TREATMENT OF FLUOROPOLYMERS IN SUPERCRITICAL CARBON DIOXIDE

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INTRODUCTION

Last years efforts of developers in all countries are guided on making competitive multipurpose materials. One of interesting directions in this field is ultrahydrofobization of different materials. Now special attention is payed to ultrafine polytetrafluoroethylene (UPTFE) as ultrahydrophobization agent. In articles [1,2] basic possibility of thin ultrahydrophobic films deposition from UPTFE solution in supercritical carbon dioxide (SC CO_2) on a surface of various materials has been shown. In this work UPTFE solubility and solution stability at different supercritical conditions were investigated.

One of the potentially perspective materials for medicine purposes are fibrous fluorinated felt. In this work fibroporous fluorine-polymeric materials of medical designation were studied for the purposes of creating of novel biocompatible antimicrobial materials. PTFE fibres were modificated with noble metal nanoparticles and biomedical compounds directly by supercritical carbon dioxide impregnation and following reduction in hydrogen media.

MATERIALS AND METHODS

Materials:

Ultradisperse polytetrafluoroethylene (UPTFE)of "Forum" trade mark (Institute of chemistry of Far East branch of the Russian Academy of Sciences, obtained by thermal gasodynamical PTFE destruction and consisting of oligo- and polymeric linear perfluorinated chains [-CF_2-] intermixture.

PTFE fibres were obtained in Institute of metallopolymer systems mechanics of Belarus Academy of Sciences by treatment of unit type polytetrafluoroethylene F-4 or F-4MB by the emission of CO_2-laser with a wavelength of 10.6 micrometer for the generation of fibrous fluorinepolymers.

Carbon dioxide (CO_2) 99,995 % MGPZ.

Ketoprofen (> 98 %) productions Sigma-Aldrich,

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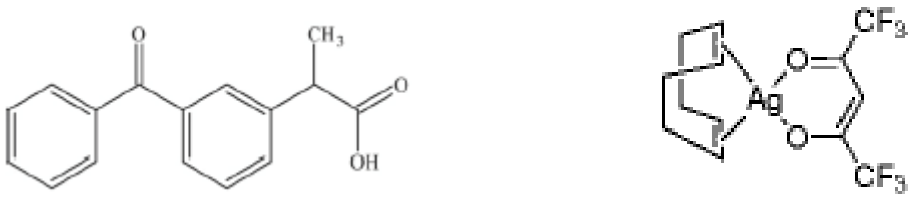
Ag compound 1,5 cyclooctadiene hexafluoroacetylacetonate (AgCOD[hfacac]) 99 %, Sigma-Aldrich.



(a) **(b)**

Fig. 1. *Chemical structure of ketoprofen (a) and argentiferous compound (b)*

Methods:

Impregnation technique and pilot unit is described in previous works [1,2]. Ketoprofen or Ag-complex were loaded into stainless steel reactor together with teflon agitator for dissolution process acceleration. PTFE fibrous material was placed on stainless steel substrate at 3-5 cm above teflon agitator. Reactor were vented with gaseous CO2 for removal of oxygen residues, sealed and placed into thermostat. On reaching of necessary temperature supercritical CO2 were submitted toreactor. Impregnation parameters - 85^{o}C, 15 MPa, 4 h. Then abrupt pressure release were carried out for removal of not-impregnated substances.

In case of AgCOD[hfacac] complex reduction were carried out in H_2 atmosphere at 65^{o}C within 6 h. Obtained composite venting were performed in vacuum oven at 80^{o}C within 3 h for removal of ligand residues.

Physical mixtures of ketoprofen and PTFE fibres were prepared by crushing and grinding in mortar.

RESULTS

Ketoprofen-PTFE fibres composites have been analyzed by IR-spectroscopy for investigation of ketoprofen physical condition incomposite (Fig. 2).

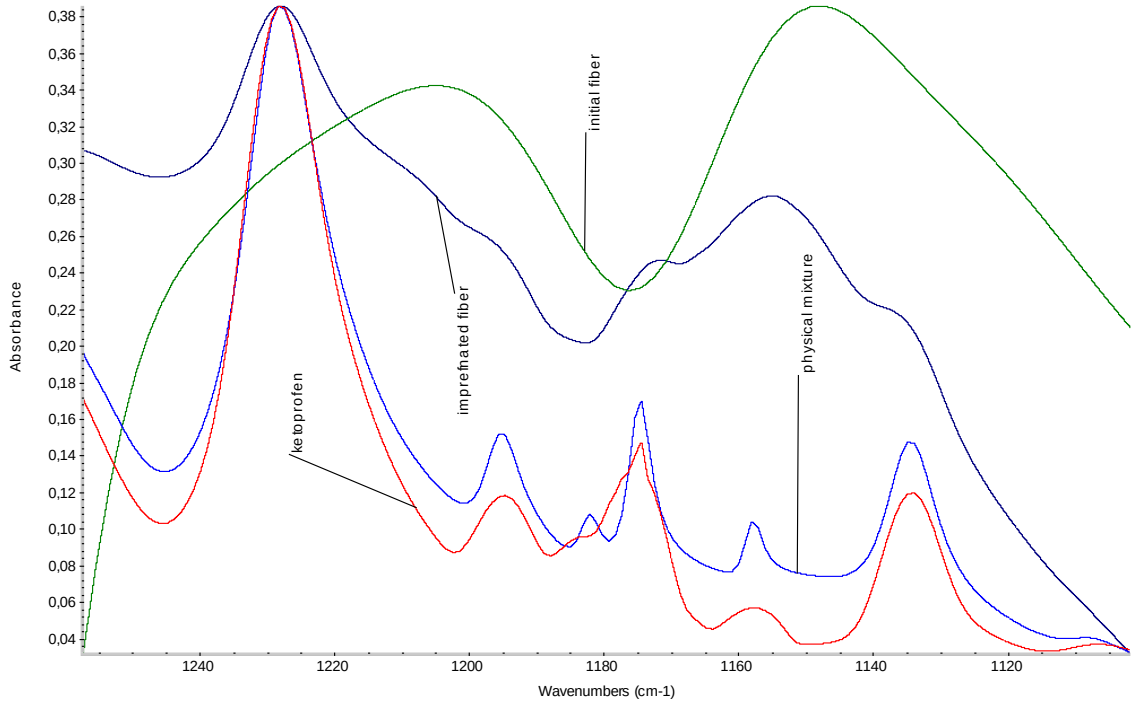
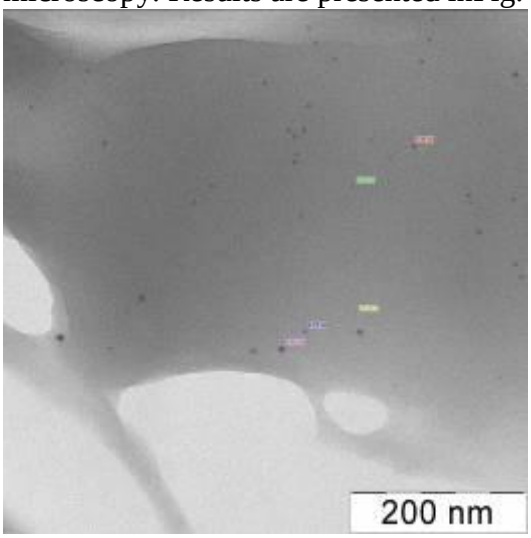


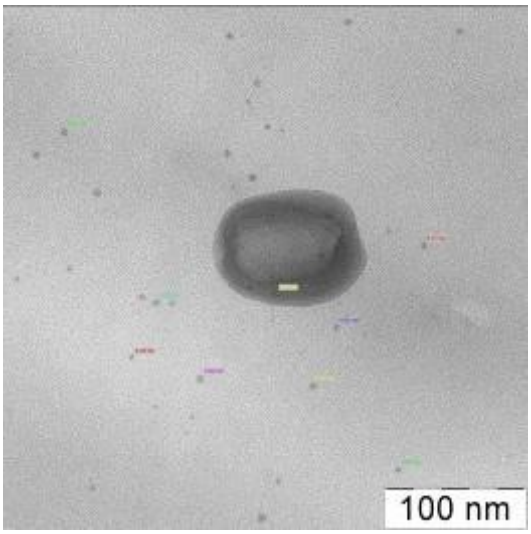
Fig. 2. *IR-spectrum of initial PTFE fibres impregnated with ketoprofen, initial ketoprofen andphysical mixture of initial ketoprofen and initial PTFE.*

In spectral range of 1150-1200 cm^{-1} significant reduction of 1195 cm^{-1} peak intensity was noted forfluorine fibre impregnated with ketoprofen. At the same time in case of fluorine fibres and ketoprofen physical mixture peak does not undergo any changes concerning initial ketoprofen that allows to drawconclusion on ketoprofen structural change in impregnated PTFE.

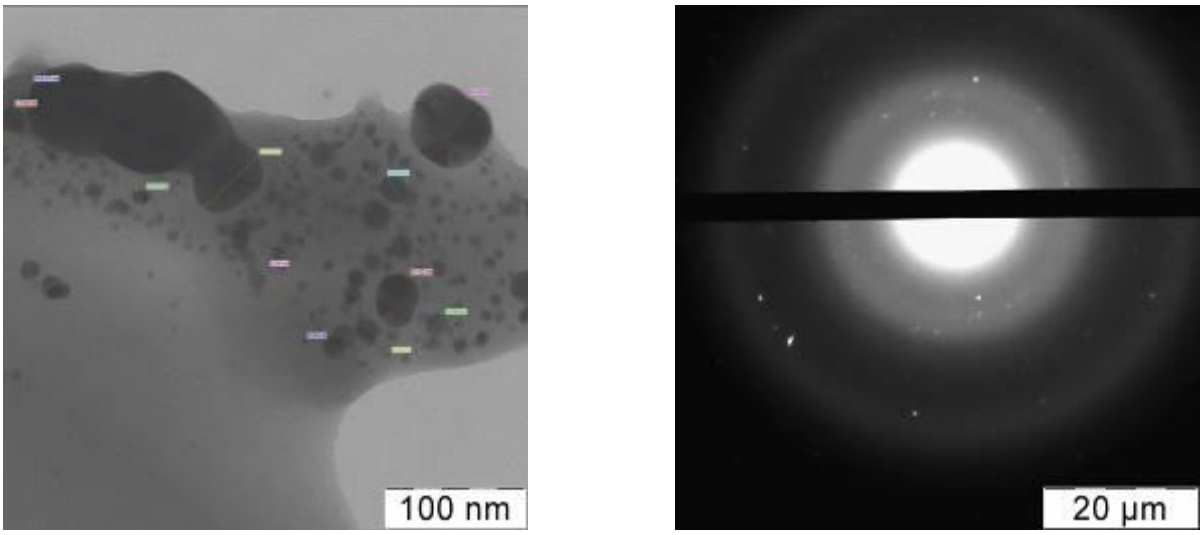
In case of impregnated fibres it was observed ketoprofen 1157 cm^{-1} band shift of 5 cm^{-1}. On this basis it is possible to conclude occurrence ofweak chemical bonding between PTFE and ketoprofen molecules which is not marked in case of ketoprofen-PTFE physical mixture.

Samples of PTFE of fibres impregnated with silver nanoparticles were investigated by TEM microscopy. Results are presented inFig. 3





(a) **(b)**



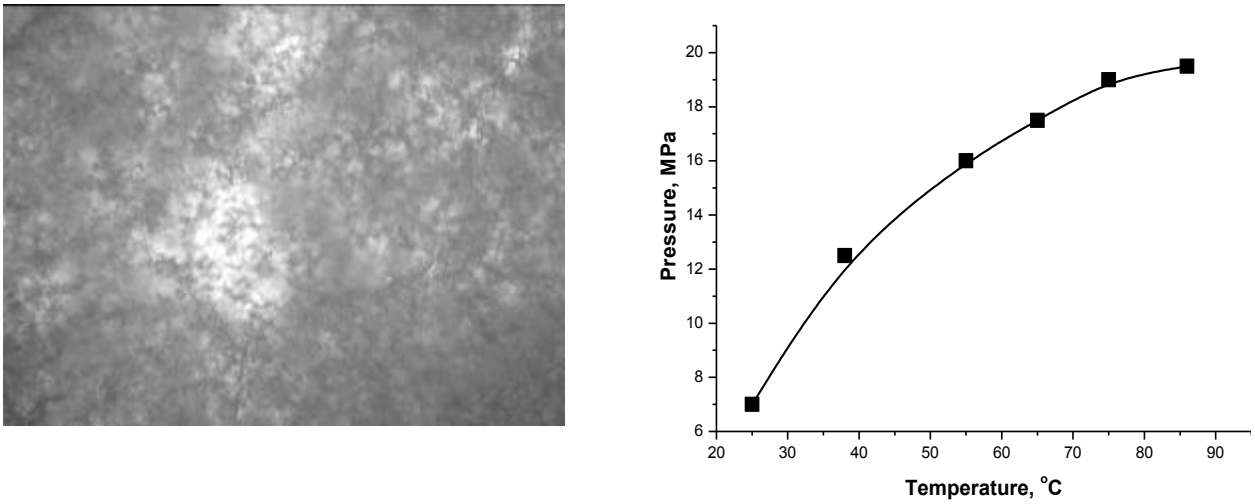
(c) **(d)**

Fig. 3. *TEM-microphoto of silver nanoparticles in matrix PTFE (a-c) and diffraction picture (d)*

Consequently silver nanoparticles with 3-10 nm mean diameter with relatively homogeneous distribution in sample were observed. It is necessary to note presence of certain particles with 50-100 nm in diameter and their aggregates.

From the analysis diffraction picture it is possible to drawconclusion on single-crystal structure of obtained nanoparticles with no significant correlation with its sizes.

Forum solubility has been explored by cloud-point method in coordinates temperature against pressure and effects are given on fig. 4.

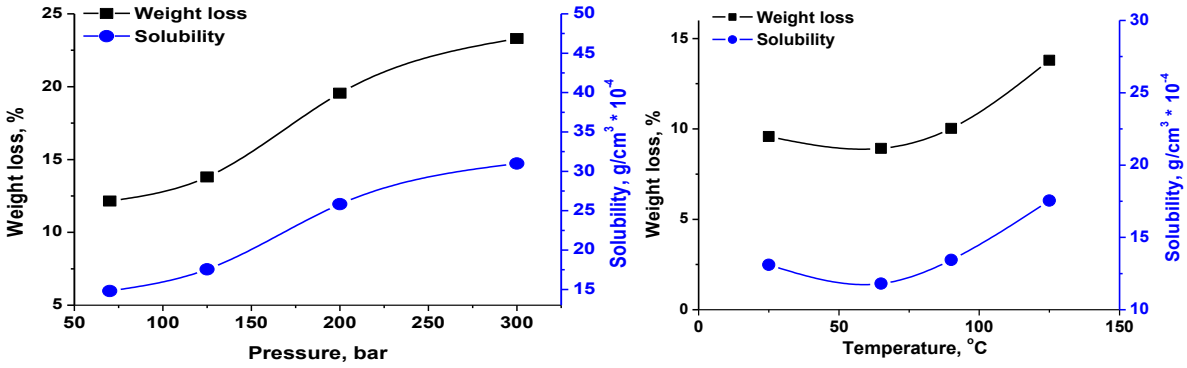


(a) **(b)**

Fig. 4. *Forum in SC CO_2 solution microphoto (a) and phase diagram (b).*

Cloud-point spectrum or the phase diagramme (fig. 4) confirms the true solubibility (i.e.

formation of molecular solution) because phase state of substance in solution (gomo- or heterogeneous system) in isothermal conditions depends on pressure whereas pressure does not affects in case of colloid solution. Due to symbasis temperature-pressure dependence Forum is characterised by low critical temperature solubility (LCST-curve).
On fig. 5a and 5b effects of weight loss measurments and Forum solubility are presented at various temperatures and constant pressure and at various pressures at constant temperature.



(a) **(b)**

Fig. 5. *Forum in SC CO_2 weight loss and solubility dependencies upon pressure at 125°C (a) and temperature at 13 MPa(b).*

From drawings 5a and 5b it can be concluded that isothermal solubility dependence upon pressure growth and tends to reach plateau above 20 MPa while isobaric solubility dependence upon temperature does not find out such tendency up to 125°C. It may be concluded that pressure acts more important part than temperature in given range of pressure and temperature
Weight loss dependence upon Forum amount in reactor has shown that soluble fraction percentage increases with Forum amount decrease and solubility remains approximately the same. It means that constant quantity of low-molecular fraction determined by equilibrium at given pressure and temperature is soluble.

CONCLUSION

PTFE fibres impregnation with ketoprofen using supercritical carbon dioxide fluid were made. Comparison of the obtained composites withphysical mixture of initial components testify to formation of weak chemical bonding between ketoprofen and PTFE fibres.
PTFE fibres impregnation with silver nanoparticles using supercritical carbon dioxide fluid were made. Silver nanoparticles with narrow size distribution were obtained. TEM microscopy data testify uniform nanoparticles dispersing in PTFE matrix.
For the first time it were observed that Forum phase diagram is characterised by low critical temperature solubility and constant low-molecular fraction amount is soluble under given conditions.

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