ATATÜRK ÜNİVERSİTESİ YAYINLARI
ATATURK UNIVERSITY PUBLICATIONS

Research Article DOI: 10.5281/zenodo.12547548

Biotribological behavior of polycaprolactone (PCL)/carbon quantum dots (CQDS) films

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ABSTRACT

Several new-generation synthetic biodegradable polymers have been developed specifically for biomedical applications in the last two decades. Polycaprolactone (PCL) was chosen as the polymer matrix in this study because it is known for its ease of synthesis, commercial availability, and excellent biocompatibility. Carbon Quantum Dots (CQDs), one of the carbon nanostructures with superior properties, were used as fillers to produce PCL film nanocomposites with improved biotribological properties. The biotribological behavior of (Sample of K-CQDs produced from Rosehip) K-CQDs filled PCL matrix nanocomposite films containing 0.3 and 2.0 wt. % K-CQDs filler were investigated in sliding against an alumina (Al_2O_3) counterface by a constant loading (2.5 N) and sliding speed (1.7 cm s^{-1}) experiments carried out in a reciprocating friction testing machine in 0.154 M isotonic salt solution. PCL/K-CQDs-2.0 film had lower friction coefficient value (0.304) with a 70% decrease, and wear rate (0.00051 mm^3/Nm; 65% decrease) compared to PCL/K-CQDs-0.3. The surface images of PCL/K-CQDs-2.0 film after the wear test indicated that the wear width trace and the adhesive wear traces decreased. In addition, the absence of cracks on the worn surface showed that both films were resistant to plastic deformation.

Keywords: Polycaprolactone, Carbon quantum dots, Nanocomposite films, Biotribology

INTRODUCTION

The application of green technologies has been one of the most studied topics in recent years, improving the properties of biodegradable and biocompatible aliphatic polyesters such as polycaprolactone (PCL) and polylactic acid (PLA).[1] PCL is readily available commercially and has high flexibility. These properties have led to its use in a variety of applications, such as the production of agricultural films, biodegradable food packages, and products used in the healthcare industry, along with the biodegradability and biocompatibility of PCL.[2,3] However, the wide use of PCL has been limited due to its significant disadvantages, such as its low mechanical properties, hardness, strength, and low gas permeability properties. It is necessary to improve the weak properties of PCL while preserving its biodegradable and biocompatible nature.[4] Various methods are used to improve the inadequate properties of PCL in order to increase its use in desired application areas.

Among these methods, nanocomposite production and extrusion with other biodegradable polymers are the most frequently used. Studies are continuing on PCL-based nanocomposites with improved properties by incorporating various types of nanoparticles such as hydroxyapatite, nanoclay, microfibril cellulose, and carbon nanotubes.[5-9] A lot of research has been done on carbon nanostructures because of their superior physicochemical, mechanical, and electrical qualities. These include fullerene, graphene nanosheets, carbon nanotubes (single and multiwalled), carbon nanofibers, and carbon nanoparticles.[10] Since carbon quantum nanodots (CQDs) offer greater qualities over the previously described carbon nanostructures, they have become the subject of numerous studies. CQDs are a brand-new class of zero-dimensional carbon nanomaterials that have special fluorescence qualities and a size of less than 10 nm. Compared to other types of nanomaterials, CQDs have a greater acidity value and surface activity because of the numerous carboxyl and hydroxyl groups that are present on their surfaces. CQDs samples are preferred due to specific chemical or physical interactions between CQDs and polymers.[11] CQDs have been produced by various methods using different carbon sources. Natural carbon sources attract attention because they are abundant, low-cost, and environmentally friendly compared to synthetic carbon sources.[12]

Recently, the use of natural substances in the synthesis of CQDs has become important with the development of green synthesis methods. Green CQDs are some of the many more reported sources, such as banana juice, onions, crab shells, glycerol, and mushrooms.[13] There are different carbon sources used for green synthesized CQDs using the hydrothermal method.[12-22]

In this study, the liquid-phase ultrasonic mixing method was used to produce the biotribological behavior of PCL nanocomposite films by adding K-CQDs samples synthesized from a natural source (Rosehip) using the hydrothermal method.[23] In the literature, the corrosion and wear behaviors of biocompatible TiO_2/PCL hybrid layers prepared via sol-gel dip coating on Ti6Al4V implants were

Received	27.02.2024
Accepted	26.03.2024
Publication Date	30.06.2024

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Cite this article: Mindivan F, Göktaş M, Makta S. Biotribological behavior of polycaprolactone (PCL)/carbon quantum dots (CQDS) films. *NanoEra*. 2024;4(1):6-10

examined.[24] And, the biodegradability behavior of a uniform PCL coating on a magnesium screw was examined in another study.[25] These studies show that this field is much newer and more remarkable. The friction and wear behavior of PCL/CQDs nanocomposite films have not been studied. This is a very original study on this subject.

EXPERIMENTAL SECTION

PCL/K-CQDs films were produced according to our previous study.[26] Images of the of PCL/K-CQDs films prepared for the wear test are given in Figure 1. PCL/K-CQDs films were subjected to wear tests using a reciprocating tribometer. The wear tests were conducted with a sliding distance of 50 m and a constant load of 2.5 N at a sliding velocity of 1.7 cm s^{-1}. A 2 mm-diameter ball made of Al_2O_3 served as the counter body. The friction force was continuously recorded by the computer with the load cell in the wear device. Following the wear test, the Nikon imaging program NIS-Elements was used to measure the 3D profiles and the Mitutoyo Surtest SJ-400 profilometer was used to measure the 2D profiles. An optical metal microscope (OM) Nikon Eclipse LV150 was used to study worn surfaces and surface pictures of Al_2O_3 balls. The wear rate was calculated using Equation (1) below. Three samples were used for each experiment.

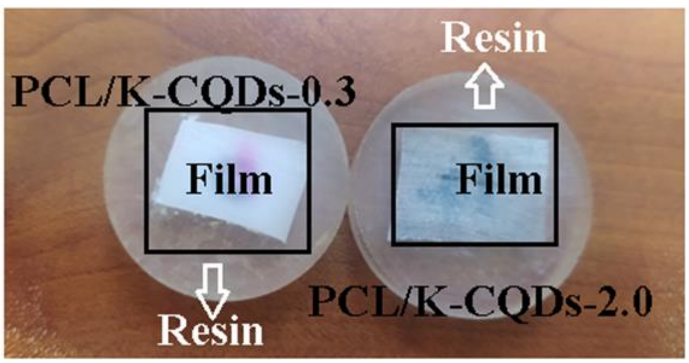

Fig 1. Images of the of PCL/CQDs films prepared for the wear test.

$$\mathbf{A} = \frac{\pi.\mathbf{W.D.C}}{\mathbf{4.S.F}} \qquad (1)$$

A: Wear rate, mm^3/Nm
W: Width of wear mark, mm
D: Depth of wear mark, mm
C: Length of wear mark, mm
S: Total sliding distance, m
F: Test load, N.

RESULTS AND DISCUSSION

The variation of the friction coefficient values obtained after the wear tests of PCL/K-CQDs-0.3 and PCL/K-CQDs-2.0 films in 0.154 M NaCl solution according to sliding distance is given in Figure 2. As seen in Figure 2, the friction coefficient values of PCL/K-CQDs-0.3 and PCL/K-CQDs-2.0 films were 1.04 and 0.304, respectively. The oscillation in the friction coefficient of the PCL/K-CQDs-2.0 film was also less than that of the PCL/K-CQDs-0.3 film. Hendrikson *et al.*[27] reported the friction coefficient as 0.529 of the PCL sample for the tissue scaffold at 1N load. In this study, the lower friction coefficient value of the PCL/K-CQDs-2.0 film as a result of the lubricating effect of the liquid medium and the wear test at 2.5 N are compatible with the literature. The friction coefficient values performed in dry environments in the wear tests are higher than the friction coefficient values in liquid environments. Because direct contact is prevented in liquid environments[28] and the friction heat is reduced. And also, it had been reported that the friction coefficient showed a more stable change in the liquid environment.[29,30]

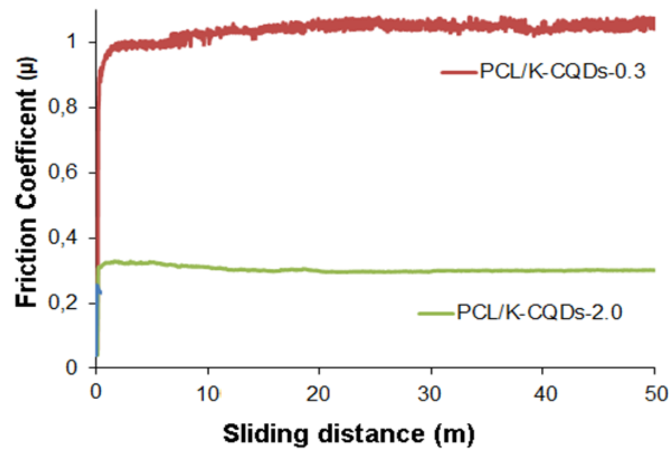

Fig. 2. Friction coefficient values of PCL/K-CQDs films.

Table 1 displays the PCL/K-CQDs films' wear volume and wear rate values. The wear volume and wear rate values of the PCL/K-CQDs-0.3 film were higher than the wear results of the PCL/K-CQDs-2.0 film (Table 1). 3D profiles of the wear track of the PCL/K-CQDs films are shown in Figure 3. It can be seen that in the wear track images in Figure 3, the PCL/K-CQDs-0.3 film had the highest wear track. 3D wear track images of the films confirmed the wear rate results. The wear volume of the PCL/K-CQDs-2.0 film was found to be 57% lower, and the wear rate was 59% lower than that of the PCL/K-CQDs-0.3 film.

Table 1. The wear volume and wear rate values of the PCL/K-CQDs films

	Wear volume (mm^3)	Wear rate (mm^3/Nm)
PCL/K-CQDs-0.3	0.21079	0.00147
PCL/K-CQDs-2.0	0.07349	0.00051

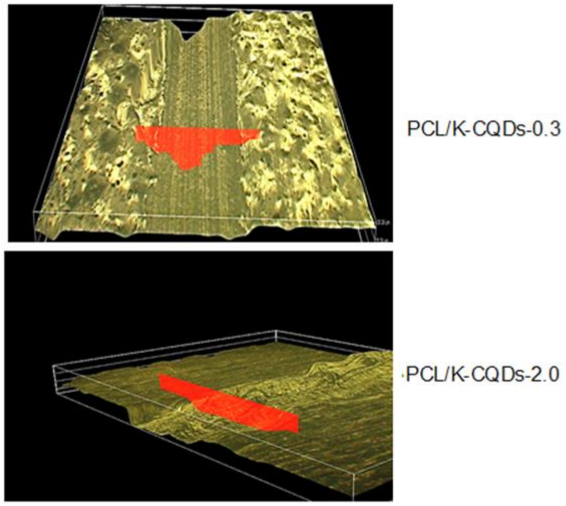

Fig 3. 3D profile of wear tracks of PCL/K-CQDs films.

OM worn surface images of PCL/K-CQDs nanocomposite films after the wear test are given in Figure 4. As seen in Figure 4, the PCL/K-CQDs-0.3 film had a higher (829.2 µm) wear track width than that of the PCL/K-CQDs-2.0 film (663.6 µm). High-magnification surface images of the films show that adhesive wear is a dominant mechanism. In a study by Bustillos *et al.*, [31] they produced graphene-reinforced PLA composites. It was reported that the heat generated on the wear surface softened the polymer, causing adhesive wear. This study was carried out in a liquid environment; therefore, frictional heat was largely prevented, and adhesive wear was the dominant mechanism in all films. In addition to adhesive wear, there are traces of large and small pieces broken off from the surfaces of films. It is understood from Figure 4 that, especially in the PCL/K-CQDs-0.3 films, delamination wear was seen in different parts of the surface, and the PCL/K-CQDs-2.0 film had delamination wear in the form of deep grooves Figure 4, the traces that can be seen as cracks on the surfaces in the high-magnification worn surface images were confirmed to be traces of adhesive wear.

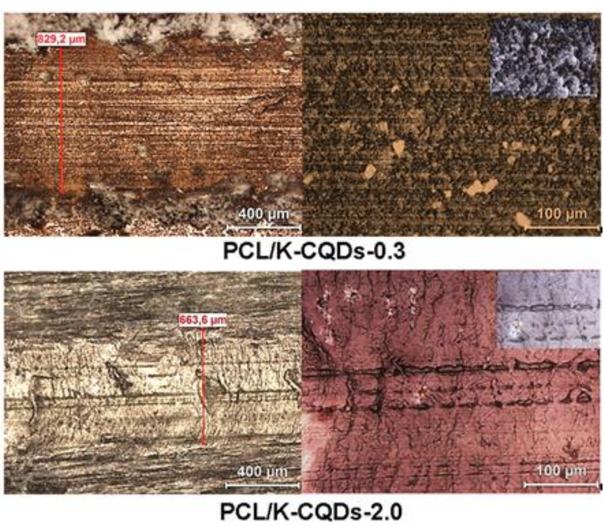

Fig 4. Low and high magnification OM images of worn surfaces generated on the PCL/K-CQDs films.

Similar to the results of this study, Min *et al.*,[32] reported that PVA and GO/PVA coatings showed similar wear mechanisms (adhesive) after the wear test, which are biodegradable polymers such as PCL. The same study attributed the observed increase in the friction coefficient to the partial delamination of composite coatings, and cracks do not appear on the surface due to their resistance to plastic deformation. The wear particles did not have an increasing effect on the friction coefficient due to the wear test being carried out in a liquid environment in this study. OM analyses of the surface morphologies of Al_2O_3 counterface were evaluated in Figure 5. In Figure 5, it is determined that the wear particles on the ball surface of the PCL/K-CQDs-0.3 film had the highest friction coefficient value. More wear particles were observed on the ball surfaces of the PCL/K-CQDs-2.0 film, which has higher wear resistance than the PCL/K-CQDs-0.3 film. It has been reported in the literature that wear particles form a lubricant film between the ball surface and the worn surface, and this lubricant film contributes to the protection of the composite surface against wear.[33] In this study, the very low presence of wear particles on the counter material of the PCL/K-CQDs-0.3 film explains the high wear volume value of this film However, there is a possibility that the resulting wear particles were removed by the liquid since the wear test was made in a liquid environment in this study. As a result, the addition of 0.3 wt% K-CQDs in this film caused poor wear resistance as it could not provide sufficient load transfer.

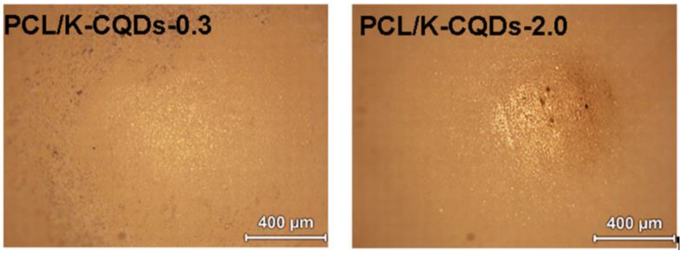

Fig 5. OM images of the Al_2O_3 balls sliding against the PCL/K-CQDs films.

Wear tests of PCL/K-CQDs-0.3 and PCL/K-CQDs-2.0 films were carried out in a 0.154 M NaCl solution. According to the friction coefficient and wear rate results, the films containing 2.0 wt% K-CQDs showed more resistance to wear. The worn surface images of films demonstrated that adhesive wear accounted for the majority of the wear mechanism, however delamination wear was also noticed. Delamination wear was also seen, however adhesive wear accounted for the majority of the wear mechanism, as shown by the worn surface photographs of the films. However, the absence of cracks on the worn surfaces of both films showed that they were resistant to plastic deformation.

Peer-review: Externally peer-reviewed.

Author Contributions: Concept - F.M.; Design - F.M.; Supervision -F.M.; Resources - F.M.; Data Collection and/or Processing - S.M.; Analysis and/or Interpretation - M.G., S.M.; Literature Search - M.G; Writing Manuscript - M.G, F.M.; Critical Review - F.M.

Conflict of Interest: The authors have no conflicts of interest to declare.

Financial Disclosure: The authors declared that this study has received financial support of the research foundation (Project no: 2021-02. BSEÜ.01-03) of Bilecik Şeyh Edebali University and TUBITAK-120M872 (The Scientific and Technological Research Council of Turkey). The authors gratefully acknowledge the support of the Surface Research Laboratory for the equipment supplied to the Mechanical Engineering Department of Bilecik Şeyh Edebali University, which was utilized in this study.

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