PREPARATION OF SMOOTH POLYETHYLENE AND POLYETHYLENE / ORGANO-VERMICULITE SURFACE

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Abstract

In this study the surfaces of pure polyethylene and polyethylene filled with organo-modified vermiculite were prepared and compared. Both polymers were prepared from industrial polyethylene powders. The polyethylene composite were filled with 3 wt. % of additive. As an additive was used vermiculite with chlorhexidine diacetate (CA). CA is antibacterial agent often used in dentist medicine. The infection is major problem of implant surgery. Smoothening of polyethylene surface may result in difficult adhesion of bacteria and viruses. Combination of smooth surface with antibacterial effect should to be very promising material for implant medicine. Two processes were compared **-** heat treatment and chemical modification (boiling in hexane). Pure polyethylene shows deep depression and sharp tips formed by preparation process. The heating method creates finer surface and more flat surfaces without sharp tips. On the other hand boiling in hexane create surface with fine roughness resulting in dissolution of polyethylene.

Keywords: Polyethylene, vermiculite, chlorhexidine diacetate, smooth surface

1. INTRODUCTION

Polyethylene (PE) is non-toxic, insoluble in water, biologically inert, stable and very often used polymer. PE is widely applied for food packaging, water purification [1], in medicine as implants (e.g. urinary catheters, vascular cannulea, tubes of respirators etc. [2,3]). The problem of implant surgery is infection caused by bacteria and viruses catch on the implant surface [4]. This problem should be solved by smoothening of polymer surface. The smoothening of polymer surface leads to make the bacteria and viruses adherence more difficult [5]. Another improving of infection effect is usage of PE contains fillers with specific effect. Polyethylene is used as polymer matrix of nanocomposites applying organically modified clay minerals as fillers [6,7]. Clay minerals are non-toxic, cheap natural phyllosilicates [8]. Layered structure of clays enables modification with organic molecules (e.g. drugs). These organic molecules can give special properties as antibacterial activity to clays. On the other hand, fixing of organic molecules on clays leads to gradual release of the drug. One of the most used organic compound is chlorhexidine diacetate (CA) - drug utilized in medicine for its strong antibacterial effect [9]. CA is very effective against Gram-positive and Gram-negative bacteria. Area of utilization of CA is bactericide. In dental application CA is active ingredient against dental plaque or oral bacteria in mouth wash. Organic modification of clay by CA is very often [10,9]. Another advantage of organo-vermiculite is utilization as polyethylene matrix due to better dispersion of filler in polymer matrix [11]. Utilization of smooth and antibacterial PE surface can solve the problem of infection. In this study two smoothening processes were compared **-** smoothening by heat treatment and smoothening by dissolution in inorganic solvent (boiling in hexane). The shape of polymer surfaces were studied by atomic force microscopy (AFM) and scanning electron microscopy (SEM).

2. MATHERIALS AND METHODS

2.1. Materials

Vermiculite from Brazil (from Grena Co., Czech Republic) was milled in vibratory mill to obtain fraction ≤ 40 μm. Monoionic Na-form of vermiculite (Na-Ver) was prepared by cation exchange with 1 mol.dm^{-3} NaCl solution.

Chlorhexidine diacetate were purchased from Sigma Aldrich Co., Czech Republic and ethanol was purchased from Vitrum VWR, Co. (Czech Republic). Polyethylene (PE) plate was prepared from powdered and granulated mixture of industrial low density polyethylene (Bralen VA20-60, Slovnaft Co., Slovak republic). Hexan p.a. was purchased from Lach:Ner, Co. (Czech Repubilc).

2.2. Sample preparation

Na-form of vermiculite was modified by chlorhexidine diacetate in concentration corresponding to 1 x cation exchange capacity of vermiculite (CEC = 106 cmol(+)/kg). Ethanolic solution of CA and aqueous solution of Na-Ver were mixed together, stirred and heated for 6h. Final product was centrifuged and dried overnight (marked as VerCA). Pure polyethylene was prepared from the mixtures of polyethylene precursors by blending mixtures in the Brabender kneading chamber (BRABENDER GmbH & Co. KG 835201.041/815604) at 150 °C for totally 10 min (two intervals were used: 10 rpm for 2 min and subsequently 50 rpm for 8 min). The PE was pressed to 100 x 100 x 1 mm plate by hand press for 3 min at 160°C. After that prepared plate was cooled down at liquid cooled press for 15 min. The polymer composite was prepared by addition of 3 wt% VerCA into the starting PE mixture. The polyethylene composite was denoted as (PE/VerCA).

For smoothening experiments were used PE and PE/VerCA plates at range 10 x 10 mm. Smoothening of the PE and PE/VerCA surfaces were prepared by heating and boiling in hexane. Heat treatment was done in oven at 150 °C for 5 min and then was the plate cooling down to laboratory temperature (PE1, PE/VerCA1). In the second process (boiling in hexane), the plate was placed into the boiling hexane solution for 8 min. Then the plate was removed form solution and washed with demineralized water and dried at laboratory temperature (PE2, PE/VerCA2).

2.3. Methods

The morphology of the samples was studied using scanning electron microscopy and atomic force microscopy. Scanning electron microscopy (SEM) images were performed using PHILIPS XL-30 equipped with energy dispersive spectrometer EDAX. The samples for SEM were coated by gold, because the polyethylene is not conductive. The brief surface morphology of the surfaces was studied using atomic force microscopy (AFM) Solver NEXT (NT-MDT) atomic force microscope equipped with semicontact (tapping) probe (NSG30) was used for imaging. The images were evaluated using Gwydion software.

3. RESULT AND DISCUSSION

3.1. Scanning electron microscopy

The characterization and antibacterial activity of polymer composites were already done in this study [6]. The **Fig. 1** shows SEM images of original polyethylene (**Fig. 1a**) and PE after thermal (**Fig. 1b**) and chemical (**Fig. 1c**) treatment.

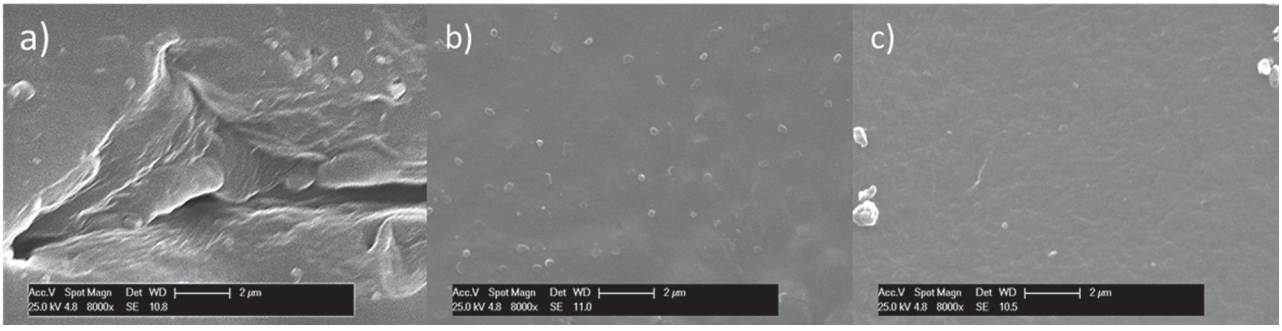

Fig. 1 SEM micrographs of a) pure polyethylene, b) PE1 and c) PE2

Original polymer exhibits rough surface with deep cracks, which may be caused during the preparation of PE plates in pressing machine. After thermal treatment (**Fig. 1b**) the surface of PE1 shows smoother surface without deep cracks and very rough surface. On the other hand, small object are visible on entire surface. These small objects should be bubbles caused by initial boiling of PE at 150°C or powdered gold from covering of samples before SEM measurement. The PE treats by boiling in hexane has also smoother surface than original polyethylene, but on the surface are visible slightly wrinkles, this might be cause by unequal dissolution of PE in hexane. Small white objects on surface are gold particles from covering of sample by gold.

On the next SEM micrographs series is polyethylene with organo-vermiculite filler before treatment (**Fig. 2a**) and PE/VerCA after heat (**Fig. 2b**) and chemical treatment (**Fig. 2c**). The original PE/VerCA (**Fig. 2a**) exhibits rough surface, but on the surface are not visible deep cracks. This should be due to presence of organo-vermiculite in PE matrix, which improves mechanical properties of polyethylene [12]. The surface of PE/VerCA after thermal treatment is smoother and does not exhibits small object, which should be also due to better mechanical and thermal stability of polymer/organo-vermiculite composite. The surface is more compact. After boiling in hexane the PE/VerCA2 surface is also smoother than starting PE/VerCA, but the surface is coarser than in the case of thermally treated PE/VerCA1. This might be caused by unequal dissolution of polyethylene in hexane. Small holes are occurred probably due to removal of VerCA particles from polyethylene matrix.

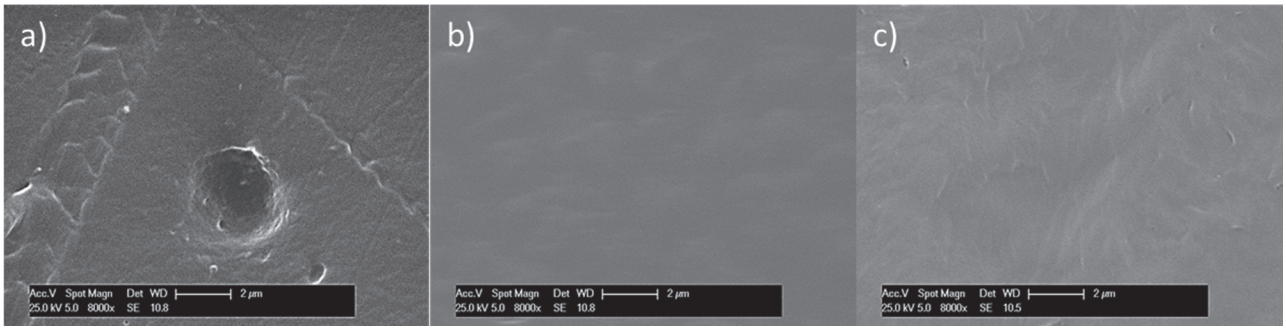

Fig. 2 SEM micrographs of pure a) PE/VerCA, b) PE/VerCA1 and c) PE/VerCA2

3.2. Atomic force microscopy

For more detailed surface study of PE and PE/VerCA at atomic level, AFM was used. **Fig. 3** shows AFM 2D and 3D images of PE before modification. PE1 after heating process and PE2 after hexane modification is on **Fig. 4** and **Fig. 5**, respectively. The surface of original PE exhibits deep valleys and sharp edges and protuberances of micrometric level. The rough morphology of surface is affected by pressing during plate preparation.

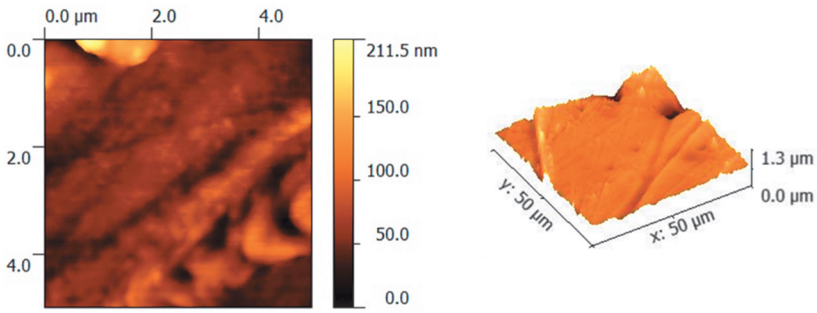

Fig. 3 AFM 2D and 3D images of pure polyethylene

PE after both surface modification processes shows very different surface (PE1 **Fig. 2** and PE2 **Fig. 3**). The heat treatment makes surface without sharp edges and protuberances. The surface also has more smooth

places (**Fig. 2** 2D image), which is determined by dark colour in the colour range. On the other hand there still are several high places (profile 0.23 μm), but this value does not reach the value of original PE (profile 1.3 μm).

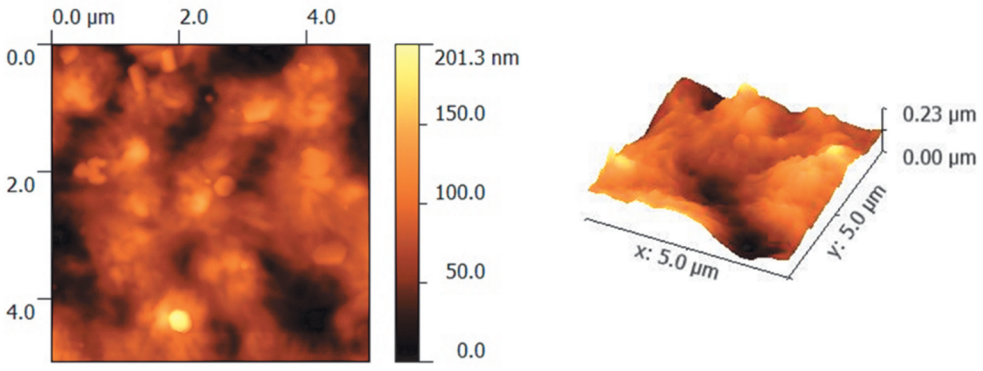

Fig. 4 AFM 2D and 3D images of PE1

In the case of hexane treatment (PE2 **Fig. 5**) the PE2 shows very rough surface with bubble-like structure. This structure should be caused by unequal dissolution of polyethylene in hexane. On the other hand, also this surface has more smooth surface profile (0.21 μm) than pure PE (1.3 μm). This structure should be suitable for biocompatibility of polyethylene implant.

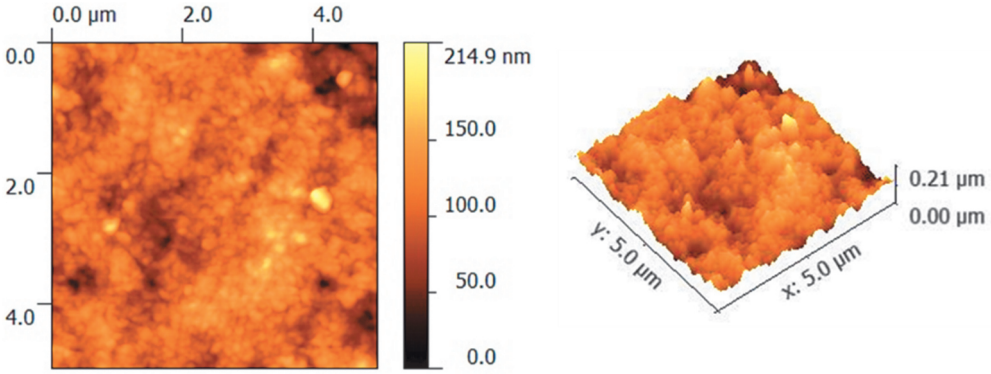

Fig. 5 AFM 2D and 3D images of PE2

The surface of original polyethylene with VerCA filler has smoother surface (**Fig. 6**) than original pure polyethylene, which could be affected by improving the mechanical properties of polymer nanocomposite by organo-vermiculite filler. Thus the preparation route of polymer plate creates the surface profile only 87 nm. The better thermal stability can leads to more stable surface against external mechanical forces during preparation of plates (pressing).

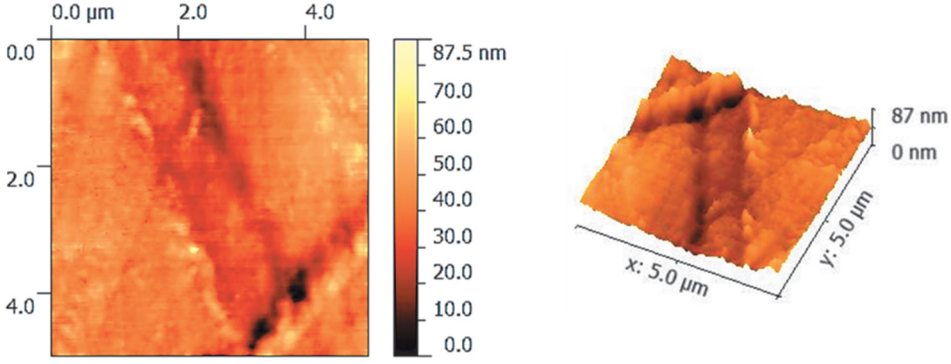

Fig. 6 AFM 2D and 3D images of PE/VerCA

The polyethylene with VerCA after heat treatment (PE/VerCA1 **Fig. 7**) exhibits surface without large amount of sharp edges and protuberances. Unfortunately, the PE/VerCA1 surface has profile in micrometric range (0.15 μm). This should be caused by bubbles because of the close boiling point of polyethylene during thermal smoothening process.

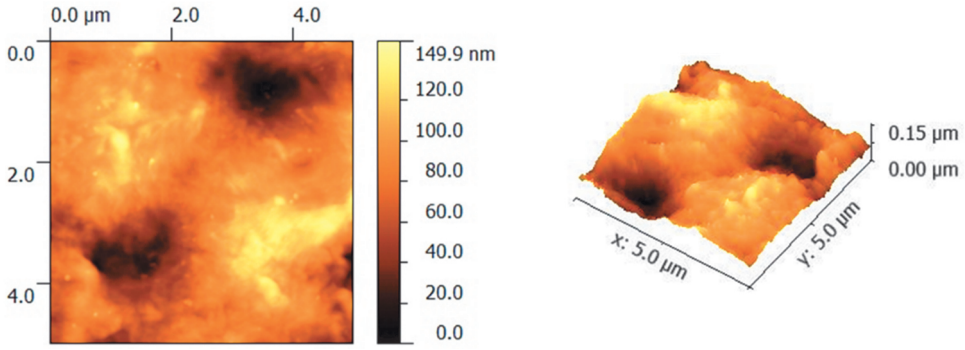

Fig. 7 AFM 2D and 3D images of PE/VerCA1

The last image shows the PE/VerCA after chemical treatment (**Fig. 8**). The PE/VerCA2 sample exhibits surface with blunt protrusions. The surface profile of the PE/VerCA2 sample is 0.35 μm which can be caused by unequal dissolution of the polyethylene in hexane. Dissolution of hexane for this sample gives better surface profile then boiling process for PE2.

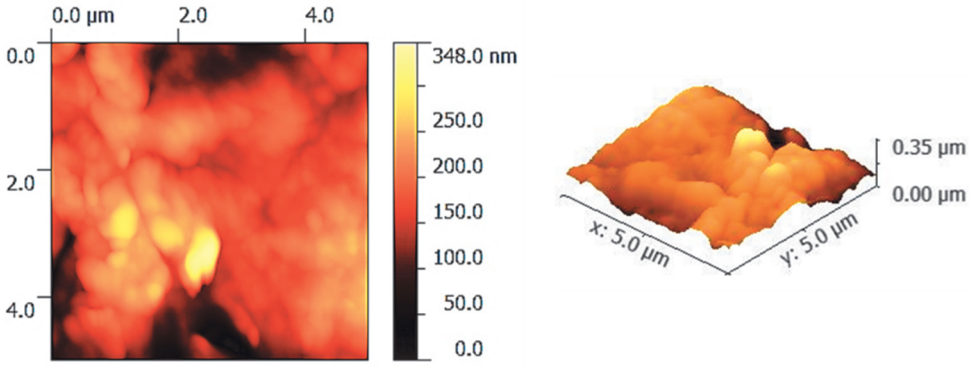

Fig. 8 AFM 2D and 3D images of PE/VerCA2

4. CONCLUSION

The polyethylene and polyethylene/organo-vermiculite surface were smoothened by thermal and chemical treatment. After both surface treatments the samples do not contain deep depression. The results show surfaces with profiles in the submicron range. The SEM micrographs show improving of surface smooth at micrometric level after both smoothening processes, no cracks were identified and surface seems to be smooth. The AFM study shows samples surfaces at nearly atomic level, where were evident remove of sharp defects. When the smoothening processes were compared, we can state that different approach will suit different sample material. For pure PE heat treatment is better, but for PE/VerCA composite chemical treatment is better.

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