

## Conference Paper

# Polymer Nanocomposites Exploited under The Arctic Conditions

A.A. Okhlopkova, L.A. Nikiforov, T.A. Okhlopkova, and R.V. Borisova

Institute of Natural Sciences, M.K. Ammosov North-Eastern Federal University, 677000

## Abstract

Several technologies of the preparation of nanocomposites based on ultra-high-molecular-weight polyethylene were developed. The first technology is based on mechanical activation of layered silicates with surfactant before addition into polymer matrix. The second technology represents mixing of ultra-high-molecular-weight polyethylene with nanoparticles by joint mechanical activation in a planetary mill. The third technology is based on mixing of ultra-high-molecular-weight polyethylene with nanoparticles in liquid media under continuous ultrasonic treatment. Common features of these technologies are reaching of filler uniform distribution in a polymer matrix and significant improvement in the mechanical properties. Also, supramolecular structure of the composites was studied.

**Keywords:** nanocomposites, ultra-high-molecular-weight polyethylene, ultrasonic treatment, mechanical activation, layered silicate, nanoparticles

Corresponding Author: A.A. Okhlopkova; email: okhlopkova@yandex.ru

Received: 9 September 2016

Accepted: 19 September 2016

Published: 12 October 2016

Publishing services provided by Knowledge E

© A.A. Okhlopkova et al. This article is distributed under the terms of the [Creative Commons Attribution License](#), which permits unrestricted use and redistribution provided that the original author and source are credited.

Selection and Peer-review under the responsibility of the ASRTU Conference Committee.

## 1. Introduction

The polar regions are characterized by extremely low temperatures and wide daily and annual temperature range. These distinctive climatic conditions cause many problems for vehicles and equipment, such as intensification of materials aging, growth of microcracks on equipment parts, decrease of strength, leaking at joints and seals, etc. There are many ways to solve these problems. One of them is use of frost resistant polymer nanocomposites (PNC). Recently, ultra-high-molecular-weight polyethylene (UHMWPE) has attracted attention of researchers as a perspective polymer for wide application fields [1-3]. Modification of UHMWPE using different types of filler can lead to significant enhancement of performance properties. PNC based on UHMWPE often exhibit enhanced mechanical and thermal properties, which can increase equipment durability [4]. Such PNC are promising materials for replacing metals and glass in equipment intended for Arctic use [5-7].

Layered silicates are interesting for researchers as filler for PNC due to their unique structure. Layers of silicates can be exfoliated in polymer volume improving properties such as strength, gas permeability, wear resistance, etc. However, preparation of exfoliated nanocomposites still remains intractable problem because of low compatibility between nonpolar polymers and polar silicates. Synthetic inorganic nanoparticles (NP) are another type of fillers. NP usually form agglomerates, which hardens PNC preparation. Thereby, prevention of agglomeration and disintegration of agglomerates are the

## OPEN ACCESS

most important tasks in PNC preparation. In this paper, we review several methods of PNC preparation which can provide uniform distribution of filler particles in a polymer matrix and improvement of mechanical characteristics.

## 2. Methods

Powdered UHMWPE (Ticona GUR 4120, Germany) with an average molecular weight of  $5 \times 10^6$  was used as a polymer matrix. Nanoparticles of  $\text{Al}_2\text{O}_3$ ,  $\text{AlN}$ ,  $\text{SiO}_2$ , and  $\text{Si}_3\text{N}_4$  (Emfutur Technologies, Spain) and Kaolinite, which is a layered silicate ( $\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$ ), were used as a filler. Cetyltrimethylammonium bromide (CTAB) was used as a surfactant. Ethanol was used as a liquid media for ultrasonic treatment.

NP and the polymer matrix were mixed in a planetary mill (Pulverisette-5, Fritsch, Germany) for 2 min before hot pressing. Surface of kaolinite was modified by mechanical activation in a planetary mill ("Activator-2S", Russia) for 2 min with the surfactant. All composites were prepared by hot pressing under 10 MPa for 20 min and 175-180 °C temperature. Filler content was varied between 0.1 – 5.0 wt.%.

PNC structure was characterized with a scanning electron microscope (SEM, JSM-7800F, JEOL, Japan) and by energy-dispersive X-ray spectroscopy (EDS, X-MAX 20, Oxford, United Kingdom) for chemical composition analysis. Mechanical tests were carried out on a universal testing machine Autograph AGS-J (Shimadzu, Japan) according state standard 11262-80.

### 2.1. Mechanical Activation of Layered Silicates with Surfactants

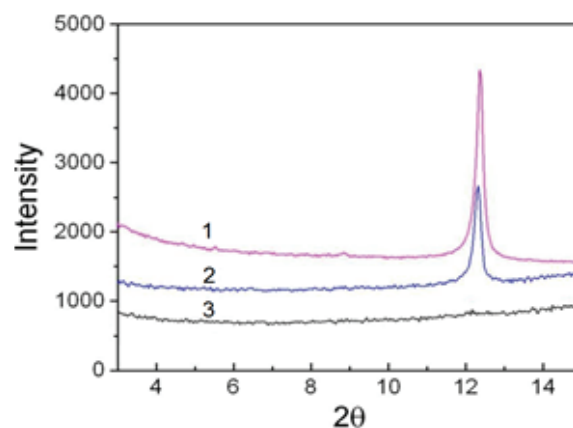
The mechanical properties of UHMWPE filled by mechanically activated kaolinite in amounts of 0.5–5.0 wt% have been evaluated [3]. Strength increased by 15% and elongation at break increased by 20% in comparison with the initial UHMWPE. The best results were shown by composites with 0.5–1.0 wt% kaolinite. Thereafter, increase of filler content lead to the deterioration of the mechanical properties of composites.

Kaolinite modified with surfactant can also be used as a UHMWPE filler. However, surfactant solution cannot be applied in the case of kaolinite, because there are no exchangeable cations between silicate layers. There is another way to modify kaolinite surface using mechanical activation in a planetary mill with surfactant. Surfactant can be used as a surface modifier due to long hydrophobic hydrocarbon chain and hydrophilic positively charged end. Composites prepared using the surfactant revealed a 17% increase in strength and 33% increase in elongation at break (Table 1) [3]. Enhanced mechanical properties can be explained by an increase in the adhesive interaction between kaolinite and UHMWPE in the interfacial layers [1, 3]. Also, surfactants can support the disintegration of the agglomerates of particles with high surface energy [1].

Composites were studied by XRD to find the explanation of mechanical properties enhancement at small amounts of kaolinite in the composites. The peak corresponding to the interlayer space of kaolinite was not detected in diffraction pattern of PNC with

Sample	Elongation (%)	Tensile strength (MPa)
UHMWPE	310-320	30-35
UHMWPE + 0.5% kaolinite	390-400	35-40
UHMWPE + 1% kaolinite	360-370	35-40
UHMWPE + 2% kaolinite	310-320	30-35
UHMWPE + 5% kaolinite	300-310	20-25
UHMWPE + 0.5% kaolinite + CTAB	435-445	36-41
UHMWPE + 1% kaolinite + CTAB	410-420	35-40
UHMWPE + 2% kaolinite + CTAB	435-445	35-40
UHMWPE + 5% kaolinite + CTAB	395-405	31-36

TABLE 1: Mechanical characteristics of composites based on UHMWPE and mechanically activated kaolinite.



**Figure 1:** XRD patterns of composites based on UHMWPE and kaolinite filler with a compatibilizer or a surfactant: (1) mechanically activated kaolinite, (2) PCM containing 5 wt% mechanically activated kaolinite, (3) PCM containing 5 wt% kaolinite with a surfactant.

surfactant (Fig. 1). Absence of peak indicates that kaolinite exfoliates in the UHMWPE volume [8]. Exfoliated silicate layers provide significant enhancement of the performance characteristics of PNC because of increase effect of silicate on the PNC structure formation process.

## 2.2. Mechanical Activation of Nanoparticles with Polymer

Determination of tensile strength and elongation at break allowed to estimate effect of mechanical activation on composite properties. As shown in Figure 2, composites with 0.5 – 1 wt.% of nanofiller possessed the best mechanical properties. At higher nanofiller content mechanical properties gradually decrease.

Use of mechanical activation led to 35 – 40% increase in elongation at break. Grinding balls of planetary mill deforms UHMWPE particles during mechanical activation and transform them into flat flakes with dimensions 50 – 200 microns [9]. This process results in increase of mechanical properties because of increase in specific surface area of polymer particles.

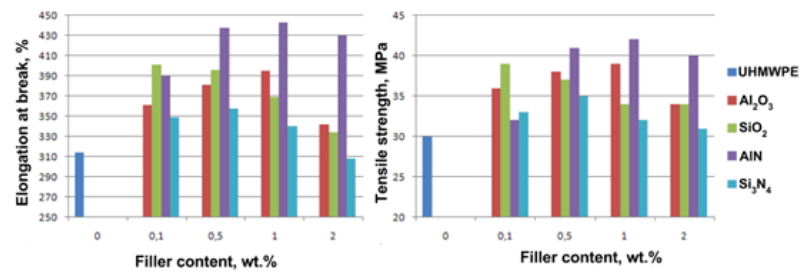


Figure 2: Elongation at break of PNCs prepared by (a) paddle mixer and (b) planetary mill.

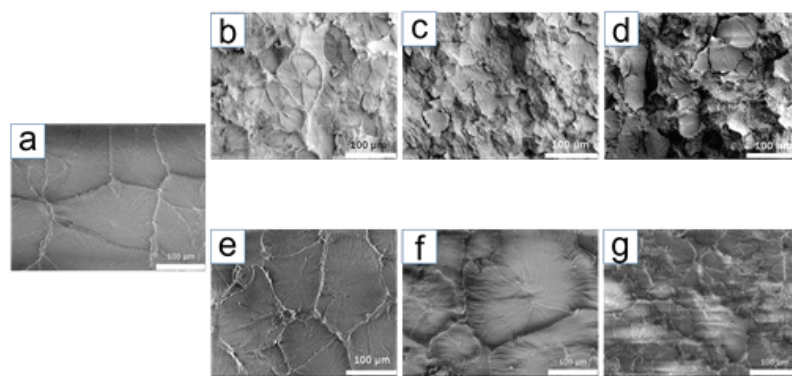
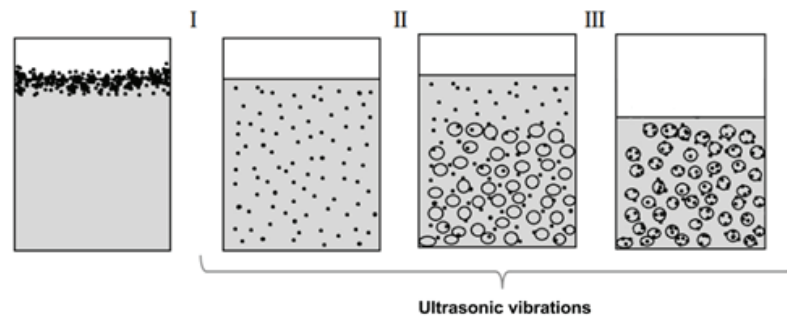


Figure 3: SEM images of (a) initial UHMWPE; and UHMWPE with various additives prepared in a paddle mixer (b) 0.5 wt% SiO<sub>2</sub>; (c) 1.0 wt% SiO<sub>2</sub>; and (d) 2.0 wt% SiO<sub>2</sub>; or mixed in a planetary mill (e) 0.5 wt% SiO<sub>2</sub>; (f) 1.0 wt% SiO<sub>2</sub>; and (g) 2.0 wt% SiO<sub>2</sub>.

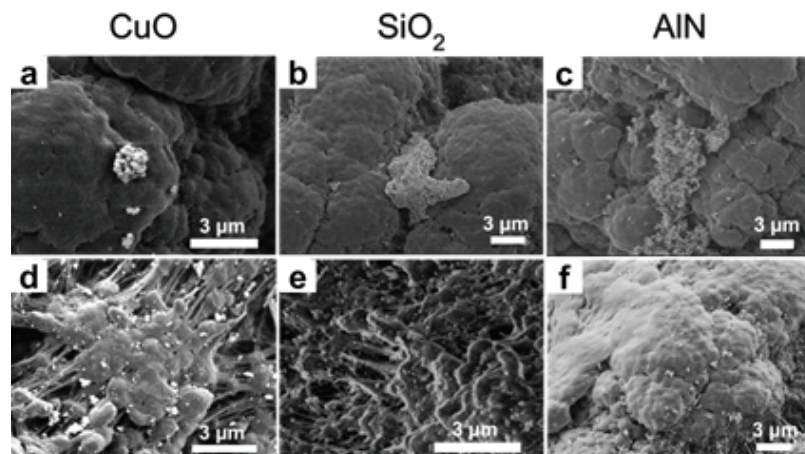
Analysis of PNC mechanical properties show that an optimal NP concentration exists [10]. Increase of filler content beyond optimal content leads to considerable decrease in mechanical properties. It is caused by the changes of adhesive interaction "UHMWPE-nanofillers". In this case, PNC's supramolecular structure consists of defective areas and deformed spherulites.

The correlation between the PNC's mechanical behavior and their microstructures is fundamentally important in determining the deformation mechanism. As shown in [11, 12], polymer deformation process consists of two major stages. The polymer's interlamellar amorphous phase is exposed to deformation at first, and this process has elastic character. After that, non-elastic deformation occurs in the spherulites.

The samples prepared in a paddle mixer are shown in Fig. 3b-d and the samples produced by joint mechanical activation in a planetary mill are shown in Fig. 3e-g. As a result, it can be concluded that the joint mechanical activation leads to more uniform distribution of the nanofiller in the polymer matrix than for composites made in a paddle mixer. Distribution uniformity is the explanation of the enhancement of mechanical properties.



**Figure 4:** Mixing stages of UHMWPE and NP: I – NP agglomerates disintegration under ultrasonic vibration impact; II – Formation of UHMWPE and NP suspension; III – Evaporation of liquid media under the ultrasonic vibrations to condense NP on the UHMWPE particles surface.

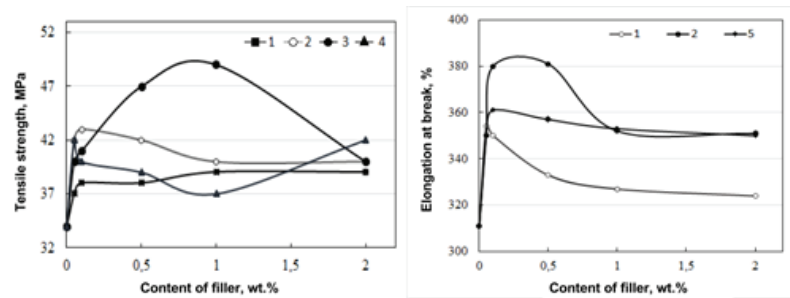


**Figure 5:** Investigation of UHMWPE particles surface and adsorbed NP: a - c without ultrasonic treatment; d - f with ultrasonic treatment.

### 2.3. Ultrasound Processing of Components during Mixing in Liquid Media

The scheme of mixing is presented in Fig. 4. Developed technology consists of three stages: 1) NP agglomerates disintegration under ultrasonic vibration impact; 2) formation of UHMWPE and NP suspension; 3) evaporation of liquid media under the ultrasonic vibrations to condense NP on the UHMWPE particles surface.

UHMWPE particles surface was investigated by SEM to estimate effect of ultrasonic treatment. As seen in Fig. 5, ultrasonic treatment provides uniform distribution of NP on UHMWPE particles surface. Distribution of filler in PNC is a critical factor for mechanical properties. Mechanical tests were carried out to clarify effect of ultrasonic treatment (Fig. 6). Significant increase of strength and elongation at break was found for all composites, but with increase of filler content mechanical properties deteriorate. Such changes of properties depend on filler content as usual for nanocomposites [3, 10]. This is due to the high surface energy of NP which increases agglomeration tendency with increase of filler content.



**Figure 6:** Mechanical properties of composites prepared by developed technique: 1 - UHMWPE +  $\text{Al}_2\text{O}_3$ , 2 - UHMWPE +  $\text{Si}_3\text{N}_4$ , 3 - UHMWPE +  $\text{ZrO}_2$ , 4 - UHMWPE +  $\text{AlN}$ , 5 - UHMWPE +  $\text{SiO}_2$ .

### 3. Conclusion

In this article, we reviewed several technologies of PNC preparation. New PNC with improved mechanical properties were obtained using these technologies. Shared feature of them is the reaching of filler uniform distribution in a polymer matrix.

Polymer nanocomposites with exfoliated structure were obtained. These nanocomposites with exfoliated silicates were prepared by treating layered silicates with surfactants during mechanical activation, and then mixing with initial UHMWPE. This type of nanocomposites exhibits improved mechanical characteristics in comparison with the pure polymer and the composites prepared without mechanical activation with surfactant.

The most perfect supramolecular and crystal structure in PNC was formed using the joint mechanical activation of composite components. Also, the presence of specific defective areas and imperfect spherulites in the supramolecular structure of the PNC reduced mechanical properties.

The technology of combining nanoparticles and initial polymer under the influence of ultrasound in a liquid media leads to the most uniform distribution of nanofiller on UHMWPE surface without any significant changes in the structure of the resulting nanocomposite.

### References

- [1] S. Sinha Ray and M. Okamoto, Polymer/layered silicate nanocomposites: A review from preparation to processing, *Progress in Polymer Science (Oxford)*, **28**, no. 11, 1539–1641, (2003).
- [2] S.-J. Park, K. Li, and S.-K. Hong, Preparation and characterization of layered silicate-modified ultrahigh-molecular-weight polyethylene nanocomposites, *Journal of Industrial and Engineering Chemistry*, **11**, no. 4, 561–566, (2005).
- [3] I. V. Kirillina, L. A. Nikiforov, A. A. Okhlopko, S. A. Sleptsova, C. Yoon, and J.-H. Cho, Nanocomposites based on polytetrafluoroethylene and ultrahigh molecular weight polyethylene: A brief review, *Bulletin of the Korean Chemical Society*, **35**, no. 12, 3411–3420, (2014).
- [4] F. Hussain, M. Hojjati, M. Okamoto, and R. E. Gorga, Review article: Polymer-matrix nanocomposites, processing, manufacturing, and application: An overview, *Journal of Composite Materials*, **40**, no. 17, 1511–1575, (2006).
- [5] S. Komarneni, Nanocomposites, *Journal of Materials Chemistry*, **2**, no. 12, 1219–1230, (1992).
- [6] L. Sherman, Nanocomposites: a little goes a long way, *M Plast Technol*, **45**, 52–57, (1999).
- [7] R. Westervelt, *Sellers launch a pricing assault. Chem Week*, 52, 161, 1999.

- [8] Y. C. Ke and P. Stroeve, Polymer-Layered Silicate and Silica Nanocomposites, *Polymer-Layered Silicate and Silica Nanocomposites*, (2005).
- [9] S. Wannasri, S. V. Panin, L. R. Ivanova, L. A. Kornienko, and S. Piriyaon, Increasing wear resistance of UHMWPE by mechanical activation and chemical modification combined with addition of nanofibers, 67-70
- [10] A. A. Okhlopkova, S. A. Sleptsova, G. N. Alexandrov, A. E. Dedyukin, E. L. Shim, D.-Y. Jeong, and J.-H. Cho, Nanoceramic and polytetrafluoroethylene polymer composites for mechanical seal application at low temperature, *Bulletin of the Korean Chemical Society*, **34**, no. 5, 1345-1348, (2013).
- [11] M. F. Butler and A. M. Donald, Deformation of spherulitic polyethylene thin films, *Journal of Materials Science*, **32**, no. 14, 3675-3685, (1997).
- [12] P. B. Bowden and R. J. Young, Deformation mechanisms in crystalline polymers, *Journal of Materials Science*, **9**, no. 12, 2034-2051, (1974).