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by Wahyu Dwi Lestari

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Wear Scar Characterization of Polycarbonate Urethane (PCU) By Raman Spectroscopy

Wahyu Dwi Lestari*, Luluk Edahwati, Ndaru Adyono, Tria Puspa Sari, Wiliandi Saputro, Ahmad Khairul Faizin, Radissa Dzaky Issafira

Department of Mechanical Engineering, Faculty of Engineering, Universitas Pembangunan Nasional "Veteran" Jawa Timur, Surabaya 60294 Indonesia

*Corresponding author:
E-mail:
wahyu.dwi.tm@upnjatim.ac.id

ABSTRACT

Until now, the need for revision surgery and implant failure is still the main clinical problem in installing biomaterials in the human body. Mechanical testing is needed to determine the life of the biomaterial before it is implanted in the human body. Mechanical testing in this study was carried out using a pin on discs simulator, run for 50000 cycles in dry condition. PCU material is used as disc components and SS 316L as a pin. The following test parameters were used: normal load F_N = 500 gram and sliding velocity 50 Rpm in dry condition. Chemical changes in the wear scar can cause a drift in friction level. This study aims to analyze the chemical surface changes in wear tracks of PCU after mechanical testing. For this, Raman spectroscopy was used to determine the chemical changes at the surfaces. The wear tracks developing between the metal on PCU were analyzed using these techniques. The results show that the chemical changes in the wear scars of the PCU disc are due to mechanical stress. Raman spectroscopy is used to observe the chemical changes on the wear scar due to the sliding test.

Keywords: Raman spectroscopy, PCU, wear scar, pin on disc

Introduction

Since the advent of modern metal-polyethylene cemented hip arthroplasty in 1962 introduced by John Charnley, the materials used for joint replacements have been continuously improved to prolong the life of orthopedic implants (Hernández-Vaquero et al., 2008). The human body has an aggressive nature towards biomaterials (Ramakrishna et al., 2001) which may adversely affect the performance of the material (Hukins et al., 1999). Long-term implantable polymers are a very important type of biomaterial for use in various biomedical applications (Hukins et al., 1999). PCU material has recently been introduced by several researchers as an alternative material for UHMWPE as bearings in artificial hip joints. Although PCU is more biostable than polyether urethanes (PEU)(Christenso et al., 2004a; Tanzi et al., 1996), PCU from explanted orthopedic implants has been reported to be degraded in the human body due to oxidation (Cipriani et al., 2013; Neukamp et al., 2015).

In biomedical cases, joint implants that use various tribological combinations are classified as hard on soft implants. An important consequence of installing soft polyethylene with hard materials is the occurrence of surface wear that causes wear debris. Osteolysis caused by wear debris is ultimately the main cause of significantly reduced life for artificial implants (Harris, 1995). Despite the many uncertainties in observed implant damage, there is a strong correlation between wear rate, aseptic loosening due to wear debris, and in vivo time. The failure mechanism

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related to the in vivo performance of implanted devices and their biomaterials can be seen with the explanted devices (Benham & Pullukat, 1976). In addition to mechanical wear and damage characterization, changes in chemical structure due to the biological environment are also required in retrieval analysis studies. There are a variety of measurements for observing wear in hard and soft pairs of biomedical components. It is believed that Raman Spectroscopy can be used to control the quality of biomedical products on the market, resulting in a better in vivo performance. Raman spectroscopy is a very effective tool in characterizing biomaterials for artificial joints. This tool does not require sample preparation because the technique is non-intrusive. In addition, confocal microscopy can be used to analyze surface micro geometries (Winogrodzka et al., 2014). The ability of Raman Spectroscopy to detect phase changes in contact that occurs at pressure has been demonstrated by several researchers (Durand et al., 2012; Affatato et al., 2013; Puppulin et al., 2016; Okubo et al., 2020; Tone et al., 2020).

Friction and wear are affected by the structure of the two sliding surfaces, test variables, and the mechanical or chemical interactions of the components (Argenson & Parratte, 2006). In vitro wear test is necessary to determine the performance of biomaterials used for orthopedic components. The present research work in this paper focuses on the analysis of the wear track made by SS 316L on PCU under dry and lubricated conditions. For this purpose, Raman spectroscopy is used to observe the possibility of changes in crystallinity based on mechanical tests. As it is known that wear is preceded and followed by changes in the microstructure of the material. Edidin et al. (1999) in their research said that the development of damage layers induced by plasticity and debris was caused by continuous mechanical loading. The advantage of using Raman Spectroscopy is to observe the surface of the wear track. Furthermore, it can also be used in combination with tribological testing for in situ measurements. The wear track on the PCU and the metal material in contact will be analyzed in this study. Observations will be made on the outside and inside of the wear track.

Research Method

Materials and tribological testing

This research uses PCU material as a disc component and SS 316L as a pin component. PCU disc components are manufactured using compression molding with a diameter of 100 mm and a thickness of 4 mm. The components of the SS 316L pin are manufactured using a turning machine with a length of 65 mm and a diameter of 6 mm, with the tip forming a radius. Wear test in this study using a pin on disk simulator. Pin on disc tests was performed with SS 316L pin rubbing against PCU discs under dry condition. A rotating pin is pressed against a stationary disc which is fixed on a support. The pin on the disc machine used in this study is shown in Figure 1. The following test parameters were used: normal load F_N = 500 gram and sliding velocity 50 Rpm in dry condition. The experiments were carried out at room temperature for 20^{0}C – 25^{0}C. Humidity was not controlled. One experiment resulted in about 50.000 data points. The data were analyzed using Origin software Graphs were smoothed to emphasize the friction trend.

Figure 1. The pin on disc wear test

Raman spectroscopy

Raman spectroscopy is a non-destructive method suitable for observing the crystallinity of polyethylene because of its high spatial resolution. Microstructural modifications on a microscopic scale can be analyzed through this tool, where oxidation occurs by itself (Puppulin et al., 2016). The wear track on PCU discs after wear testing was analyzed by Raman Spectroscopy. Raman spectroscopy (alpha 300R, Xplora, Germany) was used to check for potential alterations in the molecular structure of the PCU polymer as a result of the wear process. The Raman setup employed a 2 x-Nd: YAG laser (532 nm, Pmax ¼ 22.5 mW). The laser spot at the sample was focused on a 100x objective (Nikon NA ¼ 0.90, 0.26 mm working distance). The spectra were recorded in the inner surface of the work area. The same number of spectra is also used for the possibility of morphological changes outside the wear region due to mechanical stress.

Result and Discussion

Pre-clinical testing is important for accurate wear observations to improve the function of biomaterials. In the previous section, it was said that several researchers had made observations on materials that have undergone tribological testing by Raman Spectroscopy. Raman spectroscopy is used to observe the possibility of changes in crystallinity of the material due to mechanical stress. Confocal Raman spectra were acquired to identify any molecular-scale structural modifications in the wear track generated by the wear experiments. The measurements were performed in two positions, on the inside and the outside the wear track. The peaks with various heights were observed in the wear track due to molecular vibrations, which are shown in Figure 2. The molecular vibration peaks inside and outside the track are quite the same so that there is no indication of a change in the molecular structure. The main difference between the spectra could be observed on the fluorescence background peak at 1500 cm^{-1}, which showed a strong peak for the measurement outside the wear scar and absent within the wear scar.

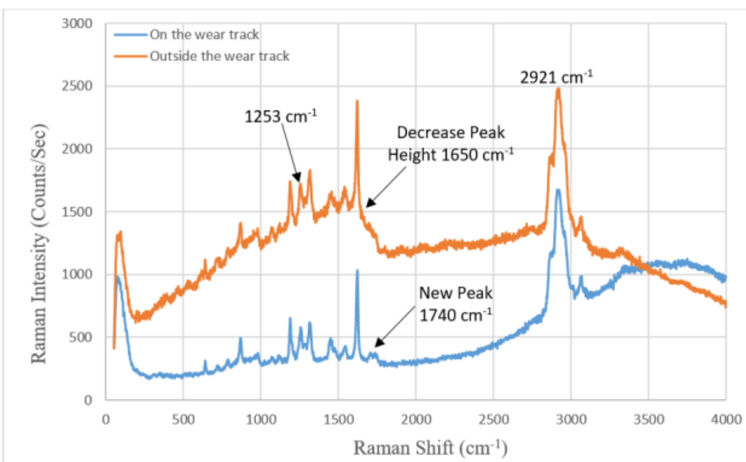

Figure 2. Raman spectrum outside and inside the wear track of the PCU disc at a sliding velocity of 50 Rpm

Further, friction and wear simulation of PCU discs using a pin on disc apparatus showed evidence of no significant physical damage on the outside wear track, while the new peak of 1740 cm^{-1} could be generated in the region (wear track) of sliding contact after 50.000 cycles. According to the literature (Christenson et al., 2004b; Shen et al., 2011), 1253 cm^{-1} is indicative of carbonate oxygen linkage, while 2921 cm^{-1} is indicative stretching $C\text{-}H_2$ of the soft segment. A decrease of the peak intensity of the band at 1600 cm^{-1} in the form of NH_2 free aromatic amine was associated with chemical changes in the hard segment. This change is an indication of chain cutting from the hard amide segment and results in free amine. Decrease peak of the 1174 cm^{-1} band was assigned crosslinking of the soft segment PCU occurring with the formation of a branched ether. A new peak of 1740 cm^{-1} was found on the wear track of the PCU disc. This may be a carbonaceous particle that is removed from the surface. These peaks indicate the non-bonded carbonate which is associated with chemical changes in the soft segments on the surface. Conversely, degradation is further developed by the loss of the peak height of the larger soft and hard segments. Interestingly, physical damage on the surface of the material over a long period of tribological testing may have resulted from critical chemical degradation. (Christenson *et al.*, 2004) reported that the PCU can undergo degradation in tribological property in vivo after being implanted for 15 months. It is proposed in terms of the present study, the disorder carbonate and hydrocarbon may take place on the surface due to the wear testing. However, further biomedical testing is required to allow the performance and compatibility of the PCU to be proven in vitro without putting patients at risk.

Conclusions

Raman spectroscopy was used to observe the scars on the PCU material produced based on mechanical testing using a pin on a disc machine. Through this measurement using Raman spectroscopy, it is known that there are chemical changes in the PCU wear track disc. Measurements were made on the inside and outside of the wear section, which showed chemical degradation during the wear testing process. Confocal Raman spectroscopy was successfully used to investigate the wear tracks. An important feature when dealing with PCU wear resistance related to the chemical changes phenomena could be identified by Raman spectroscopy.

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