

STRUCTURE AND PROPERTIES OF BALL MILLED UTRAHIGH-MOLECULAR WEIGHT POLYETHYLENE - CLAY COMPOSITES.D. Kaloshkin^{1ξ}, K.S. Ergin¹, V.V. Tcherdyntsev¹, A.V. Maksimkin¹, M.I. Petrzhhik¹, E.M. Antipov², V.A. Gerasin²¹Moscow State Institute of Steel and Alloys, Russia²Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Russia

Keywords: Polymer-clay composite, Mechanical alloying, Tribology

Abstract

In this work the composite material based on polymer matrix filled with clay is studied. The preparation of powder composition consists of mechanical activation of substances and further common ball milling of polymer and clay in a high-energy planetary ball mill. The process is divided into two stages; the first stage involves crushing of clay to obtain a nanosized powder, and in the second stage preparation of powdered nanocomposite is carried out. New clay-polymer composite shows considerable increase in modulus of elasticity and a decrease in coefficient of friction.

Introduction

Development of composite materials on the basis of polymers is one of the most priority directions in materials science. Polymeric composite materials with clay fillers are vivid example of improvement of physical, mechanical and chemical properties of polymeric matrixes without significant inputs. For example, researchers at Toyota have patented clay-nylon composites with greatly improved tensile strength, tensile modulus, and heat distortion temperature when compared to neat nylon. In these composites the improvement in the physical properties was brought about with only 5% of clay incorporation. Addition of clay can make plastics less permeable to liquids and gases, more flame retardant and tougher [1-4]. Also clays are known as nanoclays because of 1 nanometer spacing between layers (Fig. 1). The modified nanoclay is used as material with unique physical, mechanical and chemical properties, which are of interest to a number of industries. The purpose of this work was creation of a polymer-nanoclay composite with improved mechanical and tribological properties.

There are two commonly used methods for manufacturing clay-polymer composites. One of the methods, called melt blending, is based on intercalation of polymer chains into the clay interlayer space, or interlayer galleries, during melting the polymer together with the clay. The second method, *in-situ* polymerization, involves intercalation of the polymer into the clay during *in-situ* polymerization of the monomer. This process includes two steps. The first step is immobilization of a polymerization catalyst in a clay powder, and the second stage is direct polymerization of monomers in the presence of the clay. In both methods, the intercalation of polymer chains into the clay interlayer space usually leads to exfoliation of clay

crystallites on separate silicate plates. However, according to recent data, the second method is more promising for manufacturing nanocomposites with improved properties [5-9]. In this work we used another original method to prepare a new polymer-clay nanocomposite. It is alloying and mixing of separate silicate plates and polymer by mechanical influence in a planetary ball mill. Experimental work on manufacturing of a new material passed in two stages. The first stage is receiving of ultradisperse clay powder, and the second stage is alloying of clay powder and polymer.

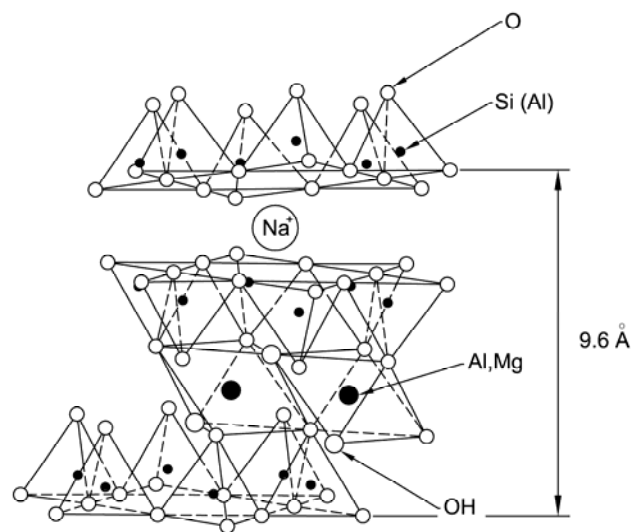


Figure 1. Structure of the montmorillonite clay

Selecting polymer matrix is one of the most important steps of creation a new polymer composite material. Working in the friction units as the bearing and sealing constructions suggests that polymer matrix should possess high (or sufficient) mechanical strength, high antifriction properties, wear resistance and resistance against aggressive environment. Ultrahigh molecular weight polyethylene (UHMWPE) and its composites are widely used as bearing components, gears, guide rails, in food treatment and medical equipment because of their excellent friction and wear characteristics, corrosion resistance and mechanical properties [10-13].

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Experimental

For polymer matrix, we used the powder of UHMWPE of GUR brand made by Ticona GmbH (Germany). The molecular weight of UHMWPE is $3-6 \times 10^6$ g/mole and the melting point is 152°C . Sodium clay Na⁺-montmorillonite with a cation exchange capacity (CEC) of 95 mgeq/100 g was used as a filler.

In the first stage, clay material was milled for one hour in a ball mill MPF-1 to get the powder of nanoclay (Fig. 2). In the second stage, composite powder was prepared by milling of UHMWPE and clay powders together in a MPF-1 planetary ball mill. Clay powder was received by 30 min milling. Jointly milling time of UHMWPE and clay powders was 30 min. Milling time was selected by experimental way. The samples of composite powder were prepared with a step of 10 mass % of clay filler.

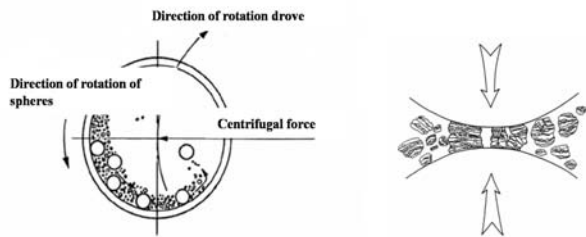


Figure 2. Process of crushing and mechanical activation in the mill MPF-1

Milled composite powders were consolidated into layers and cylinders for mechanical and tribological tests. Press-forms with powder were heated up to the temperature ($170-180^\circ\text{C}$) and exposed for 2-3 min; after exposure, press-form was cooled down with water.

For each test, 5 samples were taken. Tests were performed using test machines by INSTRO Co. and CSM Instruments. The tribological tests were performed using TROBOMETER (CSM Instruments). Figure 3 shows the schematic diagram of tribotechnical tests. Tribotechnical tests were carried out using cylindrical samples of 30 mm diameter and 2.2 mm thickness; face side of the samples were used as frictional surface. We used a ball, as a counter body, made of steel 100Cr6 with hardness 1550 HV. Normal loading of test- 1 H, linear speed - 20 cm/sec, diameter of the wear ring - 9-11 mm, duration of test - 5000 revolutions.

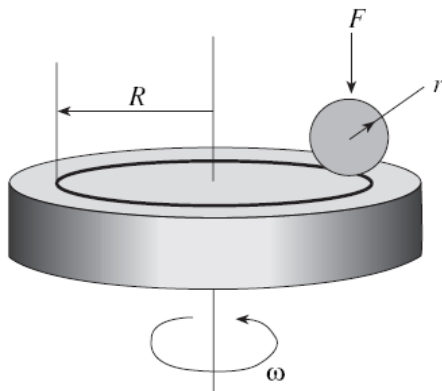


Figure 3. Scheme of tribotechnical tests

Results and Discussion

After crushing the clay, the X-ray powder diffraction analysis has been carried out. The analysis showed that the lines corresponding to inter-planar distance (a few nm) and structure of clay layers are absent in the roentgenogram. The roentgenogram and scanning electron micrograph of the crushed clay are shown in Fig. 4 and 5, respectively. This analysis shows that after mechanical process the clay represents a ultradisperse amorphous powder. Introduction of this powder in a polymeric matrix would allow an improvement in important parameters, such as wear resistance, mechanically properties like modulus of elasticity, lowering of coefficient of friction etc.

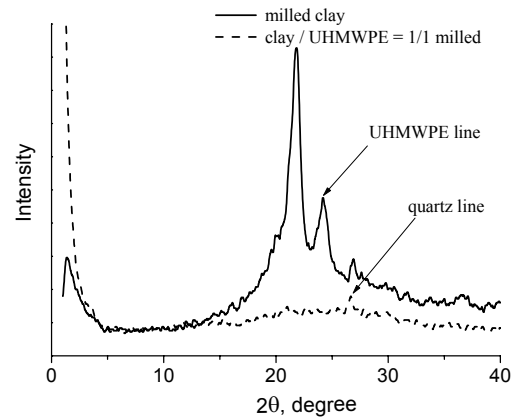


Figure 4. X-ray of milled clay and milled clay/UHMWPE composite

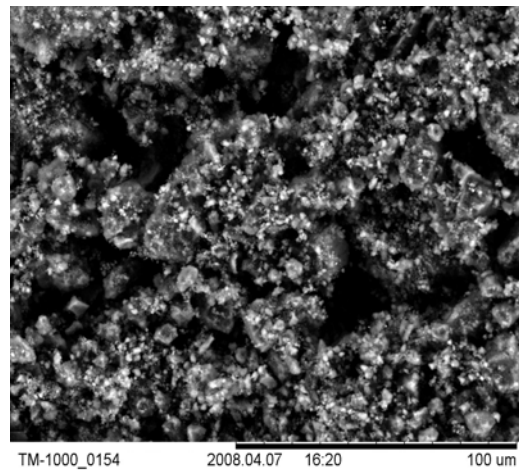


Figure 5. Electron microscope photo

In our research, following parameters were determined: modulus of elasticity (E_p), relative elongation (ε_{pp}), tensile strength (σ_{pp}), strength of fluidity limit (σ_f), coefficient of friction f and, wear resistance. The modulus of elasticity – is one of the most important parameters for a polymeric material. Modulus of elasticity E_p in Fig. 6 increases from 270 MPa to 1160 MPa with an increase in percent content of the clay from 0 to 70 wt. %.

Relative elongation ε_{pp} in Fig. 7 falls with an increase in the percent content of the clay beyond 30 wt. %. Tensile strength σ_{pp} in Fig. 8 is lower relative to pure UHMWPE, because the filler clay is fragile in nature. Figure 9 shows that strength of fluidity limit σ_f increases by 1.5 times at 70 wt. % of filler. Coefficient of friction and wear resistance data for 10 to 50 wt. % are given in Table 1. Tensile strength and relative elongation which with filling by firm particles fall, and in some cases considerably, nevertheless, remain at a high level. Tensile strength falls no more than 18 % at filling up to 40 wt. %, and relative elongation 12 % at filling up to 30 wt. %. These data show that the received composite has much higher modulus of elasticity with the minimal decrease in other mechanical parameters vis-à-vis pure UHMWPE. Two more parameters which should be lowered by introduction of ultradisperse clay - coefficient of friction and wear have been found in conditions of dry sliding which defines the most serious real challenge during loading in machines. Initial and maximal coefficient of friction of the majority of samples is at one level (the unsteady mode), but in due course the constant level of wear is established, and filled samples show less coefficient of friction. At 30 wt. % of filling, coefficient of friction decrease by 32 % in comparison with pure UHMWPE. The level of wear also falls and at 50 % filling it decreases to nearly half. Inclusions of clay particles reduce coefficient of friction at dry sliding at filling to 80 %.

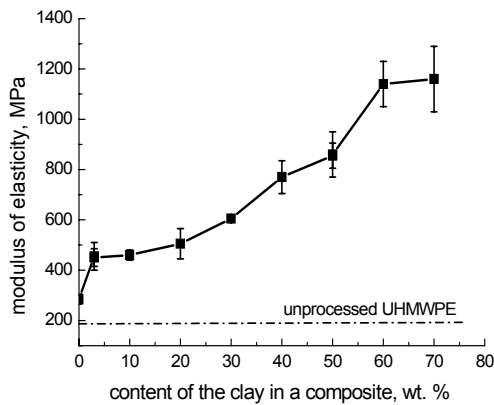


Figure 6: E_p function of the percent of the clay

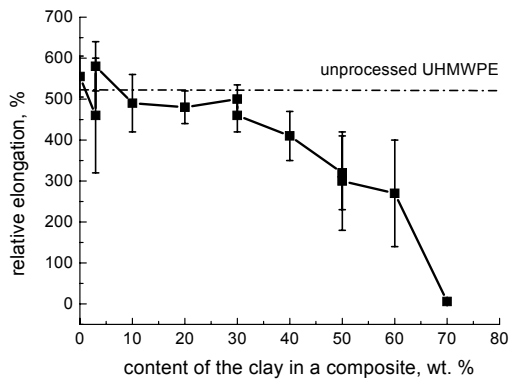


Figure 7: ε_p as function of the percent of the clay

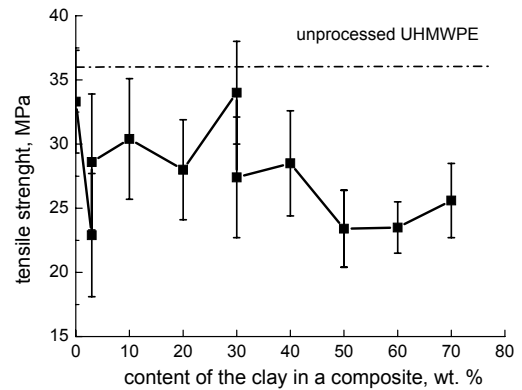


Figure 8: σ_{pp} as function of the percent of the clay

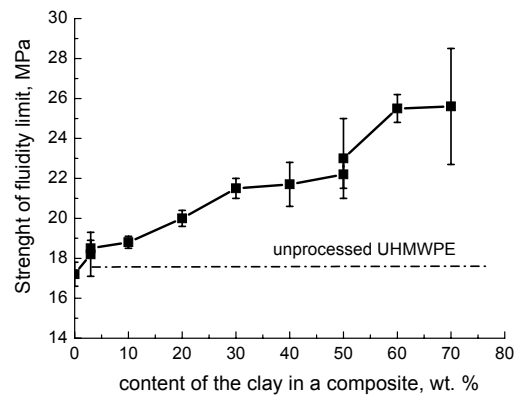


Figure 9: σ_f as function of the percent of the clay

Table 1. Wear and coefficient of friction of the samples

Content of the clay	Wear, 10^{-6} mm ³ /N.m	Coefficient of friction
0	120	0,19
10	78	0,14
30	70	0,13
50	59	0,15
70	80	0,16

Summary

Possibility of using high-energy ball-milling to produce nanoclay-polymer composite is demonstrated as a new method of producing such materials. The results obtained have indicated that ultrahigh molecular polyethylene matrix-ultra-disperse clay composites, containing 3-30 wt. % clay, show improvement in a number of important physical and mechanical properties in the new composite material.

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