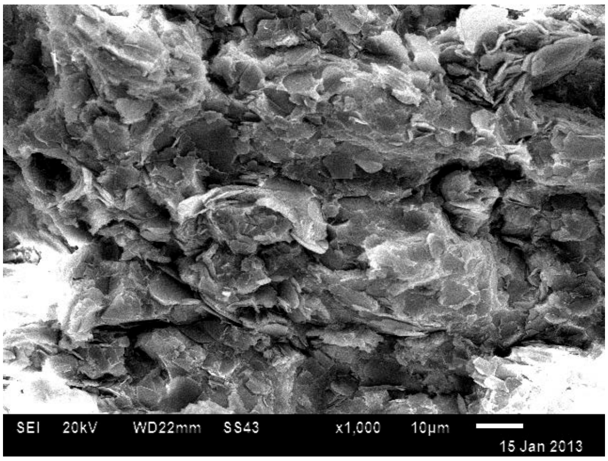

Figure 6. The structure of polytetrafluoroethylene modified by 5% boron nitride.

The stated difference between structures results from large volume changes of PTFE practically not connected by additional adhesion bond with boron nitride on melting crystalline phase in static pressed materials. This confirms again the best interaction of PTFE and boron nitride upon ultrasonic treatment and polymer monolitization with less volume changes and, therefore, small shrinkage upon baking that is very important when composite products with boron nitride are manufactured, and also the formation of the base while being treated by ultrasound on its being filled with 5% and its primary influence on material properties (Fig. 8).
The result of carried studies of cold pressing sample cleave showed on the surface of it small shells and voids are observed (Fig. 7).

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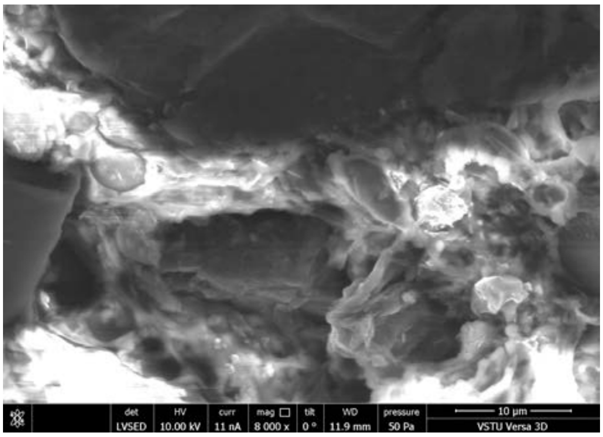

Figure 7. The micrograph of polytetrafluoroethylene containing 5% boron nitride and manufactured by static cold pressing.

On the surface of ultrasonic pressing sample cleave the shells and voids are not observed (Fig. 8).

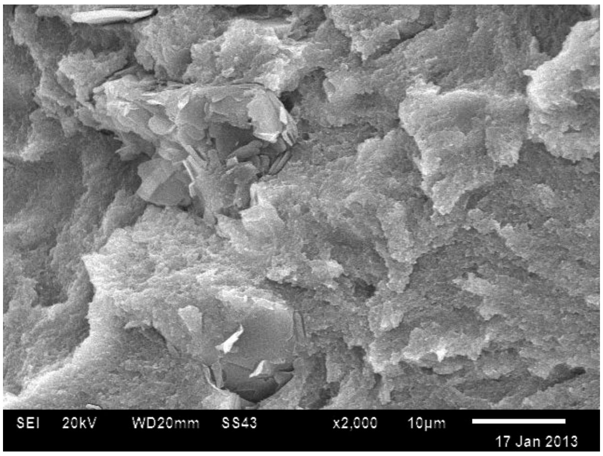

Figure 8. The micrograph of polytetrafluoroethylene containing 5% boron nitride and manufactured by ultrasonic pressing.

The decrease of composite structure defectiveness should result in increase of its density after ultrasonic treatment. For this purpose the study of ultrasonic treatment influence on changes of received PCM density was performed.
The results of synthesized composite material density are given in Fig. 9.
The density of 5 % boron nitride samples manufactured by ultrasonic pressing is seen to be 9% higher than the similar samples manufactured by cold pressing have and this confirms the structure defectiveness results received by electron microscopy.

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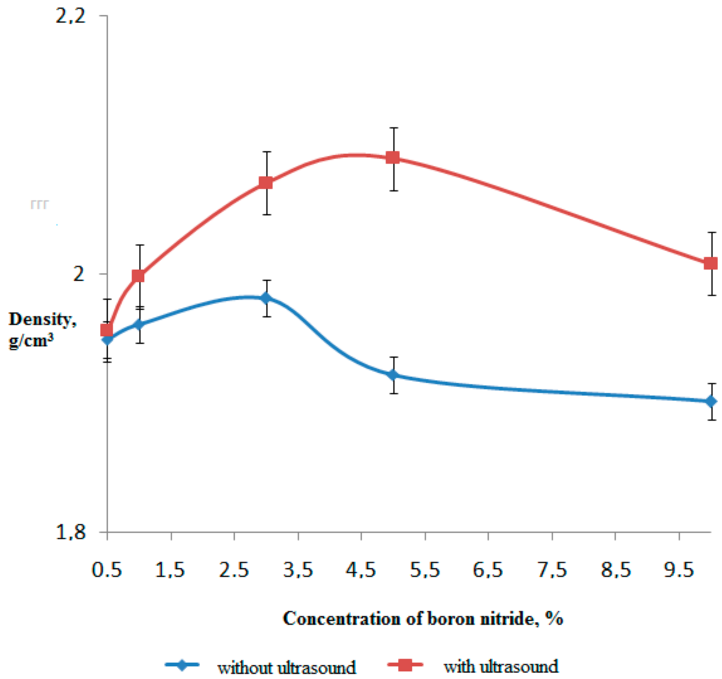

Figure 9. The influence of ultrasonic treatment and filler concentration on composite material density.

The density of polytetrafluoroethylene and boron nitride is practically similar – 2.18 g/cm^3, therefore, composite material based on polytetrafluoroethylene modified with boron nitride should have the same density theoretically (Fig. 10).

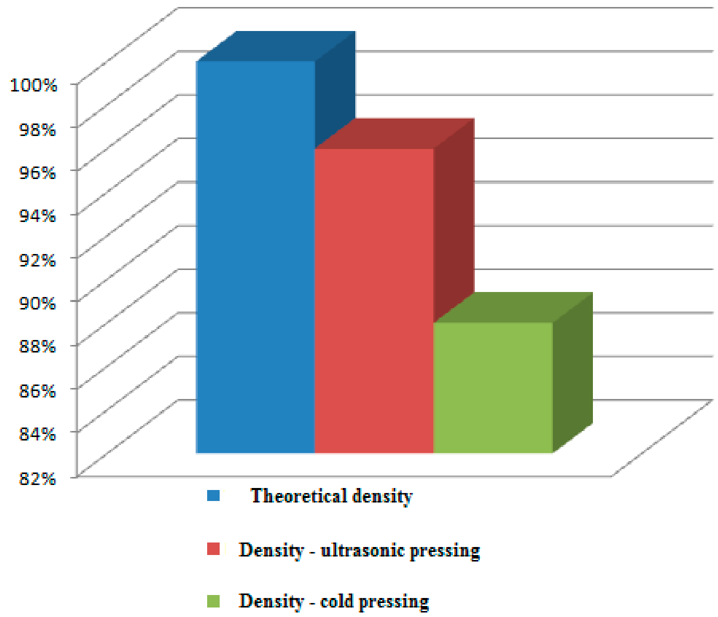

Figure 10. The density rate of composite material.

The study of quality of pressed samples from composite based on polytetrafluoroethylene and 5% boron nitride showed that 96% maximum density rate is available in material manufactured by ultrasonic pressing. PCM manufactured by static cold pressing has 88% density rate.

5. Results and discussion

The received results confirm the low adhesion strength of PCM with filler synthesized without ultrasonic exposure which acts as defect and promotes composite mixture breaking in contrast to PCM having high adhesion strength of compositions after ultrasonic treatment. On baking static pressed samples the rapid change of strain-stress polymer state is likely to occur that results in weak adhesion polymer-boron nitride bond breaking and after cooling along boundaries of metal particles pores can be formed. This confirms their lower density during baking in free condition in contrast to materials after ultrasonic treatment.

Ultrasonic treatment leads to noticeable increase of studied composite density. This result coincides with the data of supramolecular structure studies before and after ultrasonic exposure. The ultrasonic treatment of composites based on PTFE leads to fundamental change of polymer morphology, puts into operation the process of structure reconstruction. The supramolecular structure becomes more homogeneous, the porosity decreases significantly and filler particles act as structure-forming factors - centers of spherulite nucleation.

6. Conclusion

The study of ultrasonic exposure on the structure of pressed materials from polymer compositions informs of molecular interactions in powder particle surface layers promoting the process of further baking. In contrast to static pressing the promotion of phase transition in PTFE treated by ultrasound is confirmed by more advanced change of its density, strength and hardness, density of monolithic material.

The behaviour of polymers upon baking is the result of structural changes occurred during ultrasonic treatment and caused by decreasing thermal stability of crystalline formations and their lower defectiveness, as well as molecular interaction strengthening up to cross-linking during ultrasonic exposure.

The carried studies confirm that polymer composite material pressing with ultrasonic vibration is an active technology increasing efficiency of matrix structure modification and affecting significantly the structure formation processes in it.

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