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Functional properties of poly(tetrafluoroethylene) (PTFE) gasket working in nuclear reactor conditions

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ABSTRACT

In this study structural and nanomechanical properties of polytetrafluoroethylene (PTFE) used as a gasket in the nuclear reactor have been deeply investigated. In order to reveal structural changes caused by long-term pressure, temperature and irradiation (possibly neutron and gamma), methods such as SEM, X-ray diffraction and Raman Spectroscopy have been used. Nanomechanical properties such as Young Modulus and hardness were investigated by means of the nanoindentation technique. Presented study confirmed the influence of working (radiative) environment on the functional properties of PTFE. The results of Raman spectroscopy and X-ray diffraction techniques revealed shift of the major band positions and band intensities increase. Moreover, changes of hardness and Young Modulus values of the irradiated material with respect to the virgin specimen have been recorded. This phenomenon can be attributed to the modifications in crystallinity of the material. Presented work suggest that morphology of the irradiated material altered from well-ordered parallel fibers to more dense and thicker ones.

1. Introduction

Polytetrafluoroethylene (PTFE), also known as Teflon, is a commonly used material in a spacecraft design, automotive and semiconductor industry. Reported applications are associated to the fact that PTFE has excellent chemical inertness, high thermal stability and low frictional coefficient [1,2]. Therefore, it is broadly used in a range of industrial sectors where severe conditions as radiation, high temperature or lack of protection atmosphere occurs [3]. Materials subjected to aforementioned conditions are of great importance when it comes to safety assurance in nuclear facilities. Therefore, a special attention on material stability assessment and monitoring of its property changes by all regulators in all countries possessing nuclear technology (Nuclear Regulatory Commission) is put.

Studied material has been used as a gasket in a nuclear reactor for several years. The seal has been located 3.3 m under the water and was exposed to temperature fluctuations from around 20 °C–50 °C and periodic radiation (largely gamma). Moreover, hydrostatic pressure and biaxial stresses has been exerted on the material. Such aggressive conditions may lead to significant functional properties changes. The safety procedures which are in force at NCBJ are of great importance and concern the assessment of materials properties with respect to the impact of long term working conditions. The procedure for this type of material recommends its periodic replacement. For this reason, a comprehensive analysis of the Teflon gasket in its original state “witness specimen” and sample submitted to the working conditions of the installation have been performed. In case of polymers, it is commonly known that irradiation causes main-chain scission which leads to degradation of physical properties [18]. Created radiation defects, affect mechanical properties of PTFE mainly by fragmentation of the polymer chain [1,2,5,6,20]. Thus, it is crucial to perform a comprehensive study of the material in order to avoid the undesirable effects like breakage or stratification.

In general, organic insulating materials unlike inorganic ones are more vulnerable to radiation damage. According to the NASA report [4] and Lunkwitz et *al.* [5] studies, radiation effects emerging on Teflon are highly apparent. Teflon is known to have rather high susceptibility to radiation damage which can be seen by

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degradation of physical properties. This phenomenon is mainly caused by chain scission of PTFE and usually can be seen when irradiation at room temperature in air or vacuum occurs. Reported phenomena has been deeply investigated by many researchers [3,17,18]. It has been proved that during irradiation, PTFE yields defluorination which further leads to formation of macromolecular free radicals [3]. The free radicals are blocked by several reactions which results in formation of trifluoromethyl and double bonds. Moreover, importance of the environment (air, vacuum) in which the irradiation takes place cannot be dismissed. It has been reported that irradiation of PTFE in air leads to degradation of polymer chains by insertion of oxygen and initiation of the carbonyl groups [5]. Studies of structural changes in PTFE during irradiation in oxygen performed by Liu et *al.* [3] revealed creation of new groups: COF, COOH and CF_3. Despite quiet significant amount of literature data [3,5], some phenomena remain unclear. Specially, materials working at true working conditions are poorly investigated. For this reason, in this paper the influence of true working conditions of MARIA research reactor (radiation, water environment, temperature & pressure changes) on PTFE specimens were investigated with respect to structural and mechanical properties changes.

2. Experimental section

2.1. Structural analysis

Structural properties of PTFE specimens were analyzed by means of X-Ray diffraction technique. Measurements were performed by using the Empyrean (Panalytical) diffractometer with an X-ray tube with Cu anode and the focusing mirror. The measurement was performed from 10 to 80 of the 2theta angle with constant omega angle 1. The measurement step was 0.02° with measurement time of 2.4 s per step. Phase analysis was carried out using a PDF-4+2011 database. Signal analysis was performed semi-automatically by using HighScore Plus (Panalytical) code. Raman spectroscopy analysis was performed by using Jobin-Yvon T6400 Raman spectrometer equipped with 514.5 nm Ar^+ laser beam. Simple monochromatic mode in the frequency range of 100–1500 cm^{-1} has been used. Microstructure of the specimens were analyzed by means of a Scanning Electron Microscope (SEM) using Dual-Beam Auriga Zeiss microscope with energy dispersive spectroscopy (EDS) detector (Bruker). The investigated material has been covered by a several nanometers thick layer of gold in order to ensure electrical conductivity to reduce charging. Microstructure has been obtained using 2 keV secondary electrons.

2.2. Nanomechanical properties

In order to perform a full characterization of the material, complex investigation of its mechanical properties is essential. Mechanical tests at macro and micro scale such as tensile strength or hardness are considered as common and have been deeply studied until now [7,8,19,25]. However, investigation of nanomechanical properties of polymers by means of nanoindentation technique has been rarely studied until now. Nanomechanical properties of PTFE have been investigated by using NanoTest Vantage device provided by Micro Materials Laboratory. Berkovich shaped diamond indenter has been used for all nanomechanical measurements. Each experiment has been repeated at least 5 times. The indents were made by using load in the range from 0.25 to 2 mN which corresponds to over 1 μm depth. According to previous studies, it should be assumed that plastic zone developed under the indenter tip can be up to 10× bigger [21–23]. However, in our case one may assume that material changes have volume character, therefore, regardless of the depth nanomechanical response of the material should be the same (assuming no influence of the surface effects). Implementation of nanoindentation technique allowed to determine the mechanical properties such as hardness and Young Modulus [11] of the studied specimens. Nanoindentation technique is based on the Oliver and Pharr method [12,13] and allows one to measure local properties of small volumes from the load-displacement (L-D) curves [5]. A cross-section of the surface specimen geometry and nanoindentation load-displacement curve (L-D) are presented in Fig. 1A – B), respectively.

3. Results

3.1. Structural analysis

Morphology of unirradiated PTFE was studied for many years [9,14,15]. However, despite abundant amount of literature, some phenomena related to the structural changes of the material remain unclear. Therefore, focus on finding correlation between irradiation effect and structural changes of the Teflon is being made in this study. Some of performed investigations aim at explaining change of the PTFE structural properties when irradiation at temperature above its melting point (i.e. 327 °C) occurs [14]. Khatipov et *al.* [14] proved that morphology of PTFE irradiated at two temperatures below melting point 20 °C and 200 °C is almost similar to the virgin polymer. At temperature of 200 °C, visible increase of fibrillary like lamellae's were observed on the irradiated sample. In contrast, sample irradiated at temperature above its melting point demonstrated significant differences in their structure i.e. presence of spherulites with the size of about 50 μm. In this paper we present structure and morphology of the PTFE gasket exposed to working conditions (possibly gamma radiation) of a nuclear reactor. Studied sample were submitted to temperature fluctuations from 20 °C to 50 °C and periodic pressure changes.

It is a common practice to analyze the PTFE [$CF_2 - CF_2$] phase diagram system in order to understand the behavior of PTFE under pressure-temperature conditions. Moreover, understanding phase transitions phenomena over a wide range of temperatures is crucial to investigate mechanical and structural behavior of the material. Phase diagram of PTFE is shown in Fig. 2. Investigated polymer is characterized by helicoidal structure at temperature below 19 °C. The monomer unit becomes trigonal at temperatures between 20 and 327 °C and totally amorphous above 327 °C [16]. Based on the pressure-temperature phase diagram one can observe two crystalline transitions at 19 °C and 30 °C. Notably, molecular motion within the crystal below the melting point of 328 °C (341 °C in the molding powder) has been reported by Brown et *al.* [9]. The first order transition at 19 °C between phase II and IV is changing from well-ordered triclinic structure to partially ordered hexagonal

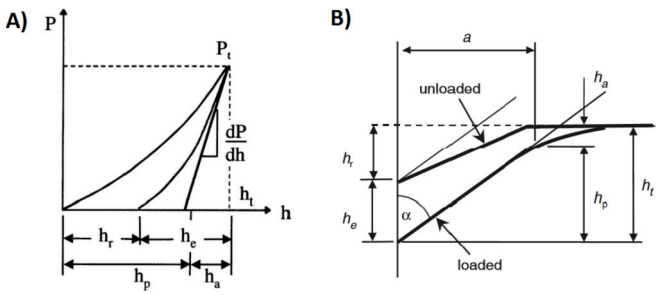

Fig. 1. A) Scheme of typical loading/unloading curves obtained during nanoindentation tests at maximum load P_t and depth h_t, B) A cross-section of the surface specimen geometry.