

SUPERCRITICAL CARBON DIOXIDE IN ELABORATION OF NANOPOROUS MATERIAL FOR MEDICAL TRIBOLOGY

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INTRODUCTION.

Numerous attempts of supercritical carbon dioxide calling for application in polymer technology [1, 2], including for modification of UHMWPE articles surface and impregnation them with nanodispersed metals are known [4, 5]. Many articles devoted to modification problems, for example, to some polymers purification from free monomers admixtures are appeared. But unfortunately too little polymer technologies have been introduced into the industry.

In this work another way of polymer systems on the base of UHMWPE modification as compared with traditional one is investigated. On a base of results received previously the new method of the polymer complex modification has been suggested at the first stage of which the UHMWPE was treated with SC CO₂ in a form of initial powder but not in block where considerable results have not been achieved. The method is founded on a structure of the UHMWPE powder which consists of porous granules with thin walls easily permeable for SC CO₂.

MATERIALS AND METHODS

A treatment was carried out in the stainless-steel reactor of cylinder form at 60-100°C and 20-50 MP CO₂ for 4-8 hours. The UHMWPE GUR 10-50 and GUR 4120 were used. CO₂ has purity 99,997 vol. %.

RESULTS

This direction started in our Institute gave the interesting results. The articles pressed from GUR- 4120 previously treated with SC CO₂ have shown the better tribotechnical characteristics as compared with untreated ones at unchanged physics-mechanical properties. GUR- 4120 articles modified with SC CO₂ treatment as seen from Fig.1 have two times lower friction coefficient and lower temperature in friction contact zone that provide more stable tribotechnical characteristics at increased sliding rate

Evidently that SC CO₂ treatment promotes to friction contact temperature decrease, in other words to substantial increase of the material lubricating properties.

Polymers modification is usually related with a swelling of articles in block in SC CO₂.

At that considerable equilibrium swelling degrees as 25 – 30 % have been achieved for amorphous polymers. High crystalline and partly crystalline polymers such as cellulose, LDPE, PTFE, PVA, Chitosan and others swell very weakly (1-3 %).

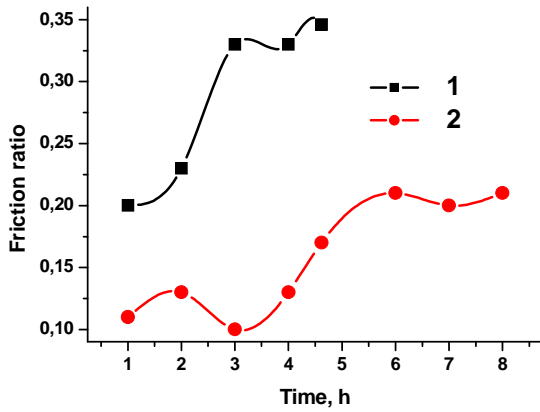


Figure 1: The dependence of friction coefficient value on abrasion time: (1) - initial sample, (2) – GUR- 4120 sample treated with SC CO₂.

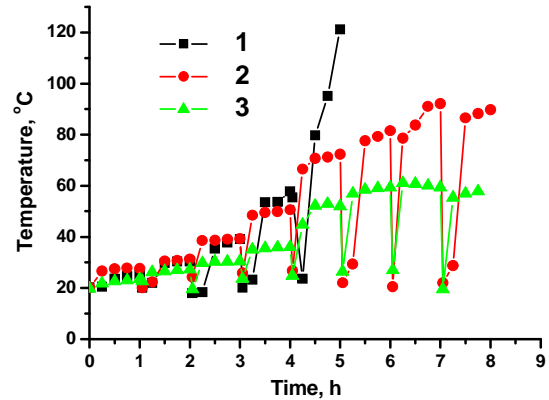


Figure 2: Contact temperature changing at increase of sliding rate: for initial sample (1), once time treated (2), repeatedly treated with SC CO₂ (3) ($P = 0.5$ MPa, sliding rate: 1 h - 0.13 m/s, 2 h - 0.25 m/s, 3 h – 0.42 m/s, 4-6 hs - 0.46 m/s).

However the articles dedicated to CO₂ desorption fullness investigation from polymers with different chemical structure and morphology are practically absent up to now.

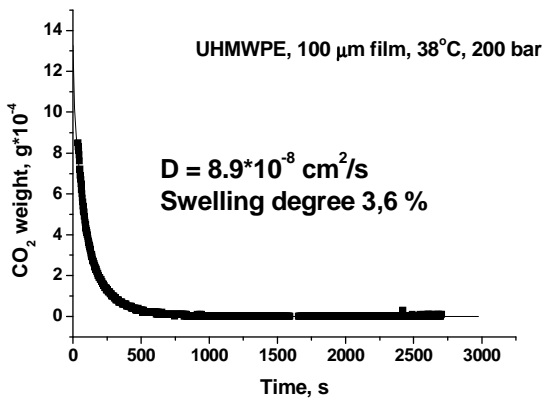


Figure 3: Gravimetric curve of CO₂ desorption from pressed thin disc with thickness of 100 μm after exposition at 38°C and 20 MPa for 6 hours (authors data). Electronic balance "OHAUS AP250D" up to within 10⁻⁵ g.

its antifriction properties remained misunderstood.

We have undertaken an investigation of structure of SC CO₂ treated UHMWPE and its surface layer chemical composition.

A presence of minor quantities of CO₂ was found in PMMA at an investigation of amorphous polymers properties in a two months after exposition in SC CO₂[5].

A SC CO₂ treatment of crystalline UHMWPE has also considerably influenced on its properties in spite of low value swelling degree.

Gravimetric technique of swelling degree and diffusion coefficients determination supposed by Berence else in 1982 year and used up to now is founded on recording of mass loss curve at fluid desorption.

It is seen that diffusion coefficient and equilibrium welling degree are very small and full desorption time is approximately 10-15 minutes.

So, the nature of SC CO₂ influence on UHMWPE giving rise to improvement of

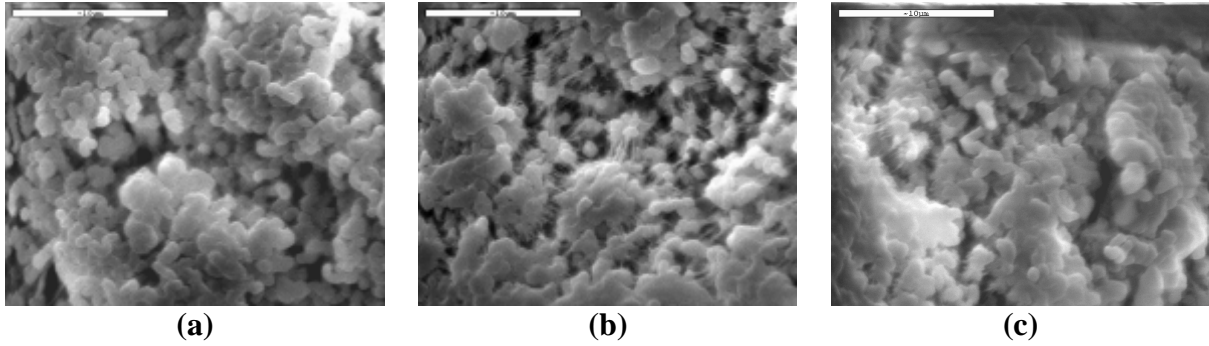


Figure 4: GUR- 4120 powder SEM microphotographs after SC CO₂ treatment (65°C, 40 MPa): (a) – initial sample, (b) – once time treated, (c) –repeatedly treated

Obviously the morphology is changed as a result of plasticization and decompression and surface area increases. A break of earlier formed tension bars is observed at repeated treatment

The structure of treated powder was studied by SAXS technique.

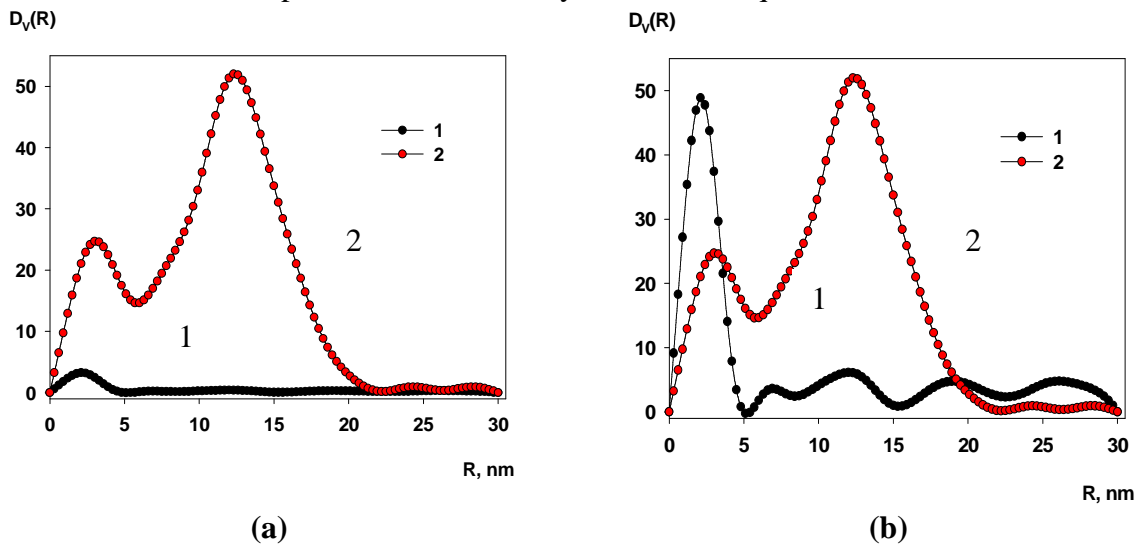


Figure 5: (a) A distribution by size (on spheres volume parts) of dispersive heterogeneities(pores) in initial matrix (1)(normalized on intensity for identification of curves maximums shifts) and in the matrix after CO₂ treatment (2).

(b) A distribution by size (on spheres volume parts) of dispersive heterogeneities(pores) in initial matrix (1) (irregular on intensity for identification of amplitudes difference) and in the matrix after CO₂ treatment (2).

An increase of contrast degree is noticed that is related with a growth of dispersive structures density gradient. A pore radius apparently increases and due this growth the material between these pores being more dense. Contrast between them increases and scattering amplitude accordingly rises.

An analysis of surface layer atom composition (~ 5 nm thickness) GUR–4120 in block after its powder exposition in SC CO₂ and following compressive pressing at 190°C was carried out by X-rays photoelectron spectroscopy (XPS) technique.

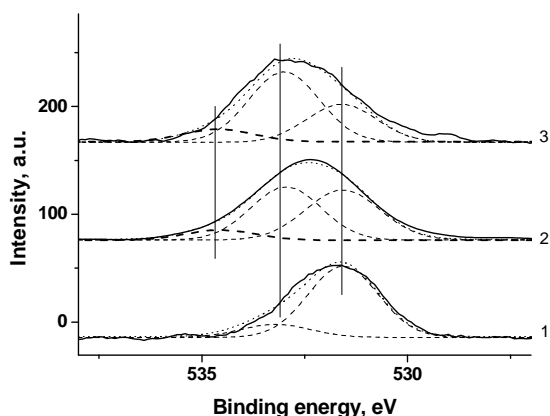


Figure 6: XPS spectra O1s of UHMWPE samples pressed from initial polymer powder (1) and after once (2) and repeated (3) treatment with SC CO₂.

which in part is bound with aromatic carbon atom (technological admixture). The state with larger binding energy (533.0 eV) is determined by binding with aliphatic carbon atom and may be identified as C–O–C and/or O–C–O, where C – aliphatic carbon (result of surface oxidation).

It was found the third oxygen state with energy 534.6 eV after SC CO₂ treatment parallel with two states typical for initial powder. It is necessary to note that parallel with high-energy state appearance the quantity of foregoing oxidized fragments (C–O–C and/or O–C–O) increases. The experiment on four- repeated treatment of UHMWPE with SC CO₂ (sample 3) was carried out for elucidation of oxide high-energy state nature which gave rise to noticeable transformation of the spectrum O1s and some growth of high-energy state.

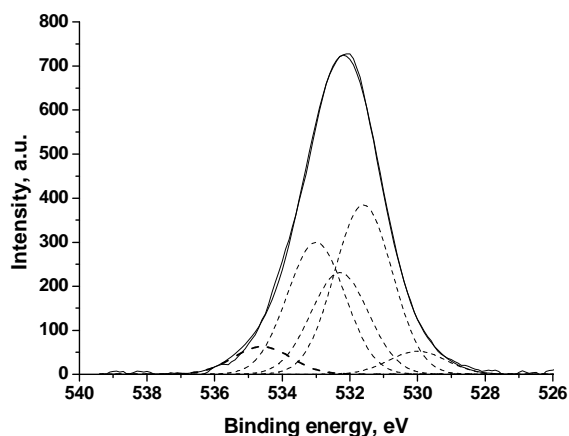


Figure 7: Spectrum O1s of the sample from polymer powder treated with SC CO₂ and pressed after abrasion on stainless steel counter-body at the conditions: $P_{sp} = 0.5$ MPa and $v \sim 0.8$ m/s for 3 hours.

in air for two months for elucidation of an influence of exposition duration in air after SC CO₂ treatment on a presence of residual CO₂ was carried out. XPS analysis data have shown at relative CO₂ concentration in both case approximately equal. This phenomenon may be

The method is unique for study of material surface properties because provides us information as about chemical structure of elements so about their concentration. The analysis of elements chemical state in CO₂ – UHMWPE system was carried out on a base of C1s and O1s spectra compare for initial sample and after different treatments in SC CO₂.

It is seen that binding energy increases with simultaneous peak widening after SC CO₂ treatment. This phenomenon may be interpret as change of different states part. Only two states are marked out in spectrum of sample 1: with lesser binding energy (531.6 eV), which may be attribute to an oxide atom combined with Ca and carbon

which in part is bound with aromatic carbon atom (technological admixture). The state with larger binding energy (533.0 eV) is determined by binding with aliphatic carbon atom and may be identified as C–O–C and/or O–C–O, where C – aliphatic carbon (result of surface oxidation).

Based on binding energy of high-energy state in the oxide spectrum (534.6 eV) and binding energy of OC(O)O state in polymers [6] (maximum value is 534.02 eV) the high-energy state may be attributed to CO₂ keeping in UHMWPE in spite of long samples residence time in superhigh vacuum ($\sim 10^{-9}$ Torr) at preparation and conducting of XPS analysis. Derived binding energy 534.6 eV is in a good correspondence with the value of 534.5 eV calculated from [7] data for gaseous CO₂ by recalibration from vacuum level to Fermi one with use of suitable bindings energy of C 1s, O1s and Ar 2p_{3/2} levels [8,9].

An analysis of two samples at once after SC CO₂ treatment and after their exposition in air for two months for elucidation of an influence of exposition duration in air after SC CO₂ treatment on a presence of residual CO₂ was carried out. XPS analysis data have shown at relative CO₂ concentration in both case approximately equal. This phenomenon may be

caused effective formation of nanopores with just thick walls preventing to diffusion of CO₂ outside.

It was interesting to determine a character of chemical state change of modified with SC CO₂ surface after active mechanical impact at friction conditions. In this case it was observed at the UHMWPE surface an oxide concentration increase up to ~ 9%.

Two additive states were found in the spectrum at that the high-energy state corresponding to CO₂ was retained (Fig. 7). An appearance of gaseous CO₂ in UHMWPE surface layers after its exposition in SC CO₂ and a little change of its concentration in the conditions of active reformation during abrasion may be caused by encapsulation CO₂ in nanopores arising at a treatment of UHMWPE with SC CO₂ and following decompression.

CONCLUSIONS:

It was shown for the first time that the carbon dioxide retains for indefinite long duration in closed nanopores of the polymer surface layer after exposition of crystalline UHMWPE in SC CO₂ and following decompression and can place a role of original tribochemical lubricant.

The effect has important meaning because CO₂ microquantities in friction contact zone are available to preserve mated bodies especially polymers from active tribochemical oxidation and therefore to improve their lubricating properties that our results of SC CO₂ influence on contact temperature and friction coefficients at UHMWPE tribological tests illustrate.

PATENTS AND AWARDS:

1. Patent RU № 2300537 C1. "Method of production of polymer articles of sliding friction for artificial implants".
2. Grant of patent decision. 3.09.2008 on Application 2007147988/04(052590) from 25.12.2007. "Polymer antifriction composition for biomedical purposes"
3. Grant of patent decision on Application 2007141757/04(045716) from 28.10.2008. "Method of production of polymer articles of sliding friction for artificial implants".
4. Gold medal on Int. Exhibition "Ideas-Inventions New Products-2008". Oct.30 - Nov. 02, 2008. Elaboration "Reinforced nanopolymer system for combined implants". Germany, Nurnberg "IENA-2008".

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