DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

ANTIFOULING PERFORMANCES OF SOME ECO-FRIENDLY BIOCIDES

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October, 2011
İZMİR

ANTIFOULING PERFORMANCES OF SOME ECO-FRIENDLY BIOCIDES

A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of Dokuz Eylül University
In Partial Fulfillment of the
Requirements for the Degree of Master of Science
in Chemistry

by
Zeynelabidin KARABAY

October, 2011
İZMİR

M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"ANTIFOULING PERFORMANCES of SOME ECO-FRIENDLY BIOCIDES"** completed by **ZEYNELABİDİN KARABAY** under supervision of **ASSOCIATE PROFESSOR LEVENT ÇAVAŞ** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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ACKNOWLEDGMENTS

The author is grateful to supervisor of this thesis, Associated Professor Levent Çavaş, for his valuable guide, help and advice, at all stages of this thesis.

I would like to thank the Henleys Propellers & Marine LTD Company and Lapinus Intelligent Fibres to provide us Lanolin based material and industrial fibres.

Also, I would like to thank to Zeynep Burcu Bayboğan and Moravia Marine and Industrial Coatings Company for their helps in the field tests and supply the chemicals.

In addition, I would like to express my gratitude to all friends for their continuous helpful encouragement and valuable supports.

I am also thankful to TÜBİTAK for financial support with the projects coded 109T512 and 109Y284.

Finally, I would like to thank my family for their limitless support and motivations.

Zeynelabidin KARABAY

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ABSTRACT

Artificial surfaces exposed to seawater are covered by marine fouling organisms. This process is known as "Biofouling". When artificial surfaces are considered as ships' hull, the biofouling processes result in undesirable consequences such as increased fuel consumption, carbondioxide emission, friction and decreased maneuverability and speed. Many attempts have so far been done to prevent biofouling process occurred on ships' hull. These processes are called as "Antifouling". There are a lot of different strategies and also paint formulations for ships' hull. However, very limited solutions, strategies and also commercial products have been available for marine propellers. Self-polishing percentages of an eco-friendly commercial product, PROP PROTECTOR (lanolin based material), developed for preventing biofouling processes on propellers' surfaces were investigated dependent on temperature, rotary rate, and fibre reinforcement in the present thesis. According to results, fibre reinforcement remarkably increased the self-polishing resistance of the lanolin based material. Field test results carried out in marine eco-system also confirmed the laboratory experiments. In conclusion, the quality of the commercial product, PROP PROTECTOR, can be developed by adding special fibres and fibre reinforced lanolin based material which might be used in the warm waters.

Keywords: Antifouling, biofouling, commercial fibres, lanolin, self-polishing.

BAZI ÇEVRE DOSTU BİYOSİTLERİN ANTİFOULİNG PERFORMANSLARI

ÖZ

Deniz suyuna maruz kalan yapay yüzeyler denizde bulunan fouling organizmalarınca kaplanması sürecine ”Biyofouling” denilmektedir. Yapay bir yüzey olarak gemi gövdeleri ele alındığında biyofouling, yakıt sarfiyatı, karbondioksit emisyonu ve yüzey sürtünmesinde artış, manevra kabiliyeti ve potansiyel hızda düşüş gibi istenmeyen sonuçlar doğurur. Gemi gövdelerinde meydana gelen biyofouling olayını engelleme adına birçok girişimde bulunulmuştur. Bu denizel olayı engellemeye yönelik gerçekleştirilen tüm çalışmalara ”Antifouling” denmektedir. Bu amaçla gemi gövdeleri için birçok strateji ve boya formülasyonları geliştirilmiştir. Biyofouling olayı gemi gövdelerinin yanı sıra pervanelerde de meydana gelmektedir. Ancak bu pervanelerde meydana gelen biyofouling olayını gidermek için geliştirilen stratejiler gemi gövdelerininkilerden farklıdır ve bu amaçla üretilen kısıtlı sayıda ticari ürün mevcuttur. Bu tezde, sıcaklık, dönüş hızı ve fiber katkısı gibi parametrelerin pervanelerde meydana gelen biofouling olayının engellemeye yönelik geliştirilen ve çevre dostu ticari bir ürün olan PROP PROTECTOR (lanolin tabanlı materyal)’in self-polishing yüzdesine olan etkileri araştırılmıştır. Elde edilen sonuçlara göre, fiber katkısı lanolin tabanlı materyalin self-polishing’e dayanıklılığını ciddi bir şekilde artırmıştır. Bu ürünün alan testleri denizel ekosistemde gerçekleştirilmiş ve laboratuvar testleriyle desteklenmiştir. Sonuç olarak, ticari ürün olan PROP PROTECTOR’in kalitesi fiber katkısı ile geliştirilmiş ve sıcak sularda da kullanılabilirliği sağlanmıştır.

Anahtar kelimeler: Antifouling, biyofouling, lanolin, self-polishing, ticari fiberler.

CONTENTS

CHAPTER ONE
INTRODUCTION

1.1 Biofouling or Biological Fouling

When an artificial surface is immersed into sea water, biological colonisation is rapidly occured on the surface. The undesirable accumulation of microorganisms, sea plants, algaes or macroorganisms on the artificial surface is named as biofouling or biological fouling (Alyuruk et al., 2010; Clare, 1996; Lewis, 1998; Wahl, 1989; Yebra et al., 2004). While the natural surfaces existing in the sea environment could be a rock fragment or a leave of a plant, the artificial surfaces could be materials such as a metal or plastic sheet, landing space, vessel, ship or a float.

Biofouling starts when organic or inorganic molecules readily present in the seawater such as polysaccharides, proteins and proteoglycans are adsorbed on the artificial surfaces. With the molecular adsorption of nutrients on the surfaces, an organic film layer comes into existence on the surface (Abarzua & Jakubowsky, 1995; Callow & Fletcher, 1994). Conventionally, the process depends on physical interactions such as Brownian motion, electrostatic interactions and van der Waals forces (Flemming, 2008). The formed organic film layer creates a nutrition environment for bacteria and diatoms. Afterwards, these organisms start to settle and colonize on the surface. As a result of colonization, a smooth bacterial and diatom based biofilm occurs on the surface. Consequently, with the settlement of bacteria and diatoms on the surface, the attachment of other species existing in the sea water becomes easier on this surface (Flemming et al., 2008; Zobel & Allen 1935). In this respect, an appropriate living environment occurs for macro organisms, larvae of crustaceans and macroalgae and then macrofoulers start to adhere and grow up on the surface (Abarzua & Jakubowsky, 1995; Dafforn et al., 2011).

1.2 Biofouling as a problem in shipping industries

Biofouling or biological fouling is observed on the natural surfaces existing in the sea or artificial submerged surfaces. As artificial submerged surfaces in seawater, the undersea parts of marine vehicles exposed to biofouling and this situation causes critical problems for the marine vehicles.

Figure 1.1 Biofouling on the vessel hull (Photo: Zeynelabidin KARABAY).

These problems are as follow; the accumulation and growing of fouling organisms on the ship surfaces cause roughness and an increase of the mass (Fig. 1.1). This roughness increases the surface friction between ship surface and sea water. Besides this, the increase of the friction and the weight result in the decrease of the capability of manoeuvre and the loss of potential speed. To overcome these negative cases, the ship started to consume extra fuel and energy; in addition to the extra consumption, it may also decrease the productivity of the machineries, due to the fact that they do extra and hard work (Rascio, 2000; WHOI, 1952).

An increasing incidence is observed in the period of dry-docking operations. In order to prevent negative situations due to accumulation of the fouling organisms, the surface of the ship needs to be cleaned. This cleaning process is named as dry-docking. This process is necessary not only for small vessels but also for big ones and it is a hard and troublesome work. Because, cleaning after disembarkation and launching again is a really expensive process. Therefore, the frequency of this process increases the cost of maintenance, resource and time. Furthermore, a large amount of toxic waste is also released into environment during this process (Abbott, 2000; Bengough & Shepheard, 1943; Rouhi, 1998).

Because of biofouling, some deformations on ship coating occur on the surface. These deteriorations cause some undesirable situations such as corrosion and discoloration (Cooney & Tang, 1999; Flemming et al., 2008).

Because of the marine transportation, the relocation of species which live in different sea environments (invasive or not native) was observed to the ecosystems in which they do not naturally exist. The transportation of these species may cause a serious ecological danger; the species in the ecosystems which they are transported to may disappear and also ecological variety may decrease (Reise et al., 1999). A good example related to this effect is Caulerpales in the Mediterranean Sea (Cavas & Yurdakoc, 2005a; Cavas & Yurdakoc, 2005b; Cevik C., Derici, Cevik F., Cavas, 2011; Cevik C., Cavas, Mavruk, Derici, Cevik F., in press; Yebra et al., 2004).

1.3 Antifouling Strategies and Antifouling Paints

Many attempts have so far been done to overcome the biofouling process occurred on ships' hull. These processes are called as Antifouling (AF). To prevent biofouling on the ships hulls, the special paints which are used to coat the surfaces is named as antifouling paint. Researchers developed several coating material which based on the dispersing a toxic material in polymeric or resin matrixes in the middle of 1800s. In this coating component, copper oxide, arsenic and mercury oxide were used as toxic material. With the aim of keeping this mixture together, linseed oil, shellac varnish, tar, and various kinds of resin were used. The history of antifouling has recentle been reviewed in Yebra et al., 2004. Turpentine oil, naphtha, and benzene were widely used as a solvent which completes this mixture (Callow, 1990; WHOI, 1952). This method underlines an antifouling paint. As well as the techniques used in the past, the method which is used to prevent biofouling is the technique of painting ships hulls with special paints named as AF paints. AF paints contain binder, toxic materials (biocides), solvent and other components (Fig. 1.2). Binder component which exits in AF paints sustains the paint. Moreover, it keeps all the materials together and homogeneous in it. Biocides are chemical toxic materials which prevent the existence of fouling organisms which cause biofouling. In addition to these main components, materials which have low percentage such as color pigments, co-biocides also exist in AF paints. A simple antifouling paint formulation contains different kinds of chemical materials and it basically consists of binder, biocides, solvent and other materials (Fig. 1.2), in this respect, so many antifouling paints have been developed so far.

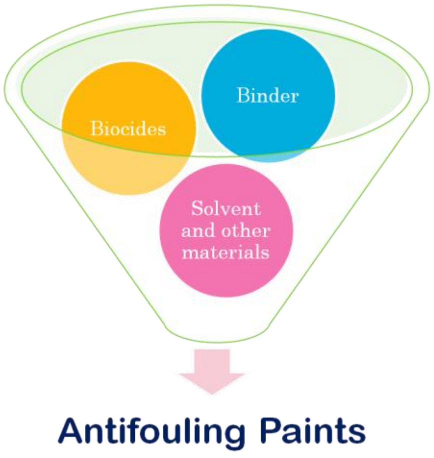


Figure 1.2 Main ingredients of antifouling paints.

Considering antifouling paints which have been developed till now, one of the most known one is tributyltin (TBT) based AF paints. The improvement of organotins have increased the performance of AF paints and completely solved the fouling problem. Throughout the AF history, TBT is a toxic compound (Fig. 1.3) which has the best AF performances and which had been developed in order to prevent biofouling problem (Champ, 2001; Gerigk et al., 1998). TBT based paints presents 5 years lifespan due to the high toxic features of TBT.

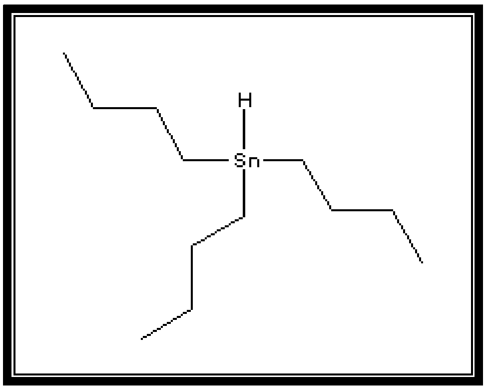


Figure 1.3 The moleculer formula of TBT.

In Archon Bay (France), so many oyster farmers observed the negative changes on oysters such as the decrese of spatfalls, abnormalities of larval development and shells malformations (Alzieu, Sanjuan, Deltreil, Borel, 1986; Yebra et al., 2004). Considering this situation, scientists proved that the negative changes were observed as a result of accumulation of TBT compounds. It was proved that even at very low concentration (20 ng/l), TBT compounds caused abnormalities (Konstantinou, 2006) such as malformation on *Crassostrea gigas'* shells and developmental defects on male characteristics of female *Nucella* sp. (< 10 ng/l) genitals (imposex) (Evans, Leksono, McKinnel, 1995; Swain, 1998; Gibbs & Brian, 1986; Yebra et al., 2004). These malformations were seen on many species in the sea environment. Considering all of these improvements, IMO reported that TBT accumulations on mammals and fishes with weakness in immunological defence, afterwards, from 1 January 2003 forward, IMO banned the applying of TBT based paints on the ships hulls and the existing TBT based antifouling paints in the ships to the date of 1 January 2008 in the congress named as AFS Convention hold in November 2001 (IMO, 2001). In accordance with the decisions of IMO, the paint industry started to develop TBT free paints instead of TBT based paints.

1.3.1 First Generation Antifouling Paints

First generation antifouling paints are defined as it contains soluble or insoluble matrix in sea water (binder), biocide, co-biocide, and other materials. When first generation AF paints containing soluble binder interact with sea water, they start to dissolve slowly. With the dissolution of binder, some roughness come into existence on the surface, biocides and co-biocides release into sea water (Fig. 1.4). As a binder, high percentage of (90 %) rosin and its derivatives (abiatic acid, levopimaric acid etc.) are used in this AF paints (Dafforn et al., 2011; Lewis, 1998; Yebra et al., 2004).

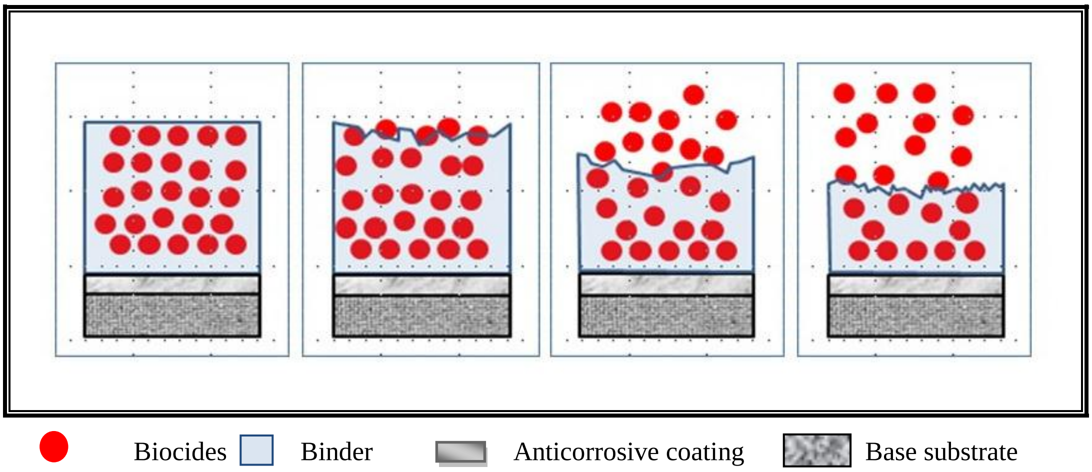


Figure 1.4 Diagram of paints with soluble matrix (was inspired by Dafforn et al., 2011).

When an AF paint which includes insoluble paint matrix interacts with sea water, the sea water molecules diffuse from the paint surface to the inside of matrix**.** With diffusion of the sea water, biocides dissolve and released to the outside from the paint (Fig. 1.5). In paints with insoluble matrix, vinyl, epoxy, acrylic, chlorinated rubber polymers are used as binder. In this type paints, the slowly release of the biocides into the seawater prevent the fouling organisms from the surfaces.

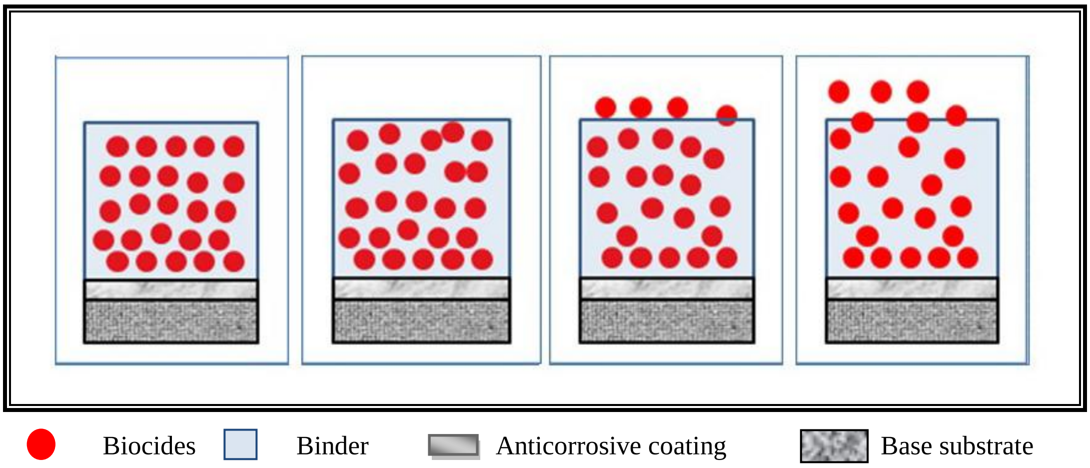


Figure 1.5 Diagram of paints with matrix which is insoluble (was inspired by Dafforn et al., 2011).

In contrast to insoluble binders, paint with soluble binder has a more controlled release of biocides and the lifespan of the releasing biocides is longer. Therefore, they are more commonly used than the insoluble matrix and have 2 years of lifespan (Dafforn et al., 2011; Lewis, 1998; Yebra et al., 2004).

1.3.2 Second Generation Antifouling Paints

Second generation paints are the paints which contain hydrolysable polymeric binder type. The matrixes of these paints have polymeric structure and they are based on the principle of the production of a new surface (self-polishing) on the paint, by leaving the surface layer by layer (Fig. 1.6). TBT based paints had the best performance up to now which were working with this principle. With the help of being hydrolyzed and departing from the surface layer by layer, foulers which have already settled on ship's hull or possible to grown are cleared off from these surfaces; besides this, the releasing of biocides more effective and controlled way. In this generation paints, TBT is head to the list of the materials used as binder and biocides. However, after the ban of TBT based paints, Zn and organosilyl based matrices were used (Dafforn et al., 2011; Lewis, 1998; Yebra et al., 2004).

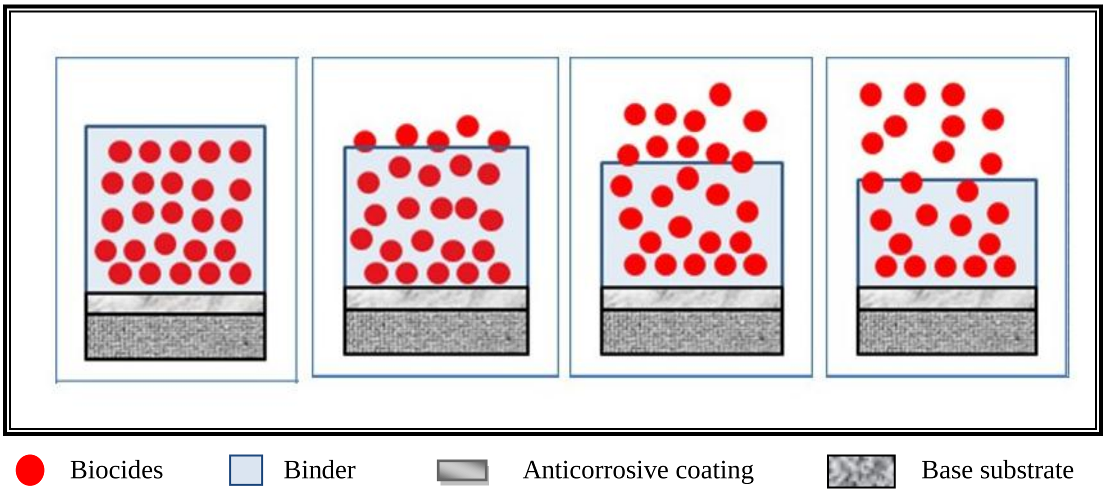


Figure 1.6 Diagram of paints with self-polishing matrix (was inspired by Dafforn et al., 2011).

1.3.3 Third Generation Antifouling Paints

Third generation AF paints are named as Foul Release or Though Type and these paints are studied extensively in recent years. Though type paints resembles highly hydrophobic structure and it does not contain any biocide as a toxic component. The surfaces of these paints have very low friction, low surface energy; and their surfaces are extra smooth. In contrast to other AF paints, the principle of third generation AF paints is not based on the release of biocide. With providing ultra smooth surfaces fouling organisms have considerable difficulties in settling. The hull of a ship which waits in the harbor is covered by the fouling organisms in the sea ecosystem. Afterwards, with the water motion made by fast cruising speed of the ship, these organisms washed off and can not adsorbed on this smooth surface (Fig. 1.7). Thus, ship’s hull is cleaned and not exposed to fouling. Typical fouling release paint performs in this way (Lewis, 1998). Present fouling release coatings are advised by Swain in 2003. AF performances of these coatings have been tested by many researchers (Wells, Meyer, Matousek, Baier, Neuhauser, 1997). In these coatings, epoxy resins, fluoropolymers, silicones and polysiloxans have been used (Brady, 2001; Swain, 2003; Thünemann & Kublickas, 2001). However, these coatings are not widely applied and used at present due to being expensive and being easily deformed (cutting, tearing and puncturing) and have poor mechanical properties (Anderson, 1998; Cough, Fothergil, Hendrie, 1994; Ryle, 1999; Swain, 2003).

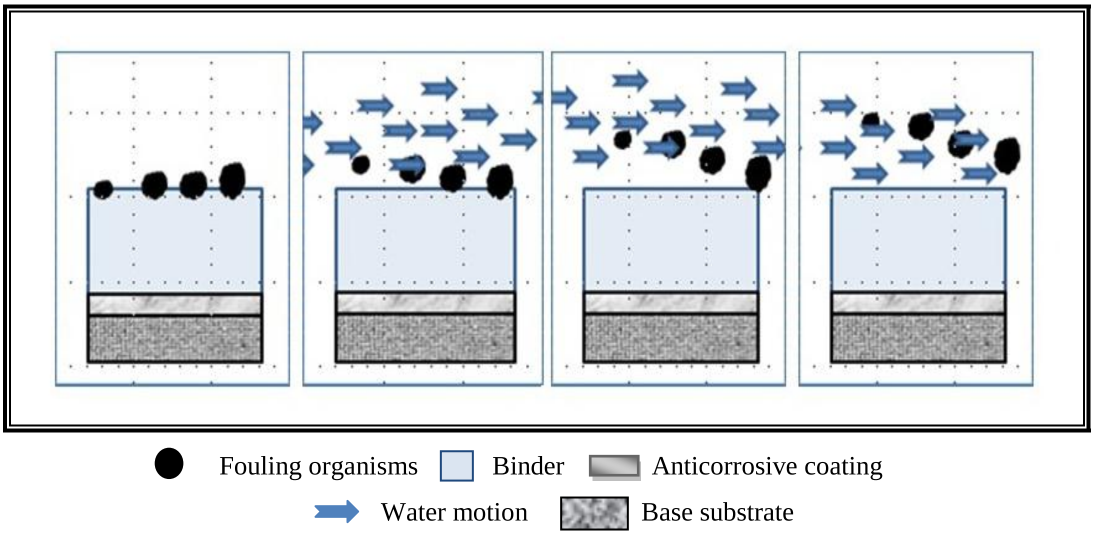


Figure 1.7 Diagram of the Foul release (Though type) paints (was inspired by Dafforn et al., 2011).

1.4 The Biocides used in Antifouling Paints

Cu_2O is an AF compound which has high toxicity used in paints and has been used widely in AF paint industry up to present. After banning of TBT based paints, paint companies increased the percentage of Cu_2O in paint; in addition to this, they started to look for appropriate materials which could complete the biocidal effect of copper. Because, although copper had high toxicity, there were some algae species which tolerated to copper toxicity in the sea environment (Foster, 1977; Reed & Moffat, 1983) and this paints containing copper were ineffective to prevent these algae species (Voulvolis, Scrimshaw, Lester, 1999). Kinds of toxic materials have been started to be added into AF paints against algae species which copper can not prevent. These materials are named as co-biocides which are added to AF paints with this aim and have highly low percentages (1-2 %). There are so many compounds used as co-biocides. The most commonly used ones are (Fig. 1.8), Irgarol-1051, Diuron, Zinc pyrithione, Sea-nine 211, Dichlofluanid, Ziram, Thiram, Chlorothalonil, Kathon 5287, Maneb ve Zineb (Gerigk, Schneider, Stewen, 1998; Omae, 2003; Voulvolis et al., 1999; Thomas, 2001). Apart from these compounds, toxic materials categorized as metal and inorganic compounds such as copper pyrithione, benzmethylamide, fluorofolpet, polypase, pyridine-triphenylborane, TCMS, TCMTB, and tolyfluanid are also used. Irgarol 1051 (2-methylthio-4-tertbutylamino-6-cyclopropylamino-s-triazine) caused so many imprecision about their environmental effects. Irgarol 1051 is generally effective on seawater and fresh water algae, but less effective on animals. In photosynthesis, Irgarol 1051 inhibits the photosystem II (PS II) by interfering with electron transport in chloroplasts. In contrast to other booster biocides, Irgarol 1051 has low water solubility and partition coefficient. It was reported that it is considerably toxic for the non-target algae and its low concentration may harm the group of micro and macro algae, endosymbiotic corals, sea grasses and indirectly herbivore sea animals such as dugong (Evans et al., 2000). The common biocides used in antifouling paint industry are; Diuron, Sea-nine 211, Kathon 5287, Chlorothalonil, Dichlofluanid, Ziram, Thiram, Maneb, Zineb, Zinc pyrithione.

1.5 Lanolin as an Antifouling coating

Coating of ships' hulls with AF paints provides protection against fouling. There are some surfaces on the ships (propeller, rudder, palm etc.) contact with seawater apart from ships' hulls. In order to protect these parts against fouling, AF coatings are used. However, AF paints used on ships' hulls are not applied on ships' propellers. The reason of this is the high rotary rate of propeller caused by the motion of itself. When a propeller coated with AF paints starts to revolve, the coating erodes faster than the coatings on the ship's hulls. The eroding of the paint on the surface of the propeller causes uncontrolled release of biocides and shortens the lifespan of the paint. Consequently, as ships' propellers exposed to more fouling, surface of friction and weight of the ships increase; therefore, when ships navigates some troubles and difficulties occur during the course of the ships (Fig. 1.9). Due to this situation occurring on the propellers, different alternatives have been investigated and used. To protect ships' propellers from fouling, surfaces of propellers are coated with the oil named as Lanolin (Fig. 1.10).

Figure 1.9 A ship’s propeller which exposed to fouling (Photo: Levent Çavaş).

Figure 1.10 Lanolin based materials

Lanolin is a material which is widely used in cosmetics industry (Fig. 1.11) in hand and body creams, balms, and lip sticks). Apart from cosmetics, it is used with many purposes such as lubricant and anticorrosive in industry. Lanolin is a light yellow, odorous and high viscous material which is produced from sheep’s wool**.** It dissolves in petroleum ether, ether, chloroform and hot alcohol without water. The melting point of Lanolin is about 40-50°C.

Lanolin is used against the fouling on ships’ propellers because of its hydrophobic character, antiseptic and antibacterial characteristics and effect of decreasing of friction. But lanolin is not appliciable to the propellers of the ships used in warm seas (above 25°C). Because lanolin based coatings easily detach from the surface of the propeller due to its low resistance against temperature. It is secreted from the sheep's skin for protection against parasites capable of living between the hairs of sheep. Sheep wool is cleared from mineral salt with a simple wash; then it is washed with water with soap and alkaline solution. In this wash, lanolin is taken from the wool. In this water with soap contains 0.5-5 % amount of lanolin. In this mixture, lanolin is in the form of emulsion and it departs from the mixture in the shape of granules. In order to take lanolin from these emulsions, centrifugation, precipitation with acid or the precipitation of Ca and Mg salts methods can be used. In order to refine lanolin, special soil filter are used. Its color is bleached. For this process, potassium dichromate, chlorine and hydrogen peroxide are used (Alzaga et al, 1999; Ash, M. & Ash, I., 1995). Due to its low melting point, it is applied on the propellers of the ships sailing in the sea of which temperature is low. They detach by melting because of its low melting point in the sea water of which temperature is high. The aim of the study is to develop lanolin based antifouling agent by adding commercial fibres for the use of ship propeller in marine industry. In the present thesis, increase in the mechanical strength of the lanolin, provided by Henleys Propellers and Marine Ltd. Firm, coated material was investigated by using special inorganic based fibers provided by Lapinus Company. The increase of mechanical strength would enable the usage of lanolin easily in the areas with high sea water temperature. Moreover, the antifouling effects of terrestrial plant extracts from *Nerium oleander* and *Laurus nobilis* and their contribution to the antifouling performance of lanolin were investigated by adding into the lanolin.

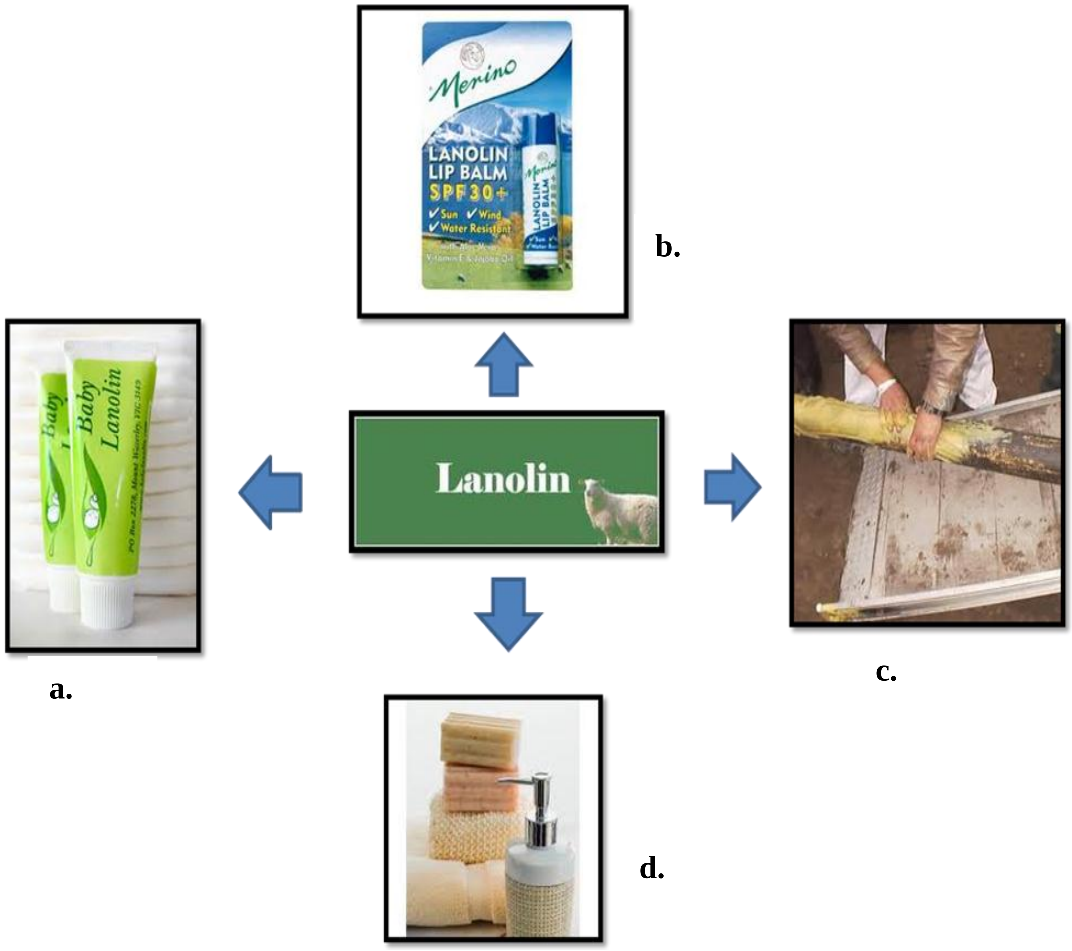


Figure 1.11 The uses of lanolin a) Cream, b) Balm, c) Industry, d) Body oil.

CHAPTER TWO

MATERIALS AND METHODS

The lanolin based material (Fig. 1.14) was kindly provided by the Henleys Propellers & Marine LTD Company in New Zealand. The special commercial fibres which are called Rockforce MS730-Roxul 1000 (Fibre 1) and Rockforce MS675-Roxul 1000 (Fibre 2) were supplied from Lapinus Company in Netherland (Fig. 2.1). These commercial fibres produced from volcanic rocks and man-made briquettes and their features were presented in Table 2.1.

Figure 2.1 The commercial fibres which provides from Lapinus Company in Netherland: (left) Rockforce MS730-Roxul 1000, (right) Rockforce MS675-Roxul 1000.

Table 2.1 The features of the commercial fibres (The values were retrieved from the web page of Lapinus Company).

Parameter	**Average/Tolerance**
Fibre index	Up to 99.9%
Fibre diameter (num. av.)	Approx. 5.5 micron
Specific surface area	Approx. 0.20 m^2/g
Fibre length	125-650 micron
Colour	Grey/green or off-white
Hardness	6 Moh
Melting point	Roxul®1000 > 1000 ºC/CoatForce® > 700 ºC
Ignition loss	Max. 0.3%wt
Moisture content	Max. 0.1%wt
Specific density	2.75 ± 0.15 g/cm^3

2.1 Preparation of glass slides and metal surfaces

The free and fibre reinforced lanolin based materials were applied on microscope slides and metal surfaces (Fig. 2.2). These glass slides which have dimensions of 26x76 mm and metal surfaces were cleaned and dried before the covering of their surfaces with free and fibre reinforced lanolin based material. The metal surfaces coat with anticorrosive material which provides by Moravia Marine and Industrial Coatings against to the oxidation. Each slide were indicated and weighted before and after the experimental processes. Afterwards, free and fibre contains lanolin based material were covered on glass slides and metal surfaces as well.

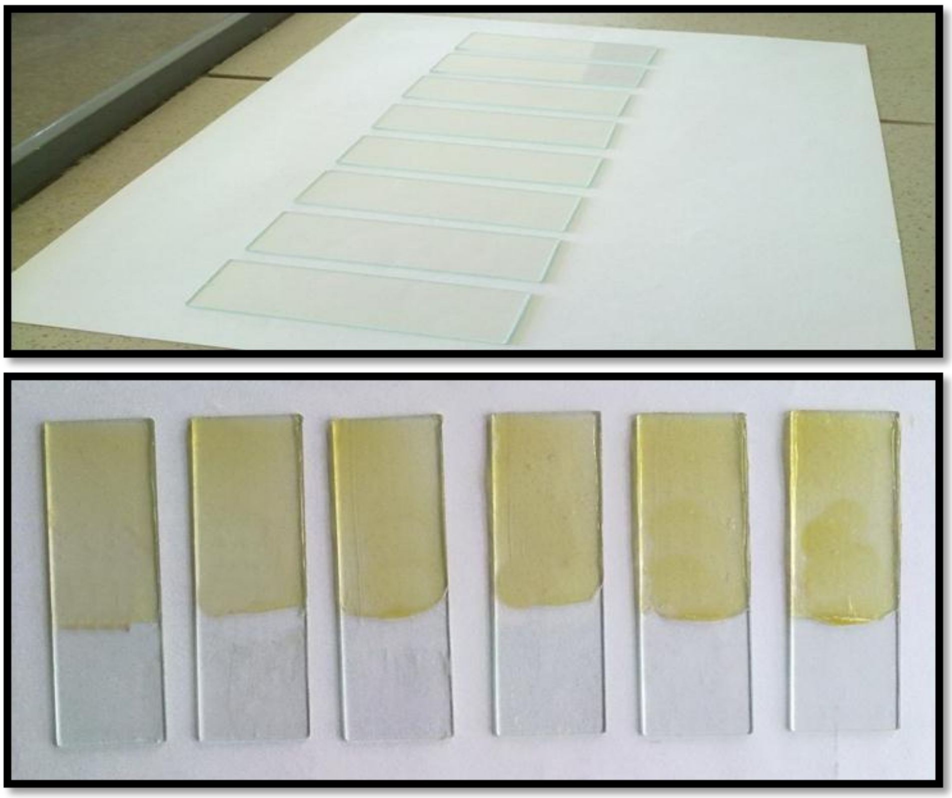


Figure 2.2 Uncovered and lanolin based material covered glass slides

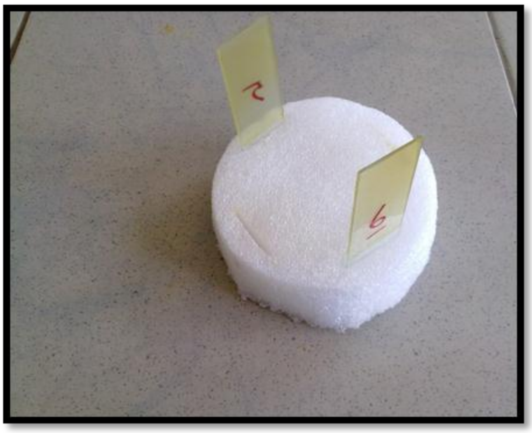
2.2 Preparation and application of free and fibre reinforced lanolin based material on glass slides and metal surfaces

In order to apply lanolin based material which is in natural wax on glass slides and metal surfaces, was melted within 25 mL beaker on hot plate at 60 ^{o}C. 200 μL of melted lanolin based material was poured onto a glass slide and metal surface which was weighted and extended onto whole glass surface carefully to obtain a homogeneous surface. Then, the covered glass slide and metal surface was waited to be cold for 10 minutes and finally weighted. The fibre reinforced lanolin based material was prepared with the melted free lanolin based material and the special commercial fibres. 0.5, 1.0 and 5.0 % (w/w) of fibres were added into the melted free lanolin based material in separately at 60 ^{o}C and then mixed for 15 minutes in order to obtain a homogeneous mixture. The same procedures which are applied for the free lanolin based material were applied for the fibre reinforced lanolin based material (Fig. 2.3).

Figure 2.3 Preparation of the fibre reinforced lanolin based material.

2.3 Self-polishing Test

Self-polishing tests of free and fibre reinforced lanolin based material were performed in rotary test system (Fig. 2.4a-b). Artificial seawater (AS) was used in rotary tests. To prepare AS, 32 g NaCl, 14 g $MgSO_4{\cdot}7H_2O$ and 0.2 g $NaHCO_3$ were dissolved in 1 L of distilled water and prepared AS was transferred into 1000 mL of beaker (Grasshoff, 1976; Yebra et al., 2005). The covered glass slides and metal surfaces were embedded into rubber disk (Fig. 2.4-a) at perpendicular axis and placed oppositely to each other. Then, rubber disk was mounted onto a beaker in downward direction and solution was stirred with magnetic stirrer at 250, 500, 750 and 1000 rpm for 1, 2 and 3 hours. After the test, glass slides and metal surfaces were removed from disk and washed with distilled water for several times and waited for one hour at room temperature. Following to dried, glass slides and metal surfaces were weighted again and related calculations were performed.



a.

b.

Figure 2.4 (a) Rubber disk and (b) self-polishing system.

2.4 Preparation of *Nerium oleander* and *Laurus* nobilis extract and eco-toxicity tests

Plant extracts were prepared by homogenization of 10 g plant leaves with 20 mL methanol. Then the mixture was centrifuged at 10000 rpm for 7 min. and the supernatant was filtered by filter paper. Afterwards the solvent (methanol) of the supernatant was evaporated with water bath at 60 ^{o}C. The same volume of water was added into the supernatant after the completely volatilized of solvent. Finally the solution was mixed well and diluted 5 different concentrations (0.50, 0.33, 0.25, 0.20, 0.17 g/mL). The same procedures were applied with another solvent such as ethanol.

Artemia salina is a well accepted test animal because of its resistance to wide range of toxic substances, high hatching ability and commercial availability (Barahona & Sanchez-Fortun, 1999; Koutsaftis & Aoyama, 2007). The use of *A.salina* in the toxicity test of antifouling agents is underlined by Koutsaftis and Aoyama (2007).

A.salina eggs were kindly provided by Ocean Life Aquarium Company in İzmir-Turkey. The eggs were placed into artificial seawater at 22-25^{o}C and conditioned for 3 days. Artificial seawater was prepared according to Grasshoff's method (Grasshoff, 1976). Actively swimming 10 individuals in 20 μL of AS were taken and placed into 96 wells microplate. Total volume of a microplate well was fixed to 220 μL by adding 200 μL biocide solution in different concentrations. All experiments were repeated for three times. Survival percentage of *A.salina* in each microplate well was determined by counting actively swimming individuals after exposure to biocide solutions at corresponding time intervals.

2.5 Corrosion tests

The corrosion tests were carried out in order to prove of anticorrosive effect of lanolin based material with metal surfaces. The metal surfaces were coated with lanolin based material according to 2.2., then these metal surfaces were immersed in artificial seawater for 6 hours.

2.6 Field tests

In order to observe the antifouling effect of the lanolin based and fibre reinforced lanolin based material the field tests were carried out. For this purpose the metal surfaces were coated with the free lanolin based and fibre reinforced lanolin based material according to 2.2. Afterwards these lanolin based and fibre reinforced lanolin based material covered metal surfaces were immersed in seawater which deep 50 cm in Zeytinburnu coast, Istanbul for about 2 months (52 days).

2.6.1 Fouling Criteria

There are many different methods to examine the antifouling performances of the materials (Arimura et al., 2004; Okimoto et al., 2005). So we have created the following criteria under the light of above mentioned patents. It is a combination of the criteria in the patents cited.

Level I. There is no any foul from fouling organisms.

Level II. There is microfilm layer formation.

Level III. There are macrofilm layer formation and the beginning of the settlement.

Level IV. There are macroalgaes and the larvae of the crustaceans.

Level V. The surfaces are covered with macroalgaes, crustaceans and many fouling organisms (>50%).

2.7 Statistical analysis

The parameters (Fig. 2.5), fibre type (Fibre 1 and Fibre 2), fibre ratio (0.5, 1.0, 5.0 % (w/w)), rotary rate (250, 500, 750 and 1000 rpm) and rotary time (1, 2 and 3 hour), were tested for determination of their effects on self-polishing percentages of the free and fibre reinforced lanolin based materials. Since the data were very large, the statistical analysis was applied in this thesis. The data was statistically evaluated by one-way ANOVA, Tukey Test and three-way ANOVA. Minitab 16.1.1 version was used for the statistical analysis.

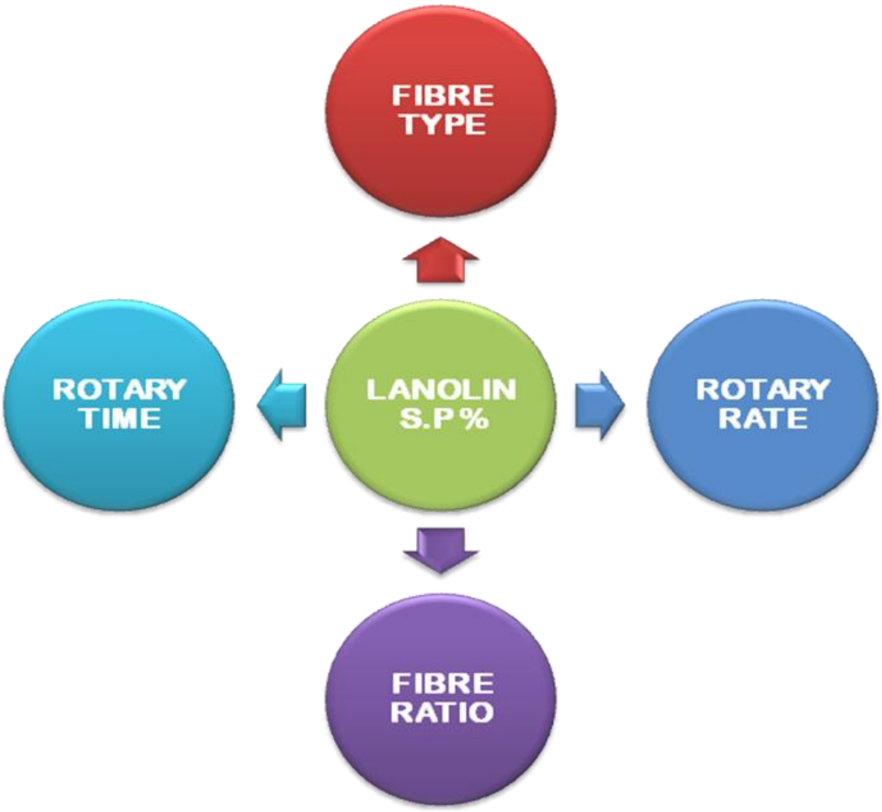


Figure 2.5 Experimental parameters which affected the self-polishing percentages of the materials developed.

CHAPTER THREE
RESULTS AND DISCUSSION

The biofouling process on marine propellers has a great importance which compared to biofouling process that occurs on ships' hull inasmuch as there are many alternative antifouling paints for ships' hull. However, when the marine propellers are considered, number of the products is lower than those for ships' hull (Clare, 1996; Lewis, 1998; Wahl, 1989; Yebra et al., 2004). Lanolin is a natural product, produced from wools of sheep. The number of the sheep in New Zealand is higher compared to other countries, the most of lanolin in world is provided by New Zealand. Although lanolin has many uses in cosmetics, it is also used as antifouling coverage of marine propellers. Lanolin covered marine propellers are protected by fouling organisms very well in temperature below than 25 ^{o}C. But the seawater temperature negatively affects the self-polishing rate of the lanolin from marine propellers. According to our observations it is completely removed from surface of propellers in the Mediterranean Sea. In the present thesis, newly developed/modified fibre reinforced lanolin is recommended for propeller protection and the strength of lanolin against self-polishing is increased by adding commercial fibres.

The self-polishing percentages of the free and fibre reinforced lanolin based materials were carried out in laboratary experiments. Free and fibre reinforced lanolin based material covered glass slides and also metal surfaces are investigated in the rotary systems in different rotary rates (250, 500, 750 and 1000 rpm) and temperatures (30, 40 and 50 ^{o}C). Self-polishing test of free lanolin and fibre reinforced lanolin based material were carried out with three parallel covered glass slides.

3.1 The effect of experimental conditions on self-polishing percentages in glass slides

The self-polishing percentages of free lanolin based material were appeared in Fig. 3.1. This figure shows that the effects of temperature, rotary rate and rotary time on the self-polishing percentages of free lanolin based material covered glass slides. The experimental conditions of self-polishing procedure were 250, 500, 750 and 1000 rpm rotary rate, 1, 2 and 3 hours rotary time and the temperature of artificial seawater is 30 ^{o}C. Considering this figure, the max and min self-polishing percentages of free lanolin based material were observed in 1000 rpm rotary rate – 3 hours rotary time and 250 rpm – 1 hour rotary time, respectively. The results of 1 hour rotary time did not show any significant differences between four different rotary rate ($p>0.05$). Moreover, 750 and 1000 rpm rotary rate were remarkably different ($p<0.05$), whereas 250 and 500 rpm rotary rate have not significantly differences in 2 hours rotary time. Table 3.1, 3.2 and 3.3 depicted that the effect of the rotary rate on the glass slides at 30 ^{o}C and 1, 2 and 3 hour respectively. Although, any rupture was not observed on the lanolin based material covered glass slides for 250 and 500 rpm rotary rate in these tables, quite distinctive rupture was observed for 750 and 1000 rpm rotary rate in Table 3.2. According to Fig. 3.1, the self-polishing percentage was obtained as 6.16 ± 1.52 for 3 hours at 1000 rpm. This number can be considered as low self-polishing, but when surfaces are examined, these surfaces have great problems (Table 3.1). To the best of our knowledge, any problem which is occurred on homogenous lanolin surfaces is resulted in heavy fouling by foulers.

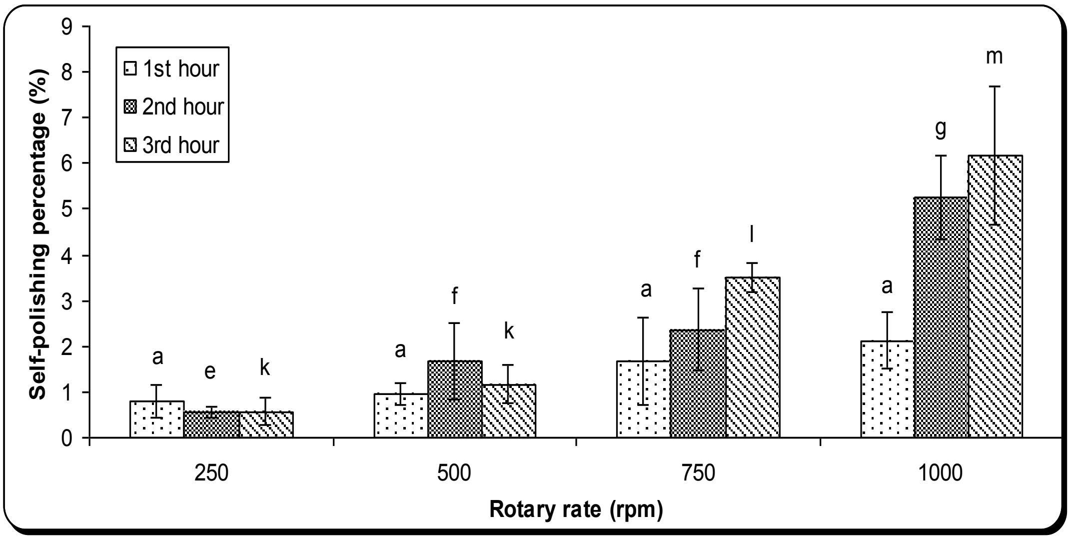


Figure 3.1 Effect of rotary rate on the self-polishing percentage of free lanolin based material at 30 ^{o}C. The lanolin based material covered glass slides were applied in rotary system 1, 2 and 3 hours, respectively.

Table 3.1 The images of the free lanolin based material covered glass slides at 30 ^{o}C, after 1 hour.

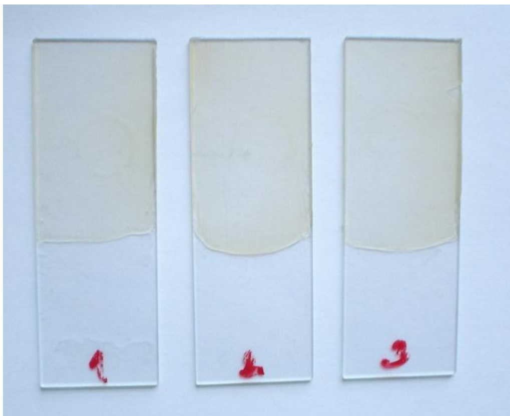
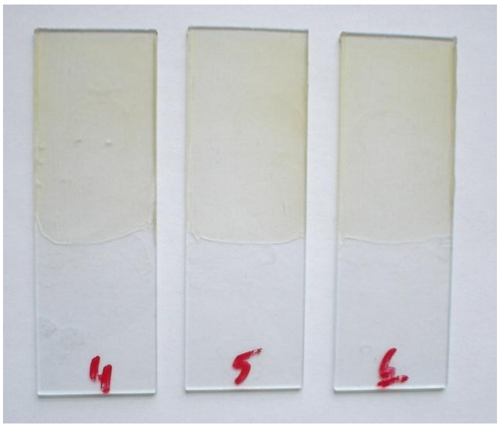
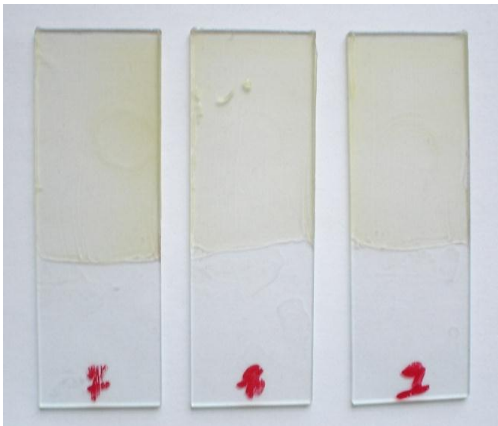
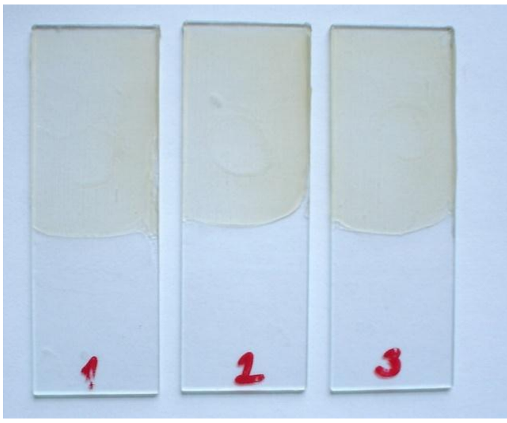
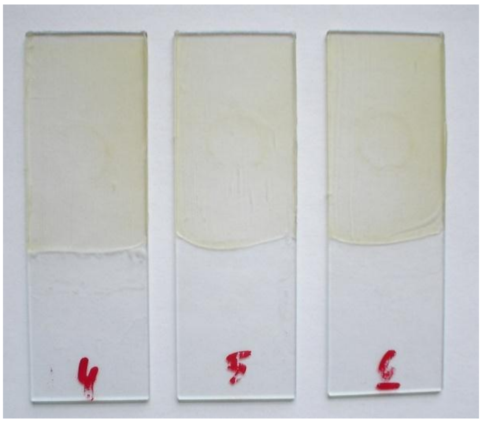
 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

Table 3.2 The images of the free lanolin based material covered glass slides at 30 ^{o}C, after 2 hours.

<table>
<tr>
<td>

A. 250 rpm</td>
<td>

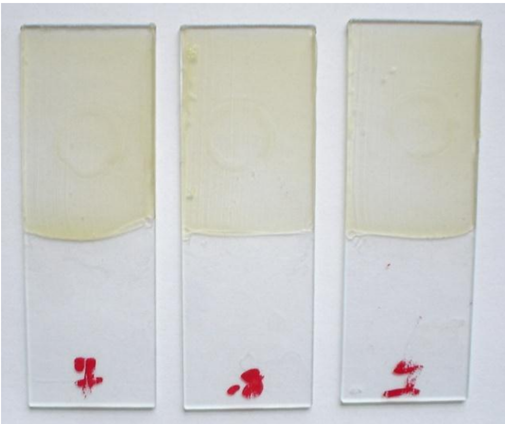
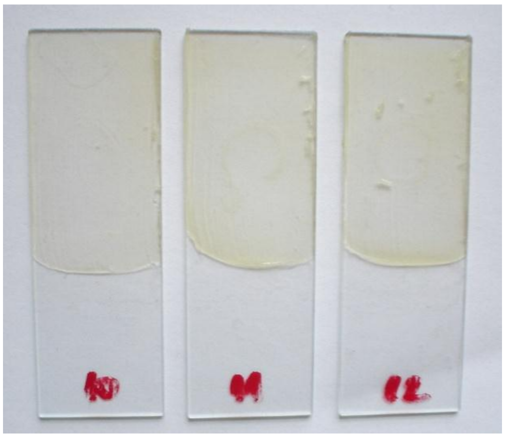
B. 500 rpm</td>
</tr>
<tr>
<td>
C. 750 rpm</td>
<td>
D. 1000 rpm</td>
</tr>
</table>

Table 3.3 The images of the free lanolin based material covered glass slides at 30 ^{o}C, after 3 hours.

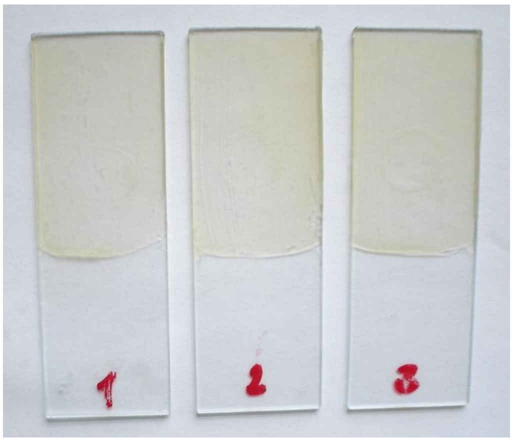
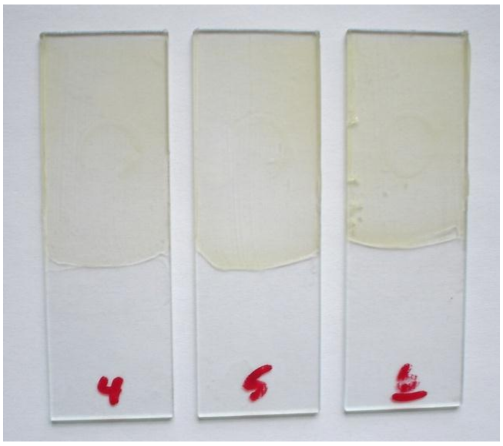
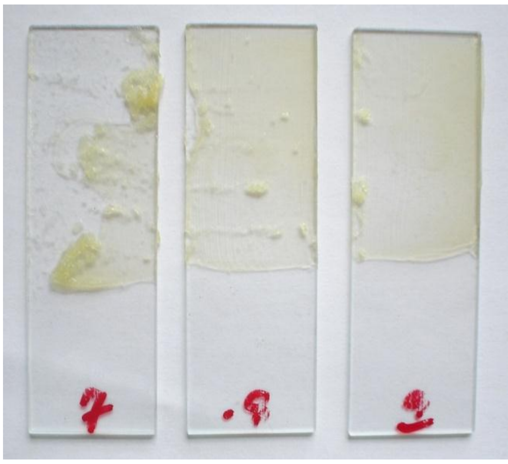
 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

Fig. 3.2 and 3.3 show that the effects of experimental conditions on self-polishing percentage of free lanolin based material at 40 and 50 ^{o}C sequentially. In these figures, the self-polishing percentages of free lanolin based material were observed to increase in comparison with Fig. 3.1. According to Fig. 3.2, the max and min self-polishing percentages of free lanolin based material were determined in 1000 rpm rotary rate – 3 hours rotary time and 250 rpm – 2 hour rotary time and according to Fig. 3.3, 1000 rpm rotary rate – 3 hours rotary time and 250 rpm – 1 hour rotary time respectively.

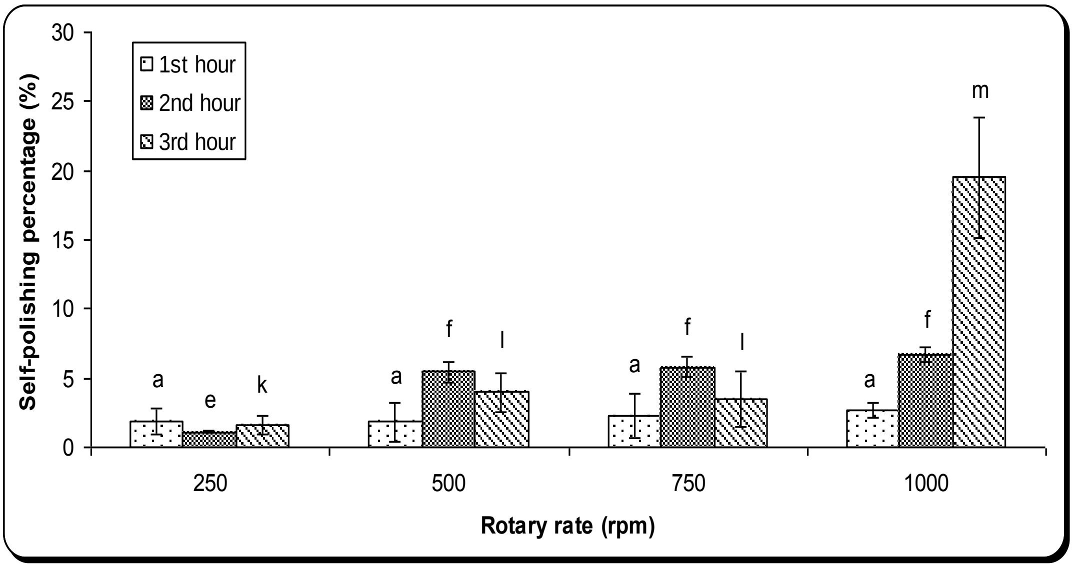


Figure 3.2 Effect of rotary rate on the self-polishing percentage of free lanolin based material at 40 ^{o}C.

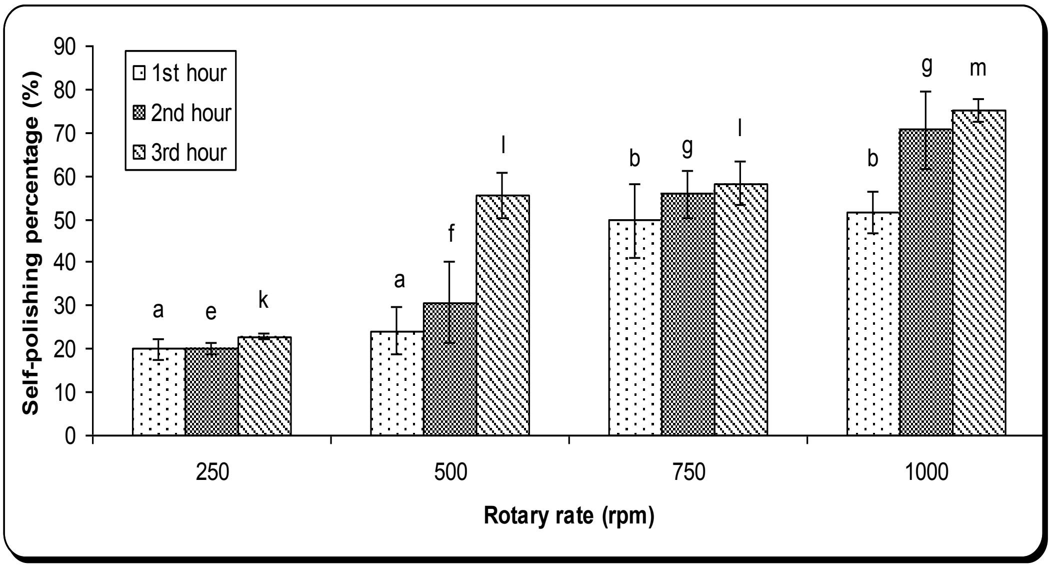


Figure 3.3 Effect of rotary rate on the self-polishing percentage of free lanolin based material at 50 ^{o}C.

Self-polishing percentages of fibre reinforced lanolin based material which contains 1% Fiber 1 (w/w) were depicted in Fig. 3.4. The results were indicated that, the self-polishing percentages of lanolin based material which contains 1% Fibre 1 (w/w) quite decreased with respect to free lanolin based material in all rotary rates at 30 ^{o}C. In the results of 1 hour, there were not any differences between the 250 and 500 rpm ($p<0.05$) and between the 750 and 1000 rpm respectively. In 2 hours rotary time, although there were not any significant difference between the 500 and 750 rpm, 250 and 1000 rpm were statistically different from them. Table 3.4 shows that the pictures of 1% Fiber 1 (w/w) reinforced lanolin based material covered glass slides, after the self-polishing test under the 250, 500, 750 and 1000 rpm. Table 4 shows that the effects of rotary rate on 1% Fiber 1 (w/w) added lanolin based material end of the 1 hour and at 30 ^{o}C. As can be seen from the Table 3.6, any deformation was not observed from the fibre reinforced lanolin based material covered glass slides for the all rotary rate experiments. On the other hand in Table 3.6, quite little roughness was observed on the glass slides for 1000 rpm rotary rate. Table 3.6 indicates that the effects of the 3 hour rotary time for the same fibre ratio and temperature on the surfaces. In this table, whereas 250, 500 and 750 rpm rotary rate shown good performances on these conditions, only 1000 rpm rotary rate did not show the same success.

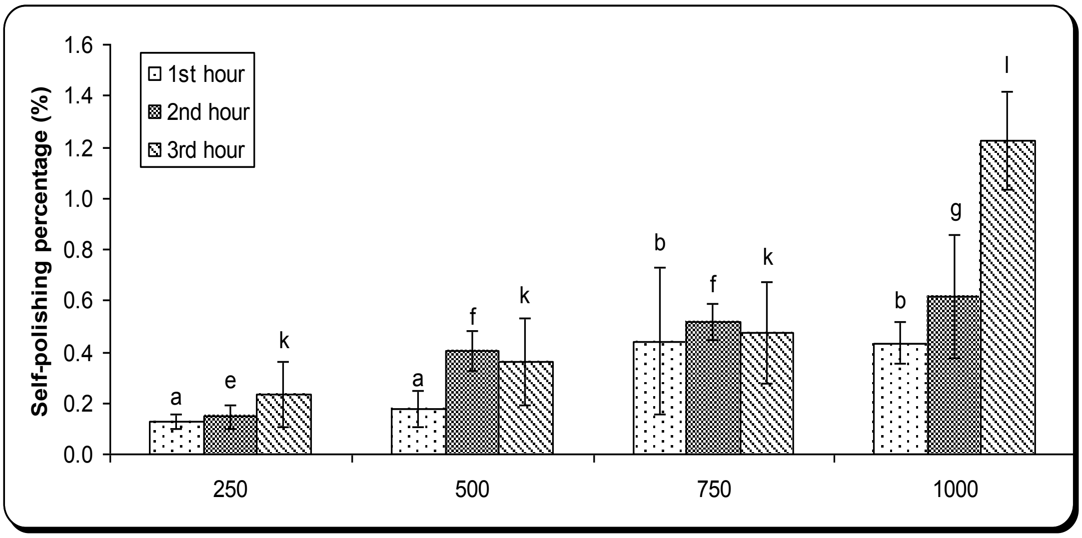


Figure 3.4 Effect of rotary rate on the self-polishing percentage of fibre reinforced lanolin based material which contains %1 fiber 1 (w/w) at 30 ^{o}C.

Table 3.4 The images of the 1% Fiber 1 reinforced lanolin based material covered glass slides at 30 ^{o}C, after 1 hour.

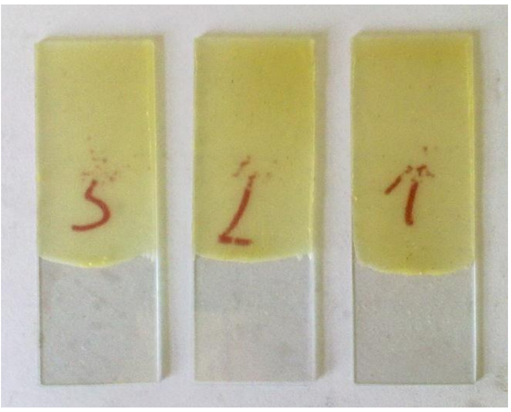
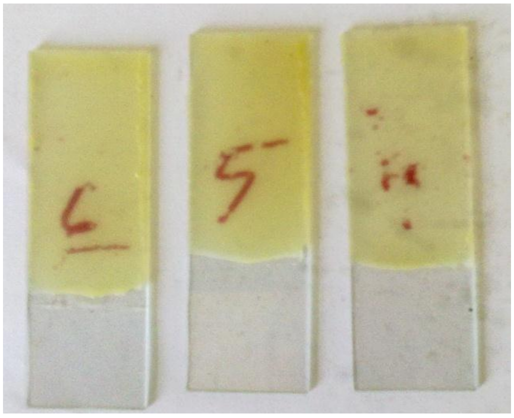
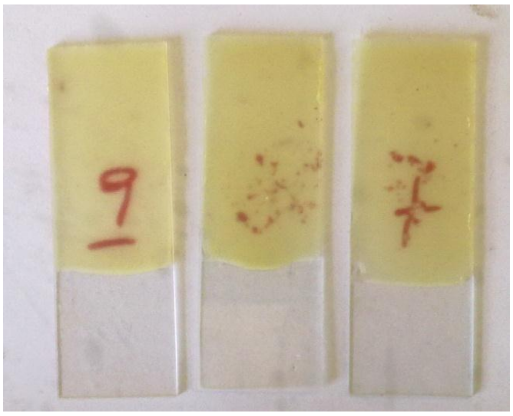
 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

Table 3.5 The images of the 1% Fiber 1 reinforced lanolin based material covered glass slides at 30 ^{o}C, after 2 hours.

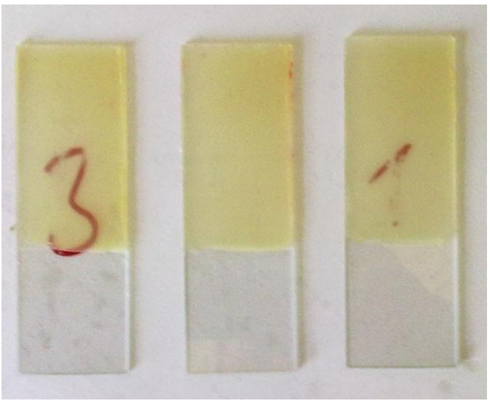
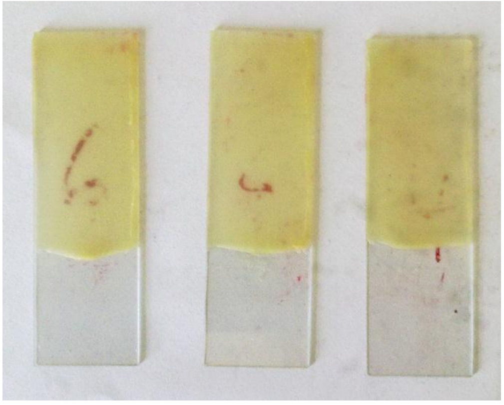
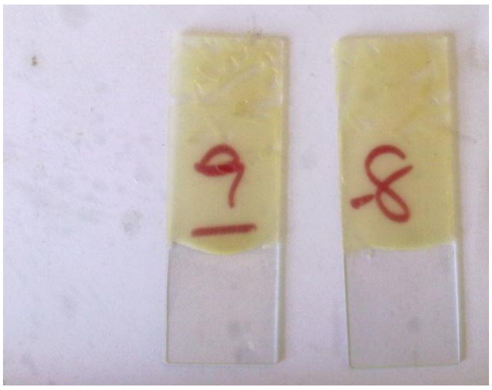
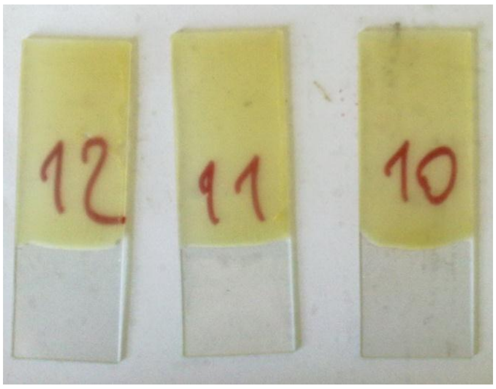
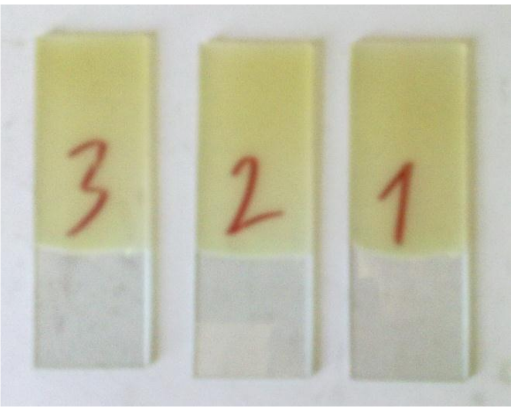
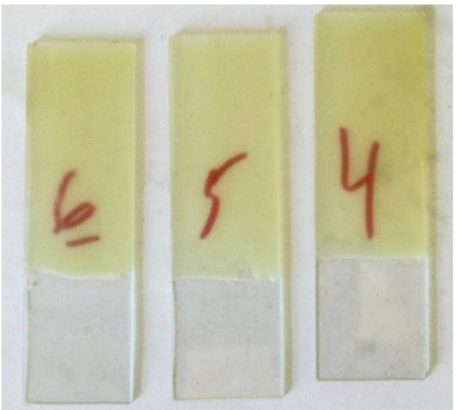
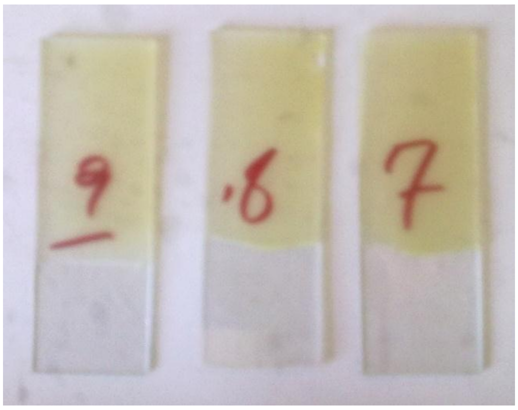
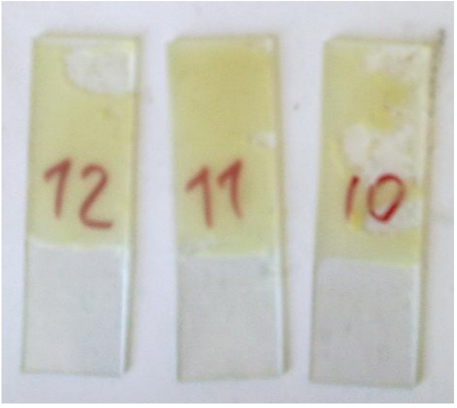
 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

Table 3.6 The images of the 1% Fiber 1 reinforced lanolin based materia covered glass slides l at 30 ^{o}C, after 3 hours.

<table>
<tr>
<td>

A. 250 rpm</td>
<td>

B. 500 rpm</td>
</tr>
<tr>
<td>

C. 750 rpm</td>
<td>

D. 1000 rpm</td>
</tr>
</table>

Fig. 3.5 and Fig. 3.6 show that the effect of self-polishing percentages of lanolin based material covered glass slides which contain 1% Fibre 1. The self-polishing percentages increased with the increasing of rotary rate and rotary time in Fig. 3.5 and Fig. 3.6. Both of these figures, the max self-polishing percentages were observed in experimental groups which have 1000 rpm rotary rate and 3 hours rotary time. According to experimental results from the test group which exposed to 3 hours rotary time in Fig.5, there were not any significantly differences between the 250, 500 and 750 rpm ($p>0.05$), and 1000 rpm statistically different ($p<0.05$) from them. As it can be seen from Fig. 3.5 and 3.6, the results which obtained from 1000 rpm rotary rate in Fig. 3.6., the self-polishing percentages have 6 times high value when compared with the results of Fig. 3.5.

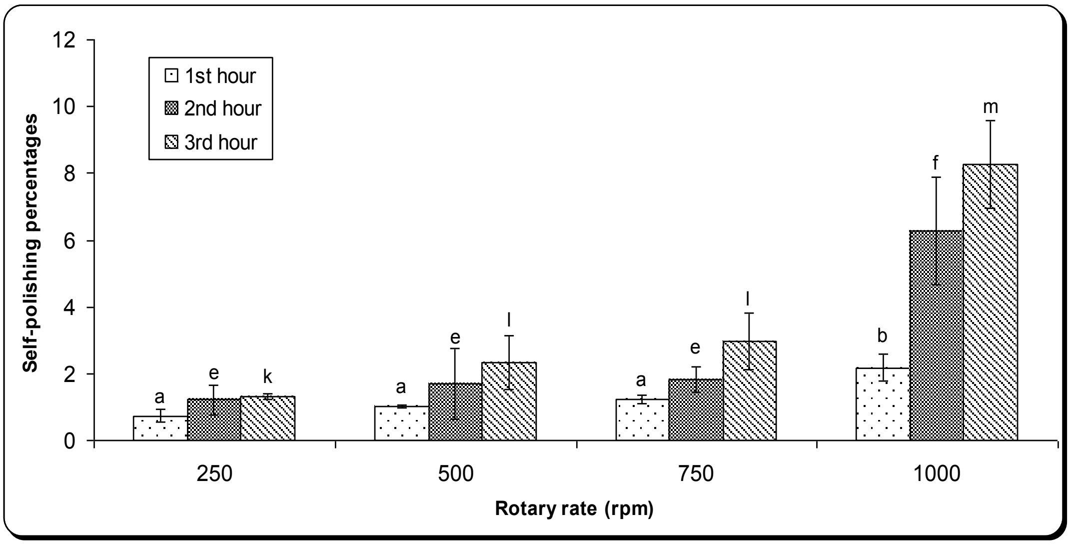


Figure 3.5 Effect of rotary rate on the self-polishing percentage of fibre reinforced lanolin based material which contains %1 fiber 1 (w/w) at 40 ^{o}C.

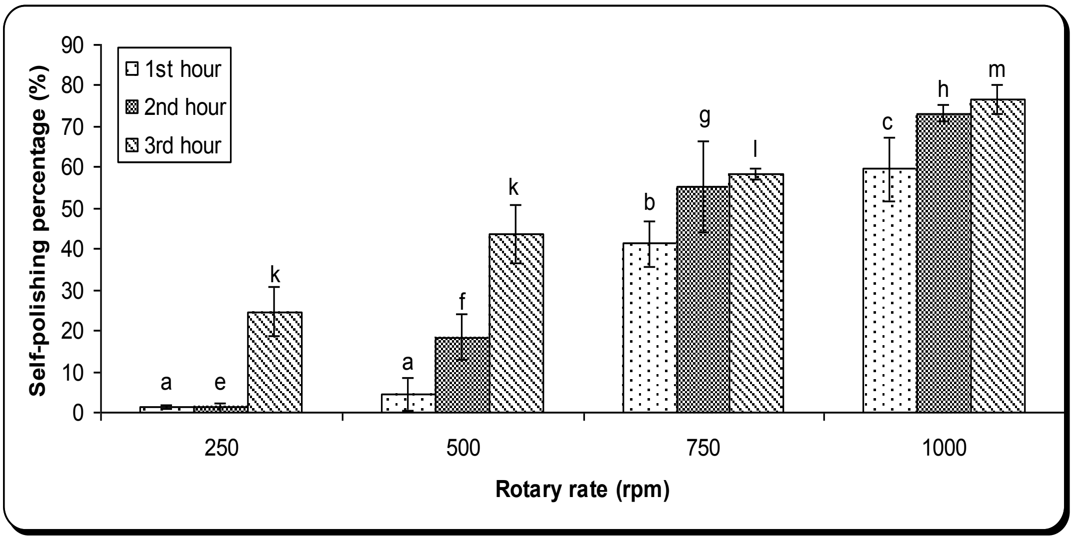


Figure 3.6 Effect of rotary rate on the self-polishing percentage of fibre reinforced lanolin based material which contains %1 fiber 1 (w/w) at 50 ^{o}C.

The self-polishing percentage of the 5% Fiber 1 (w/w) reinforced lanolin based material were seen in Fig.3.7, 3.8 and 3.9 at 30, 40 and 50 ^{o}C. According to these figures, the max self-polishing percentages evaluated from 1000 rpm rotary rate – 3 hours rotary time in Fig. 3.7 at 50 ^{o}C. In addition to this, the min self-polishing percentages were observed in 250 rpm rotary rate in Fig. 3.9. Statistically, 500, 750 and 1000 rpm rotary rate have not any significant differences ($p>0.05$) and 250 rpm is different from them at 2 hours rotary time in Fig. 3.8.

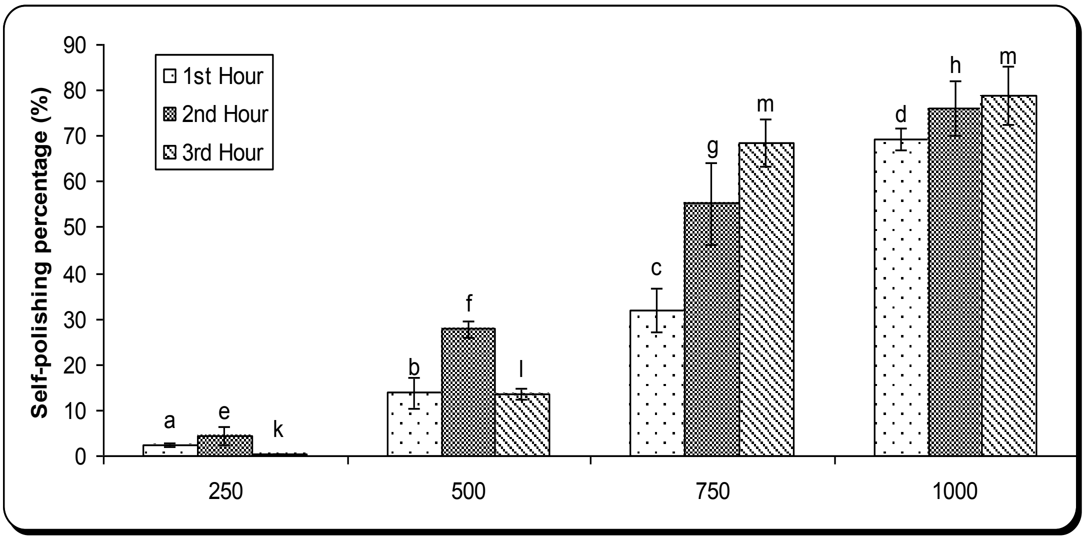


Figure 3.7 Effect of rotary rate on the self-polishing percentage of fibre reinforced lanolin based material which contains 5% Fiber 1 (w/w) at 50 ^{o}C.

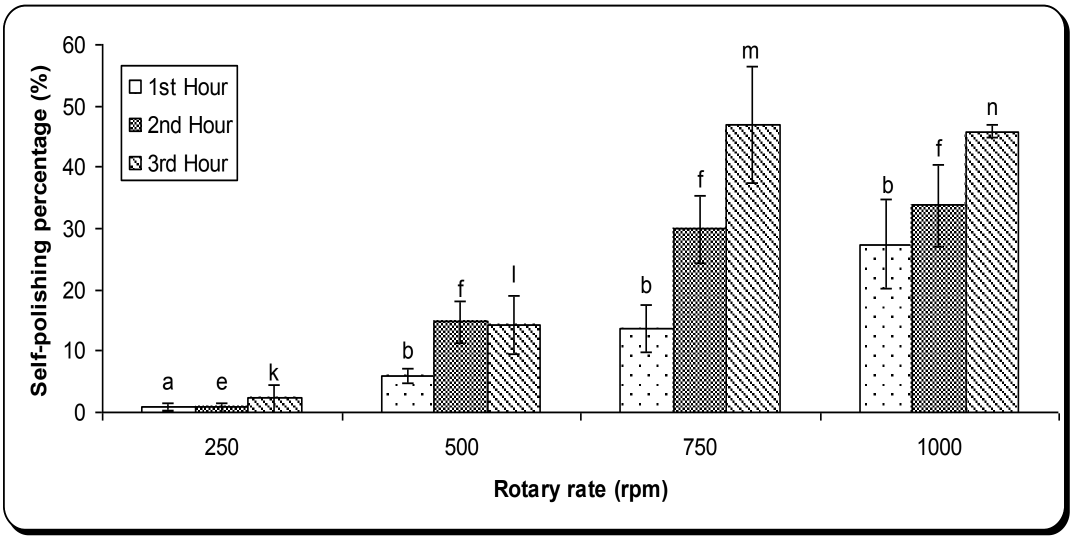


Figure 3.8 Effect of rotary rate on the self-polishing percentage of fibre reinforced lanolin based material which contains 5% Fiber 1 (w/w) at 40 ^{o}C.

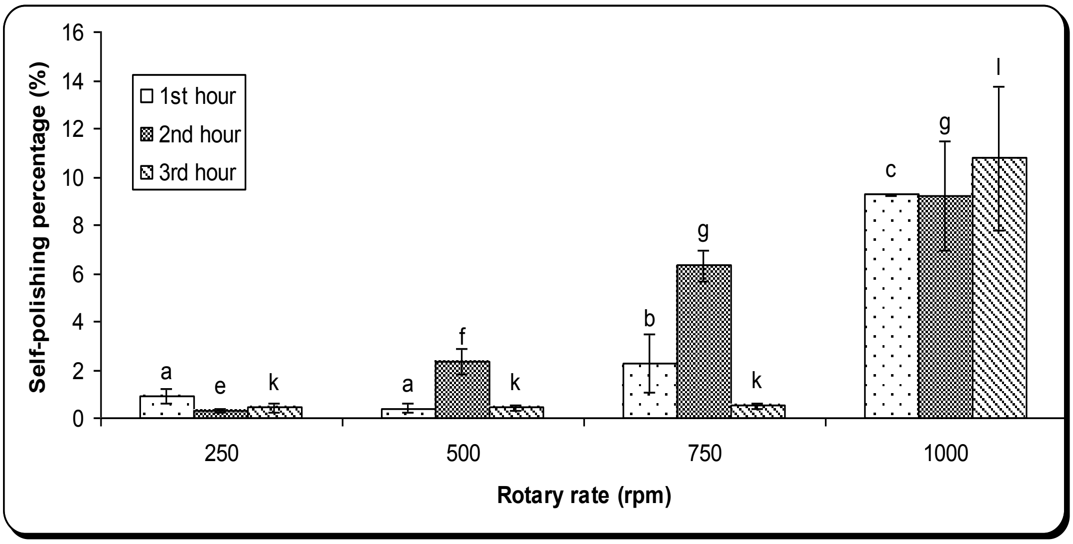


Figure 3.9 Effect of rotary rate on the self-polishing percentage of fibre reinforced lanolin based material which contains 5% Fiber 1 (w/w) at 30 ^{o}C.

The self-polishing percentages of 5% Fibre 2 (w/w) reinforced lanolin based material were appeared in Fig. 3.10, 3.11 and 3.12. at 30, 40 and 50 ^{o}C respectively. Considering all these figures, the self-polishing percentages were increased with the rotary rate and rotary time. Furthermore, the self-polishing percentages were also increased with the temperature (30-50 ^{o}C). The min and max self-polishing percentages were observed in 250 and 1000 rpm rotary rate respectively, in addition, the max percentage was seen in 50 ^{o}C for the 5% Fibre 2 (w/w) reinforced lanolin based material. Moreover, in the results of 2 hours rotary time, there were not any remarkable differences between the 250, 500 and 750 rpm rotary rate ($p>0.05$), and 1000 rpm statistically different ($p<0.05$) from these condition.

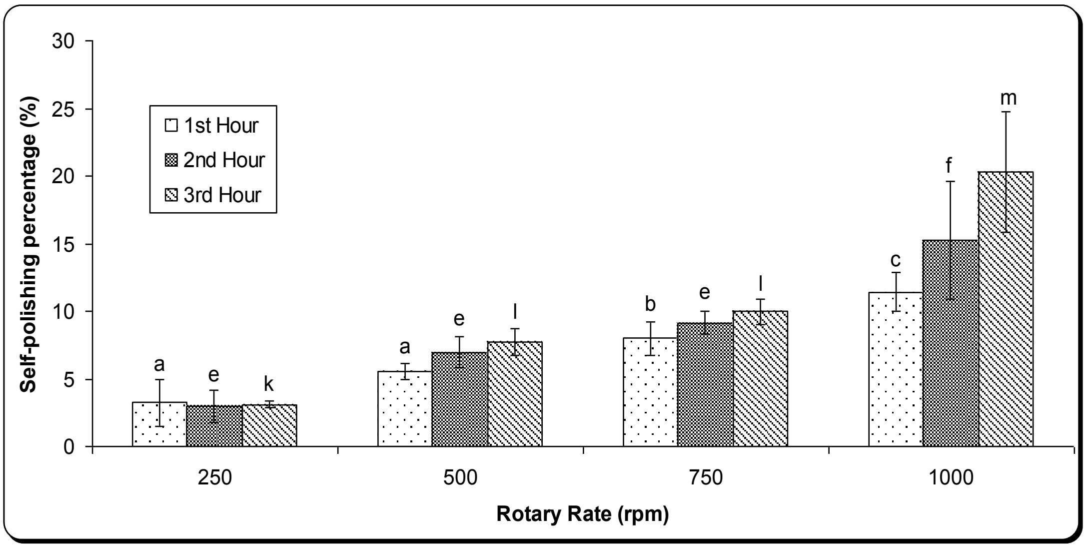


Figure 3.10 Effect of rotary rate on the self-polishing percentage of fibre reinforced lanolin based material which contains 5% Fiber 2 (w/w) at 30 ^{o}C.

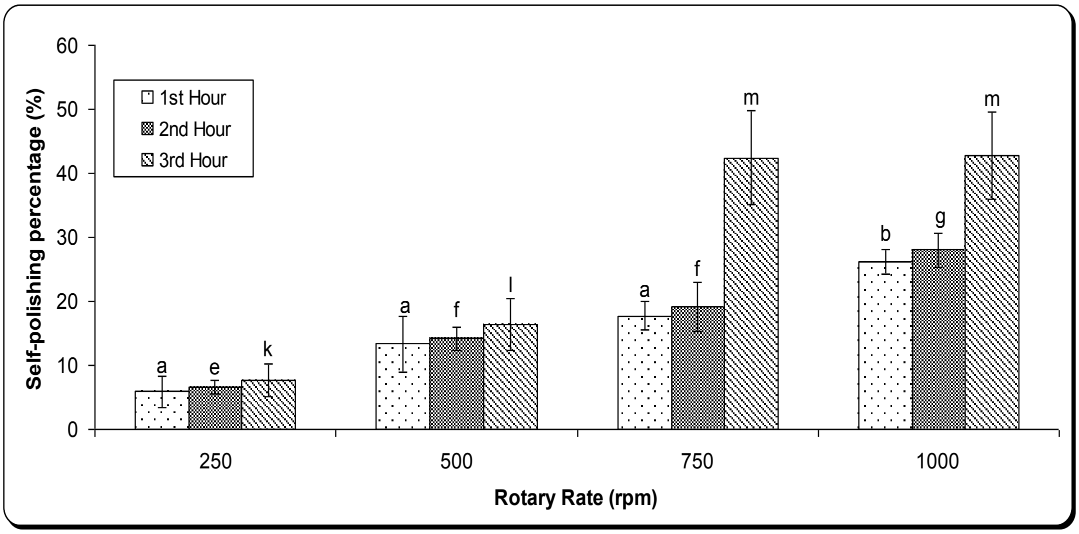


Figure 3.11 Effect of rotary rate on the self-polishing percentage of fibre reinforced lanolin based material which contains 5% Fiber 2 (w/w) at 40 ^{o}C.

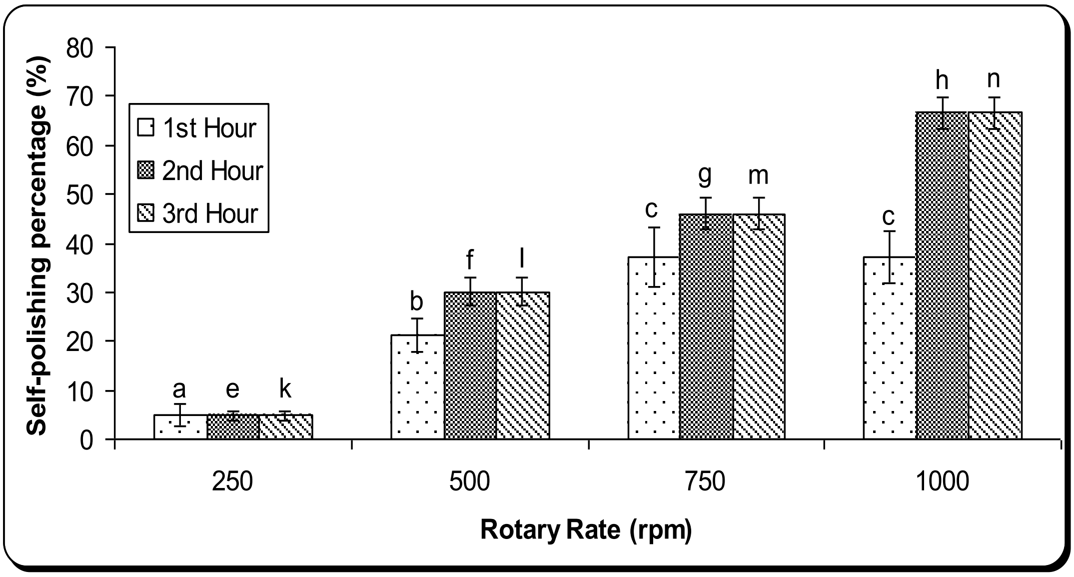


Figure 3.12 Effect of rotary rate on the self-polishing percentage of fibre reinforced lanolin based material which contains 5% Fiber 2 (w/w) at 50 ^{o}C.

The melting point of the lanolin based material is about 40-50 ^{o}C and due to the fact that the experiments which belongs to Fig. 3.13, 3.18 and all experiments which has 50 ^{o}C were carried out for completely testing the effect of temperature on the fibre reinforced lanolin based material. The self-polishing percentage of the 0.5% Fibre 1 (w/w) reinforced lanolin based material was quite higher than the results of the 30 ^{o}C because of the temperature of artificial seawater was 50 ^{o}C. In theoretically, the max self-polishing percentage had to be determined from 3 hour 1000 rpm, but the max self-polishing percentage was observed from 1 hour, 1000 rpm due to the condition temperature in the Fig 3.13. But, as it can be seen from this figure, the results of 1000 rpm fairly close. Moreover, the Fibre 1 was indicated the better effect (lower self-polishing percentage) than the Fibre 2 at the same fibre ratio.

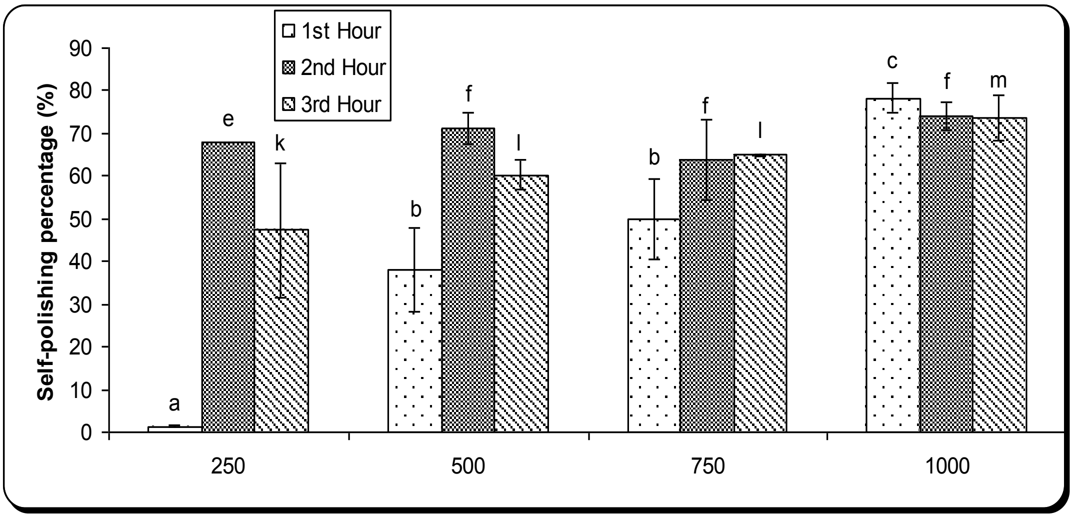
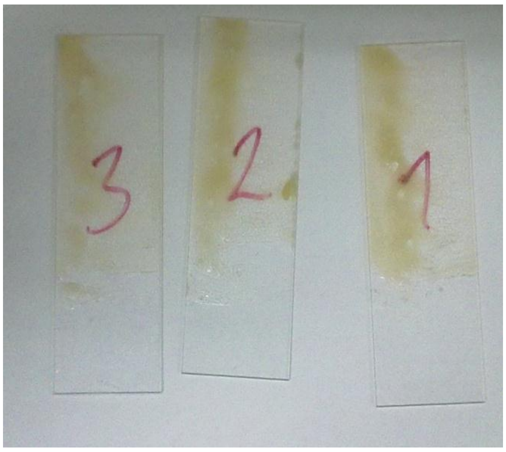
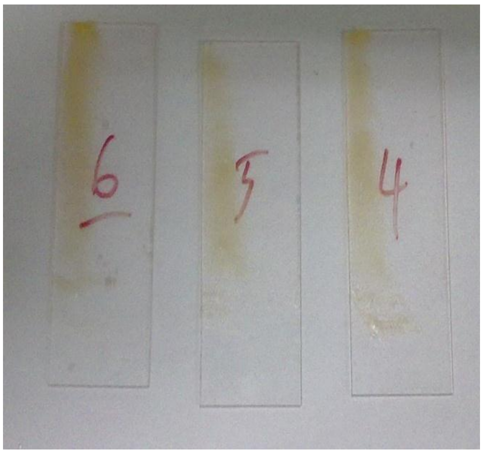


Figure 3.13 Effect of rotary rate on the self-polishing percentage of fibre reinforced lanolin based material which contains %0.5 fiber 1 (w/w) at 50 ^{o}C.

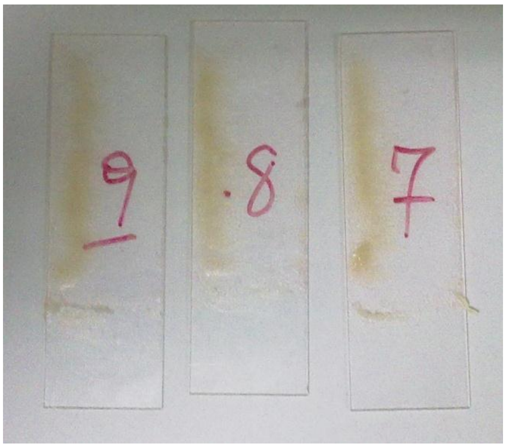
Table 3.7 The images of the 0.5% Fiber 1 reinforced lanolin based material covered glass slides at 50 ^{o}C, after 1 hour.



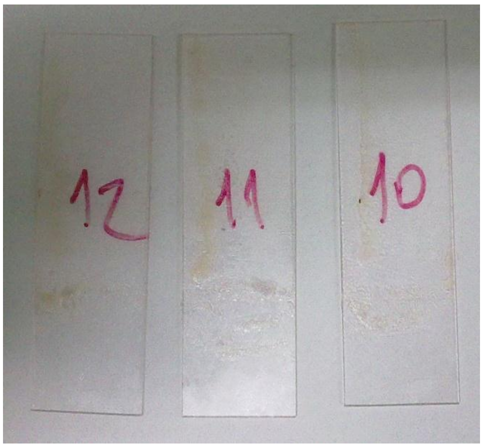
A. 250 rpm



B. 500 rpm



C. 750 rpm



D. 1000 rpm

Table 3.8 The images of the 0.5% Fiber 1 reinforced lanolin based material covered glass slides at 50 ^{o}C, after 2 hours

<table>
<tr>
<td>

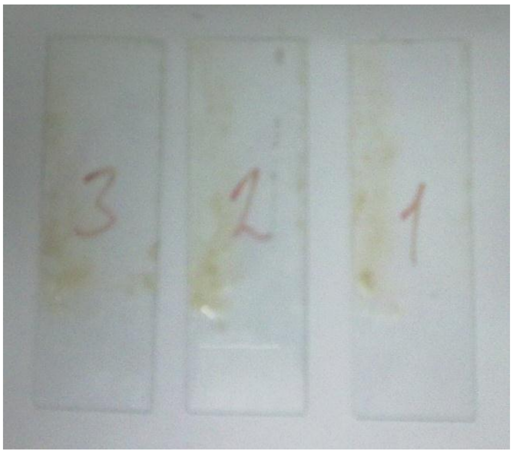
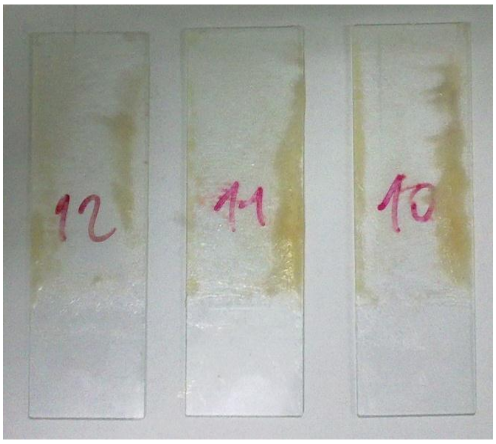
A. 250 rpm</td>
<td>

B. 500 rpm</td>
</tr>
<tr>
<td>

C. 750 rpm</td>
<td>

D. 1000 rpm</td>
</tr>
</table>

Table 3.9 The images of the 0.5% Fiber 1 reinforced lanolin based material covered glass slides at 50 ^oC, after 3 hours.

 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

The effect of rotary rate on the self-polishing percentages of 0.5% Fiber 1 (w/w) reinforced lanolin based material covered glass slides were shown in Fig. 3.14 at 40 ^{o}C. The max self-polishing percentage was observed in 1000 rpm rotary rate, 3 hours. On the other hand, 250 rpm rotary rate was shown the min self-polishing percentages. According to the 1 hour rotary time results, there were not observed any significant differences between the 250, 500 and 750 rpm rotary rate, on the contrary, 1000 rpm results contain statistically differences from preceding experimental groups. As it can be seen from Table 3.10, 3.11 and 3.12, many deformations occurred on the 0.5% Fiber 1 (w/w) reinforced lanolin based material covered glass slides after the self-polishing tests.

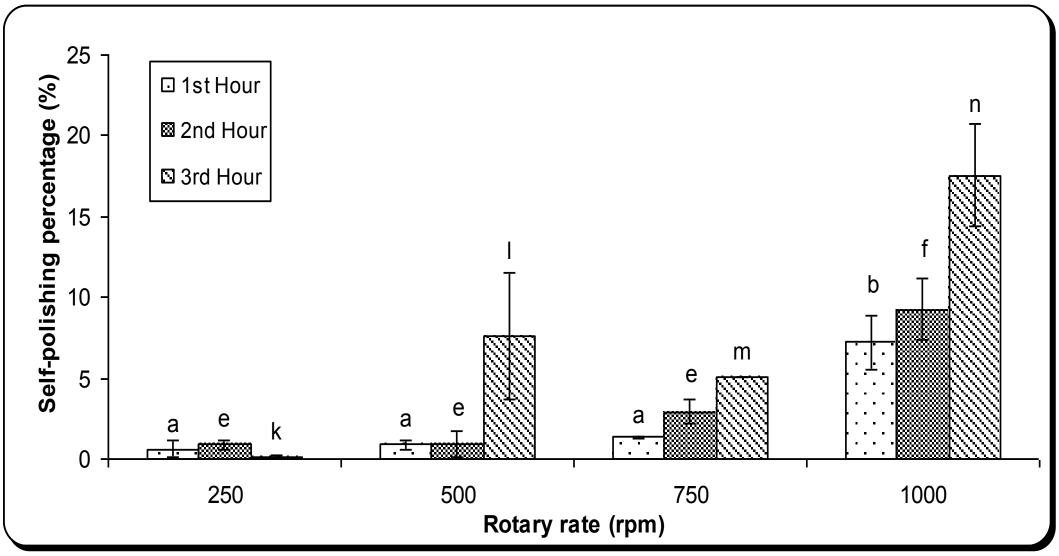


Figure 3.14 Effect of rotary rate on the self-polishing percentage of fibre reinforced lanolin based material which contains %0.5 fiber 1 (w/w) at 40 ^{o}C.

Table 3.10 The images of the 0.5% Fiber 1 reinforced lanolin based material covered glass slides at 40 ^{o}C, after 1 hour.

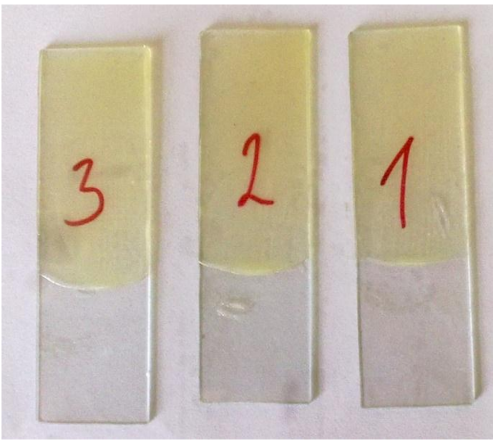
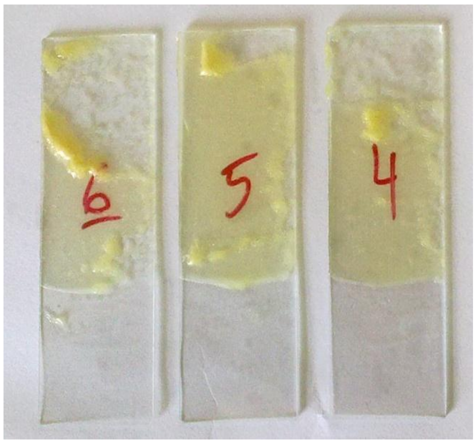
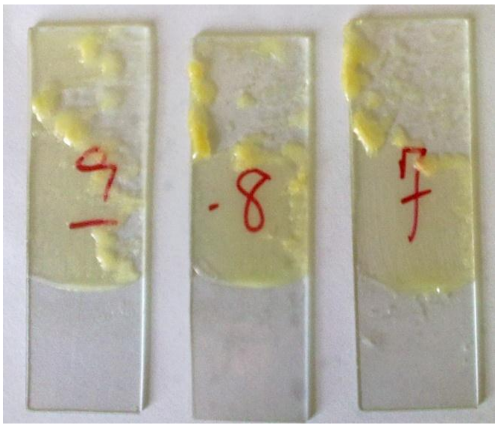
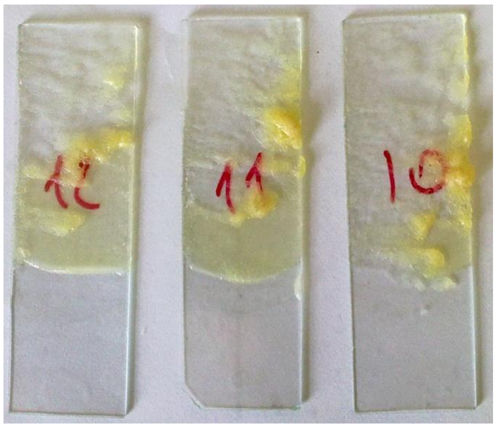
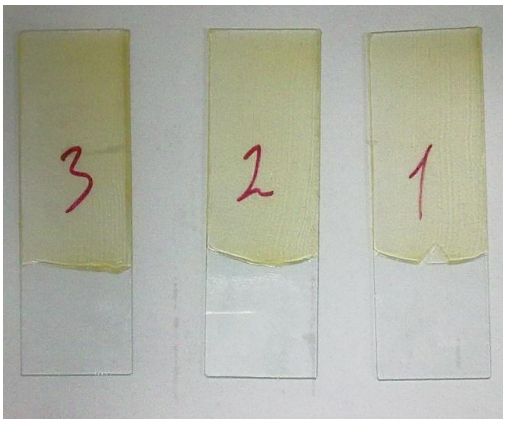
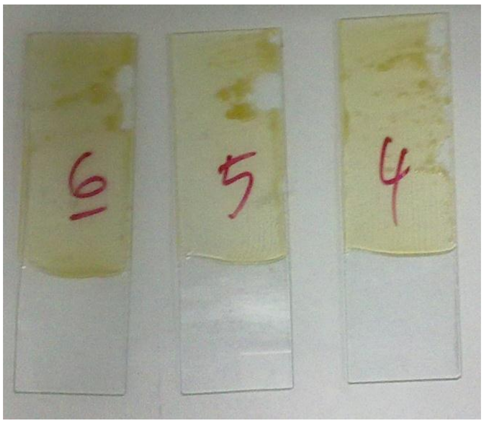
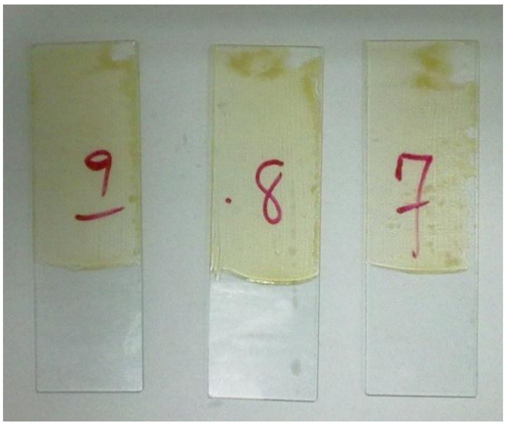
 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

Table 3.11 The images of the 0.5% Fiber 1 reinforced lanolin based material covered glass slides at 40 ^{o}C, after 2 hours.

<table>
<tr>
<td>

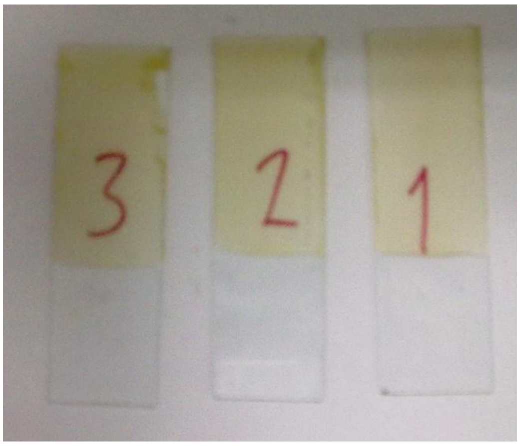
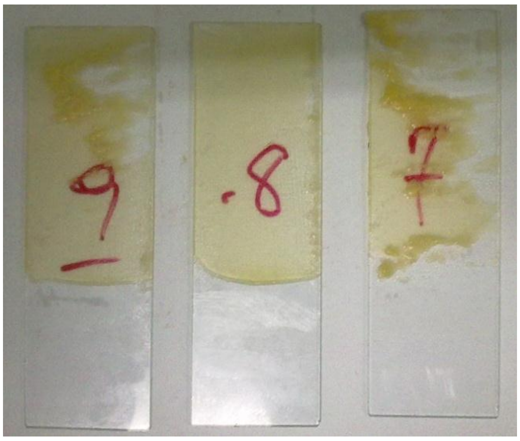
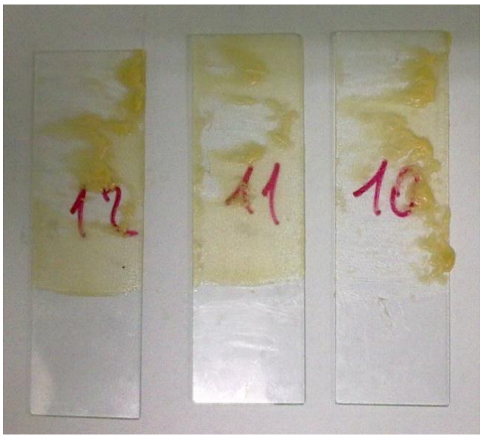
A. 250 rpm</td>
<td>

B. 500 rpm</td>
</tr>
<tr>
<td>

C. 750 rpm</td>
<td>

D. 1000 rpm</td>
</tr>
</table>

Table 3.12 The images of the 0.5% Fiber 1 reinforced lanolin based material covered glass slides at 40 ^{o}C, after 3 hours.

 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

The effect of experimental conditions on the self-polishing percentage of 0.5% Fibre 1 (w/w) reinforced lanolin based material was presented in Fig. 3.15. As it can be seen from this figure, self-polishing percentages were increased with the rotary rate. Table 3.13, 3.14 and 3.15 show that the images list of the 0.5% Fibre 1 (w/w) reinforced lanolin based material after the rotary test which 1, 2 and 3 hour respectively. Comparison with the other ratio of Fibre 1 (1%), the results was found that worse than the 1% Fibre 2 (w/w) reinforced lanolin based material. Statistically, there was no any significantly differences between the all rotary rate in 1st hour ($p>0.05$). The max self-polishing percentage was determined from the 3 hour and 1000 rpm.

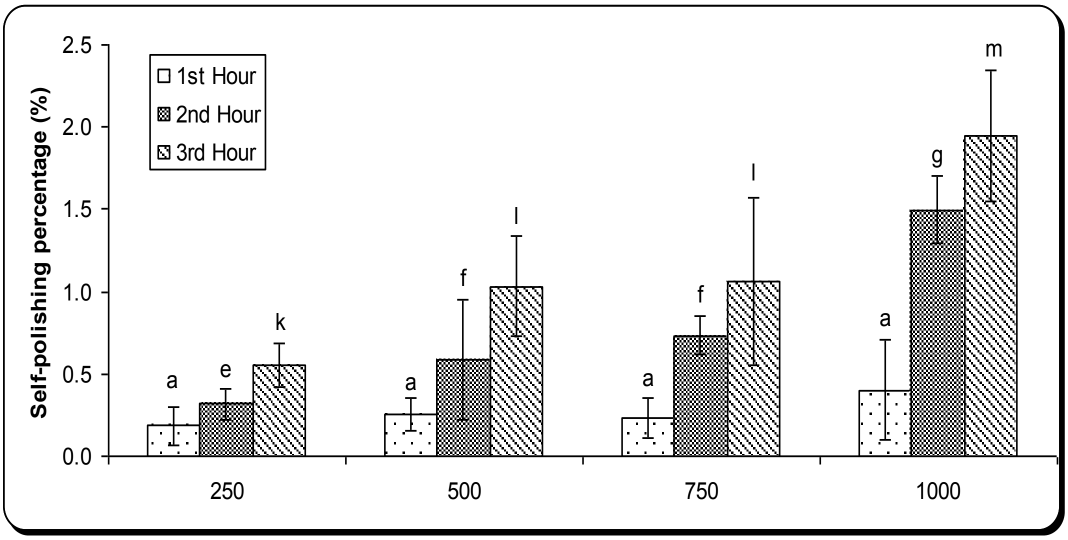
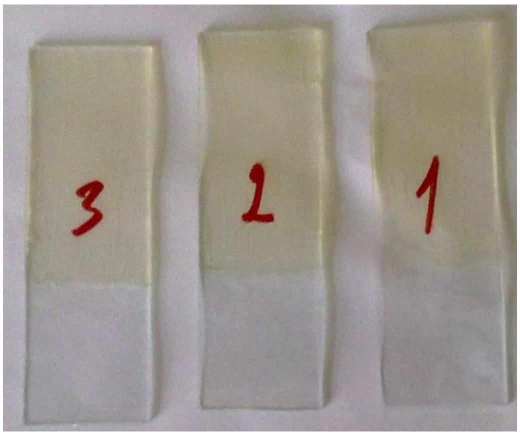
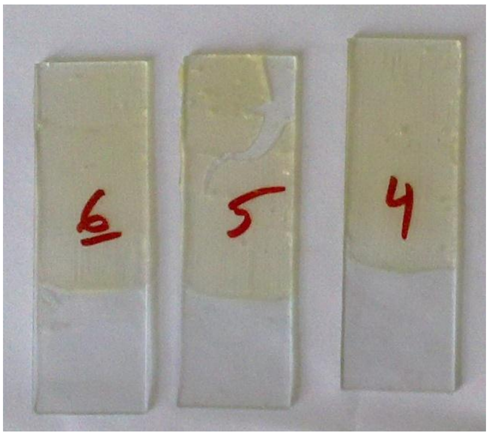


Figure 3.15 Effect of rotary rate on the self-polishing percentage of fibre reinforced lanolin based material which contains %0.5 fiber 1 (w/w) at 30 ^{o}C.

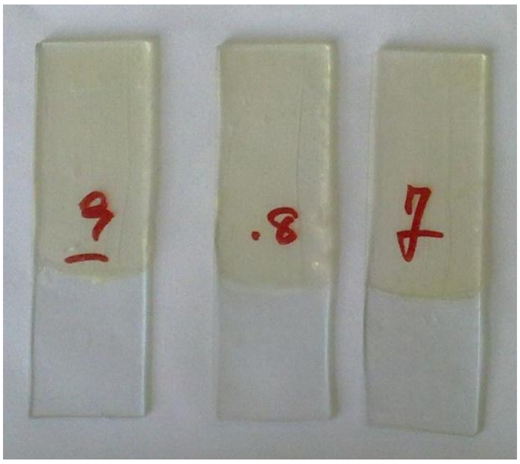
Table 3.13 The images of the 0.5% Fiber 1 reinforced lanolin based material covered glass slides at 30 ^{o}C, after 1 hour.



A. 250 rpm



B. 500 rpm



C. 750 rpm

D. 1000 rpm

Table 3.14 The images of the 0.5% Fiber 1 reinforced lanolin based material covered glass slides at 30 ^{o}C, after 2 hours.

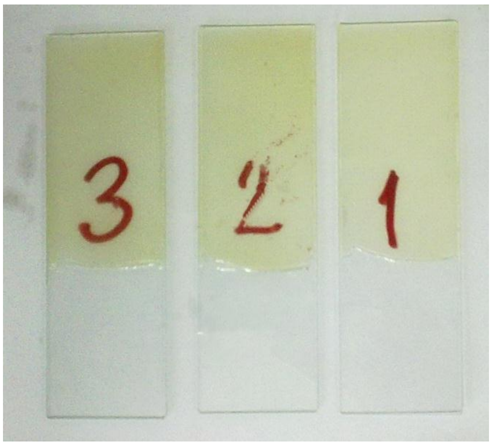
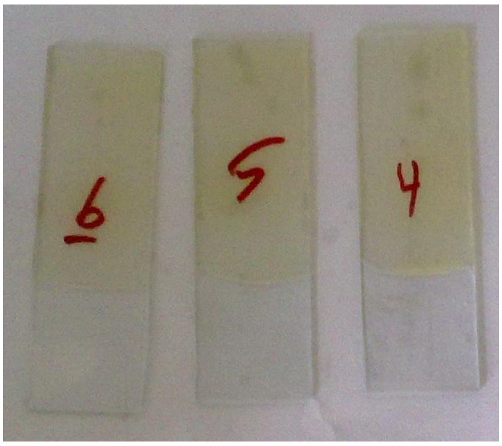
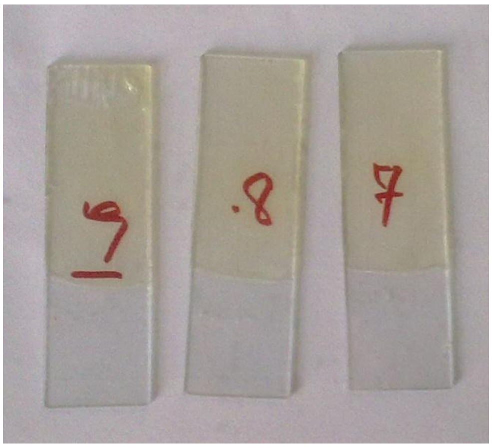
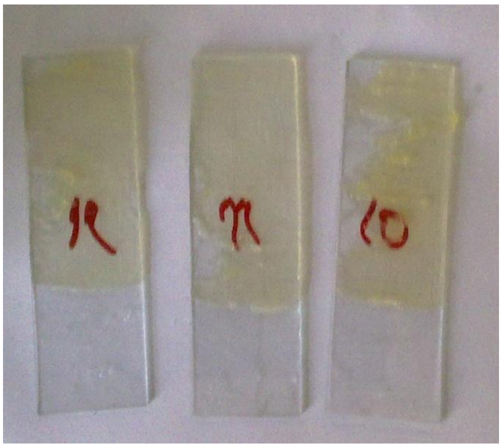
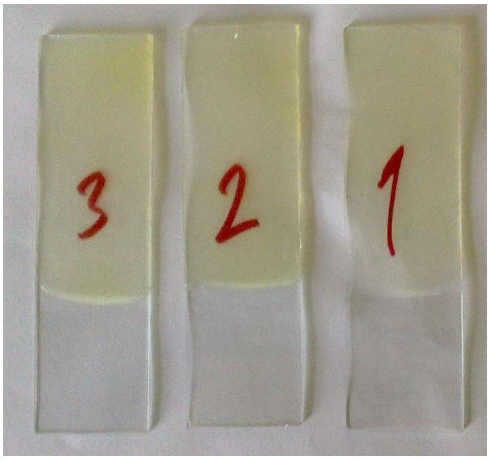
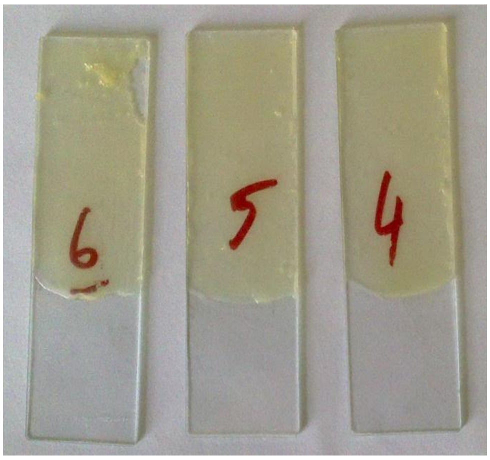
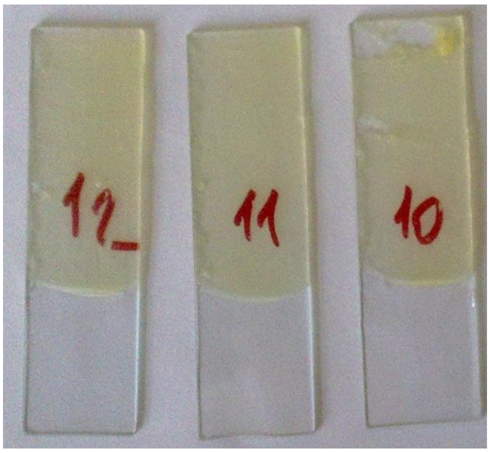
 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

Table 3.15 The images of the 0.5% Fiber 1 reinforced lanolin based material covered glass slides at 30 ^{o}C, after 3 hours.

 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

At 30 ^{o}C the self-polishing percentages of the 0.5% Fiber 2 (w/w) reinforced lanolin based material was shown in Fig. 3.16 and the effect of rotary rate on glass slides was presented in Table 3.16, 3.17 and 3.18. Although the results of 250 and 500 rpm rotary rate were observed low self-polishing percentage, conversely the percentage of 750 and 1000 rpm were found quite high. In Table 3.16, it can be seen that the surfaces of 250 and 500 rpm are quite smooth. However, this smoothness was not observed on the surfaces of 750 and 1000 rpm. Table 3.17 shows that, except for the surfaces of 250 rpm the fibre reinforced lanolin based material covered glass slides have roughness in the all rotary rate.

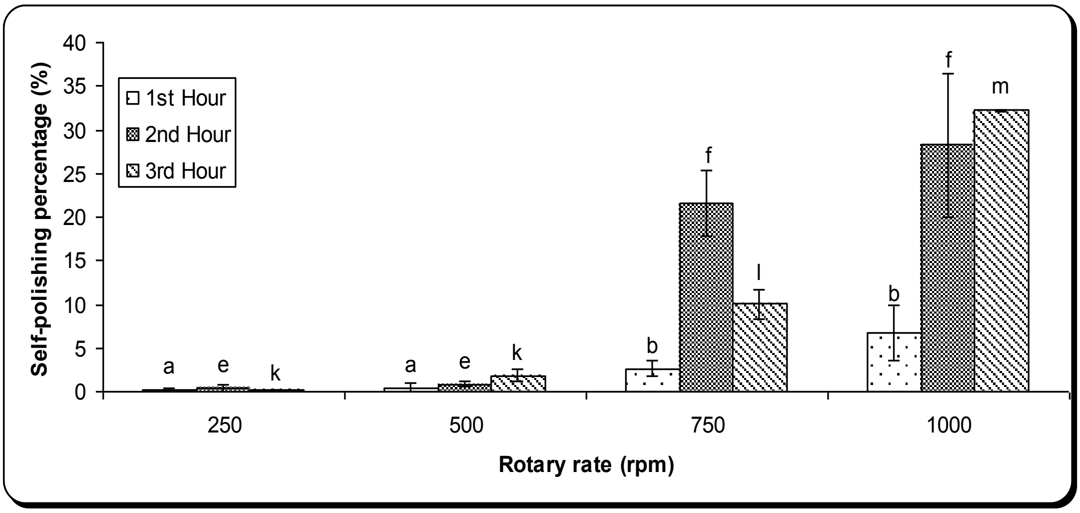


Figure 3.16 Effect of rotary rate on the self-polishing percentage of fibre reinforced lanolin based material which contains %0.5 fiber 2 (w/w) at 30 ^{o}C.

Table 3.16 The images of the 0.5% Fiber 2 reinforced lanolin based material covered glass slides at 30 ^{o}C, after 1 hour.

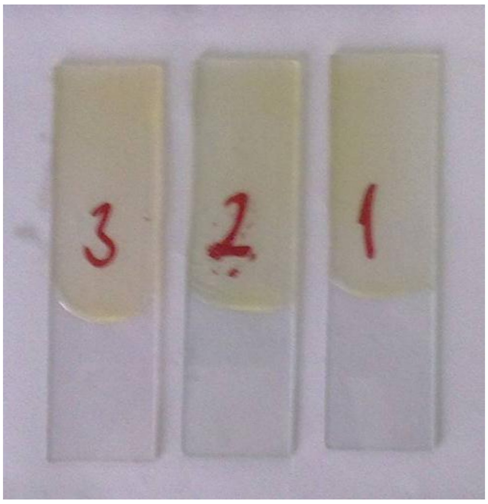
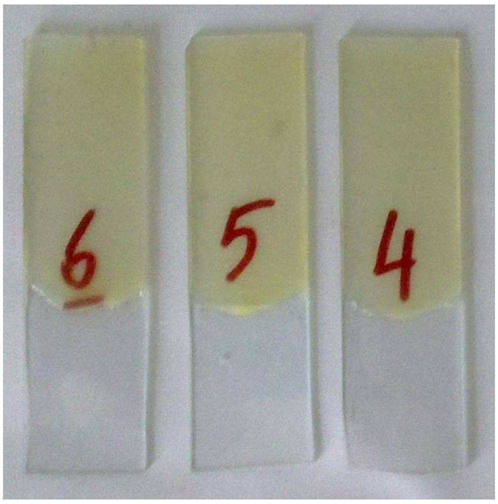
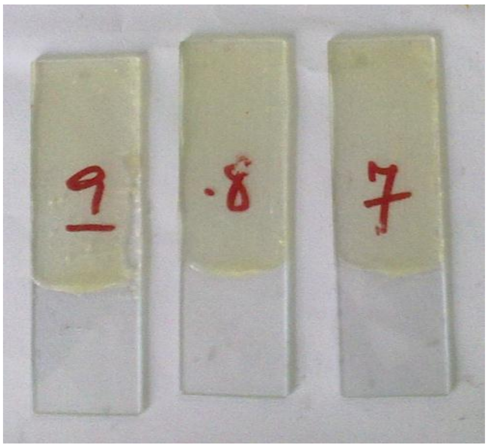
 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

Table 3.17 The images of the 0.5% Fiber 2 reinforced lanolin based material covered glass slides at 30 ^{o}C, after 2 hours.

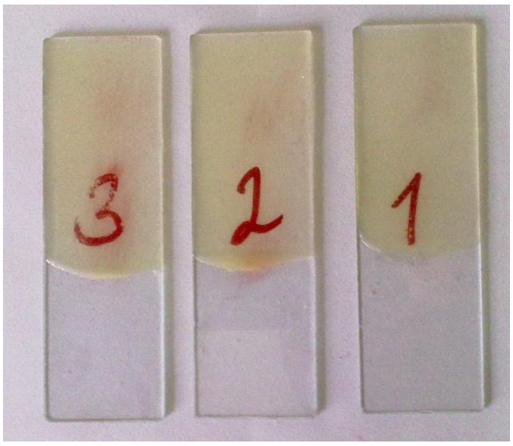
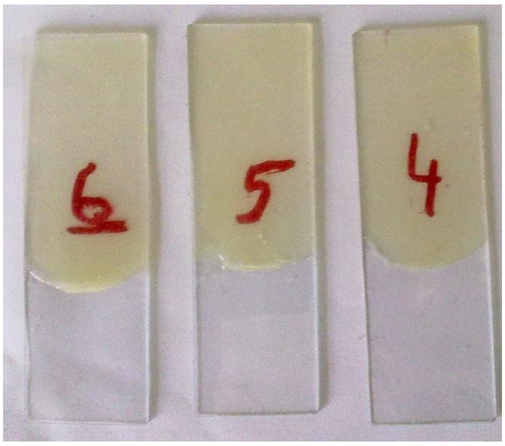
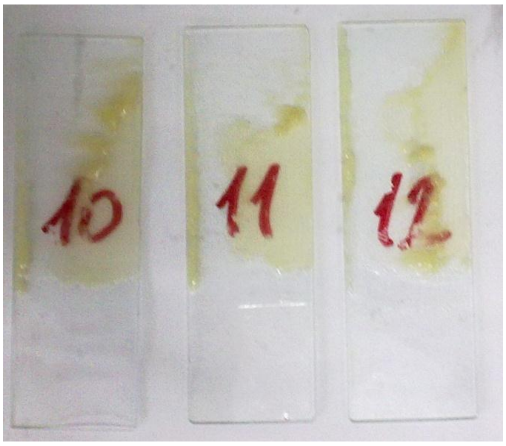
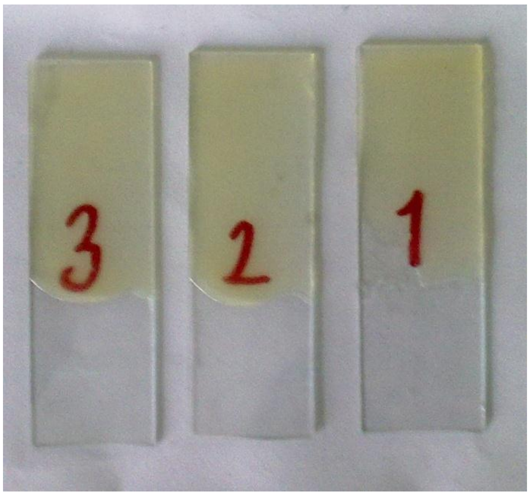
 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

Table 3.18 The images of the 0.5% Fiber 2 reinforced lanolin based material covered glass slides at 30 ^{o}C, after 3 hours.

<table>
<tr>
<td>

A. 250 rpm</td>
<td>

B. 500 rpm</td>
</tr>
<tr>
<td>

C. 750 rpm</td>
<td>

D. 1000 rpm</td>
</tr>
</table>

The self-polishing percentages of the 0.5% Fiber 2 (w/w) reinforced lanolin based material were presented in Fig. 3.17 at 40 ^{o}C and Table 3.19, 3.20 and 3.21 show that the images of the 0.5% Fiber 2 (w/w) reinforced lanolin based material covered glass slides after the self-polishing tests, respectively. In these results, the min and max self-polishing percentages were observed in 250 rpm rotary rate – 1 hour rotary time and 1000 rpm rotary rate – 3 hours rotary time respectively.

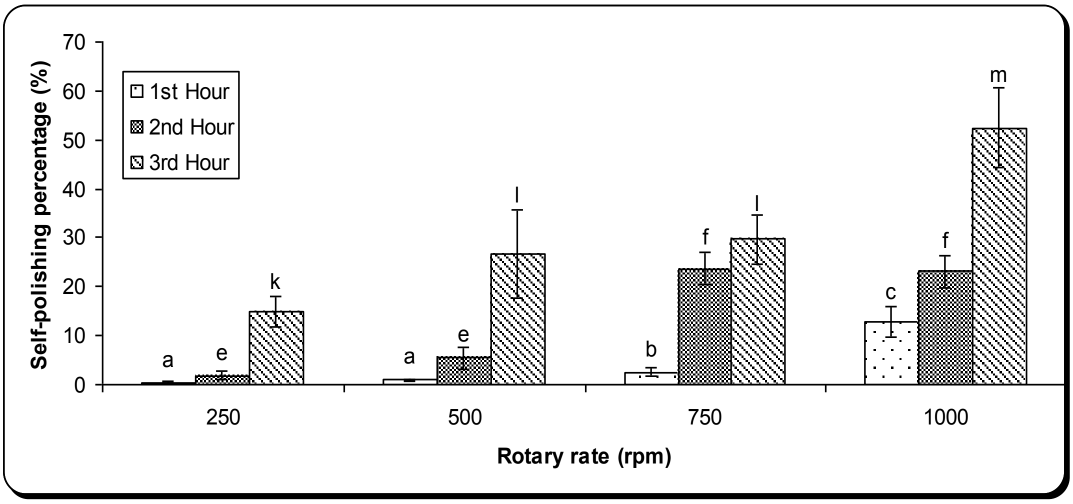


Figure 3.17 Effect of rotary rate on the self-polishing percentage of fibre reinforced lanolin based material which contains %0.5 fiber 2 (w/w) at 40 ^{o}C.

Table 3.19 The images of the 0.5 % Fiber 2 reinforced lanolin based material covered glass slides at 40 ^{o}C, after 1 hour.

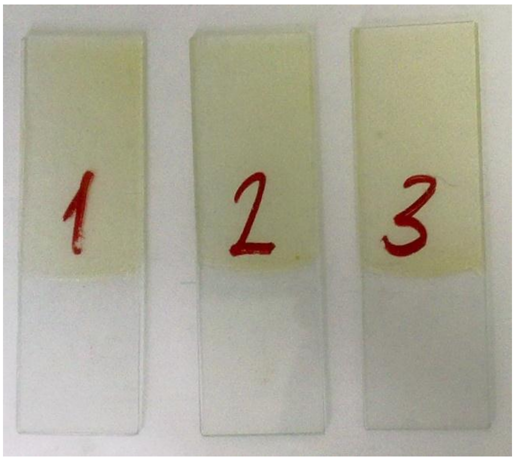
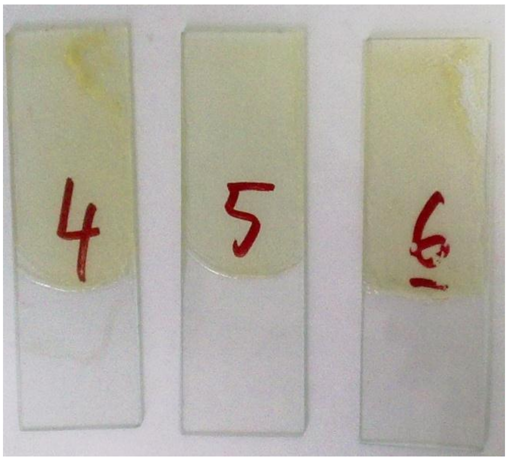
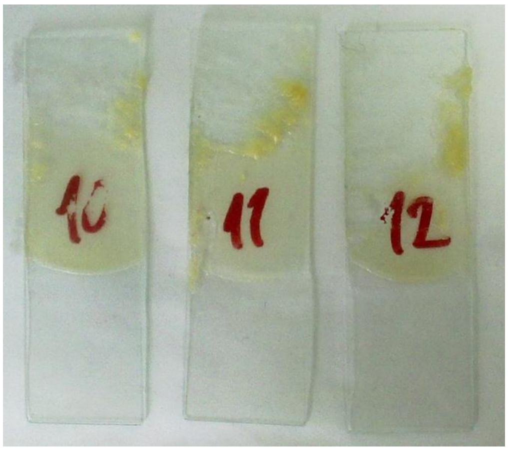
 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

Table 3.20 The images of the 0.5 % Fiber 2 reinforced lanolin based material covered glass slides at 40 ^{o}C, after 2 hours.

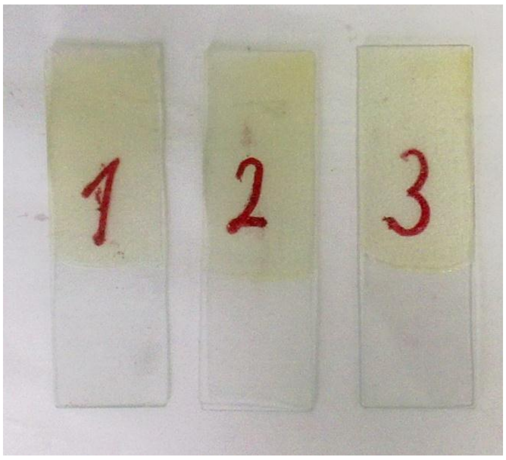
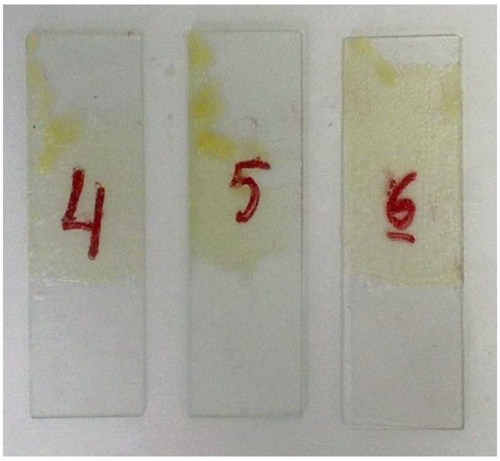
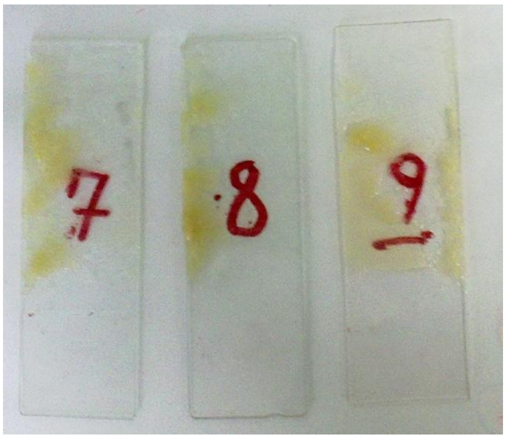
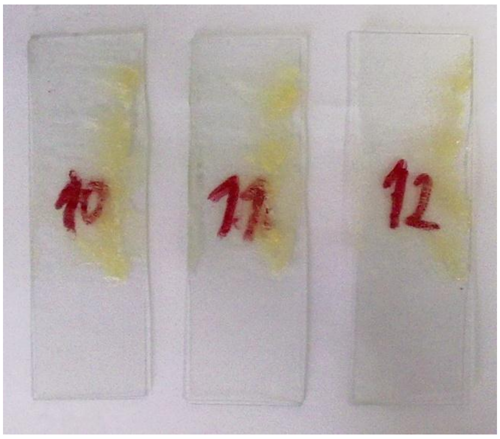
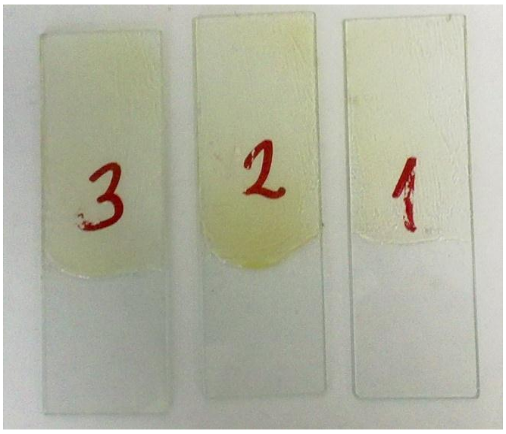
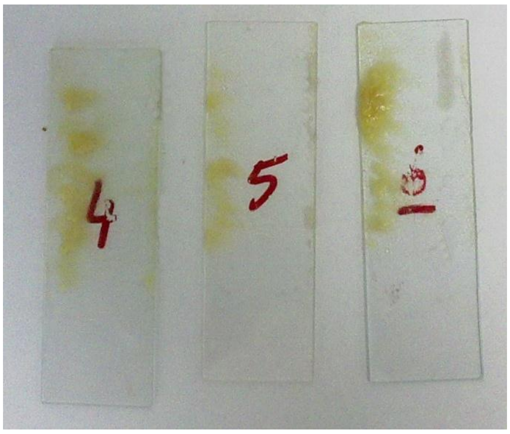
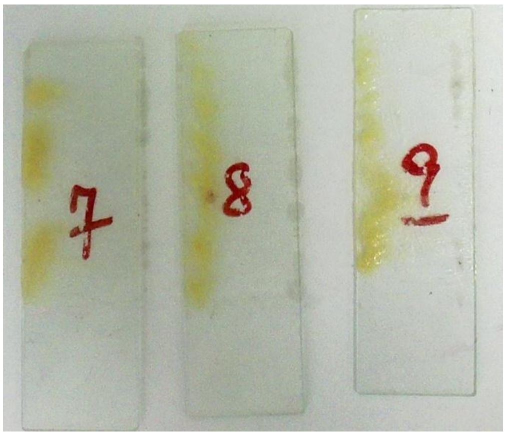
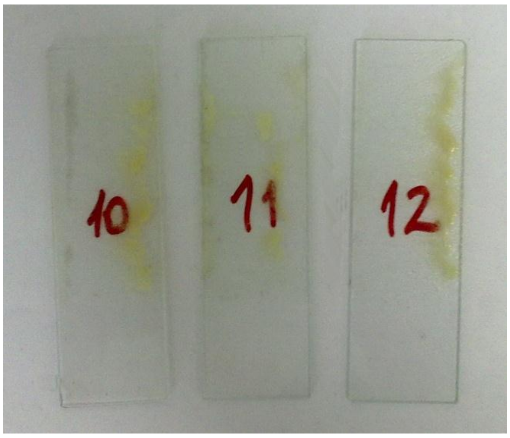
 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

Table 3.21 The images of the 0.5 % Fiber 2 reinforced lanolin based material covered glass slides at 40 ^{o}C, after 3 hours.

 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

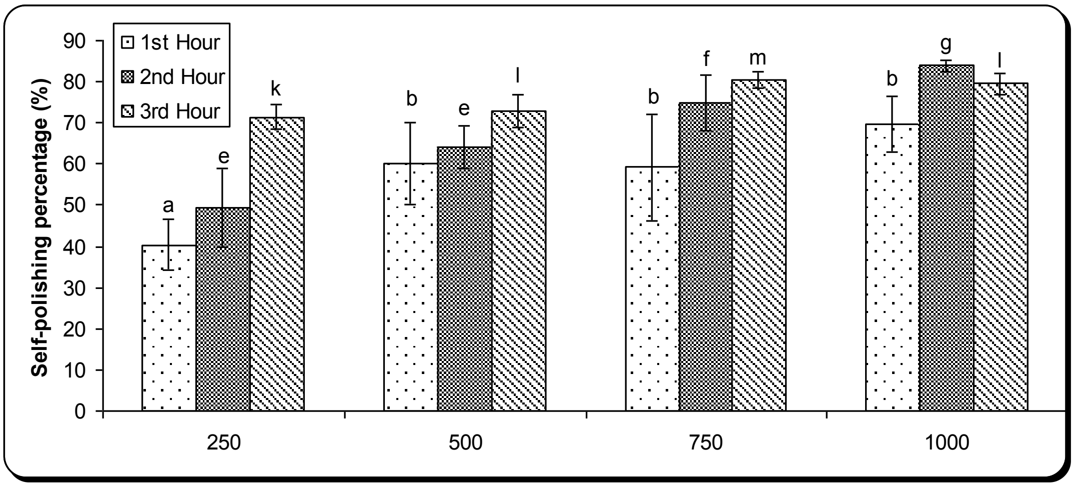


Figure 3.18 Effect of rotary rate on the self-polishing percentage of fibre reinforced lanolin based material which contains %0.5 fiber 2 (w/w) at 50 ^{o}C.

Table 3.22 The images of the 0.5 % Fiber 2 reinforced lanolin based material covered glass slides at 50 ^{o}C, after 1 hour.

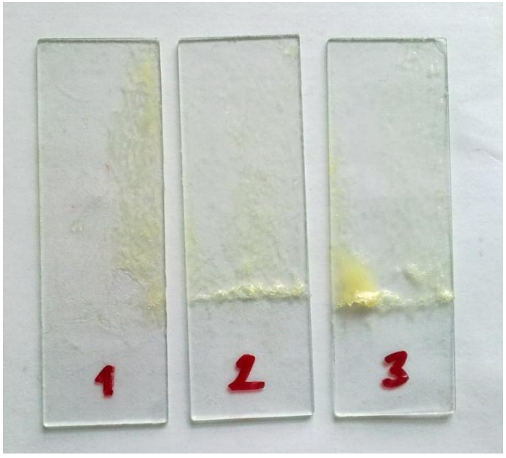
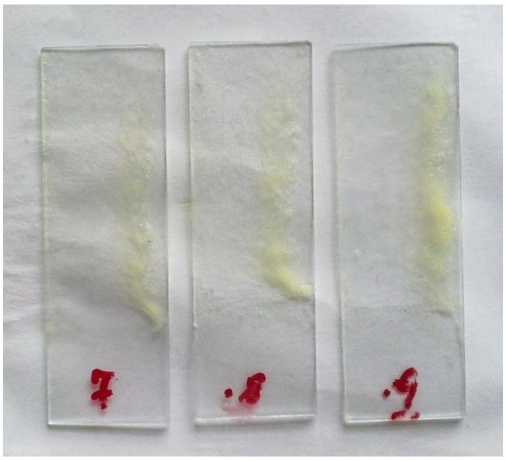
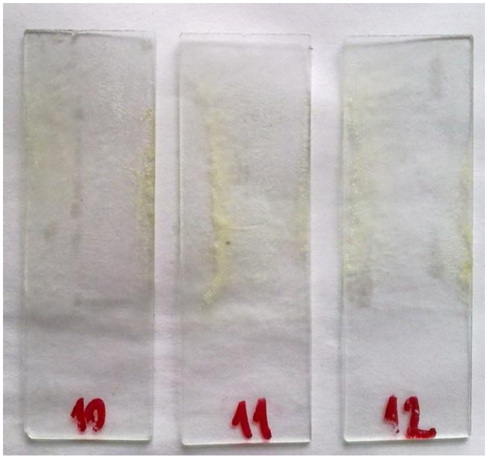
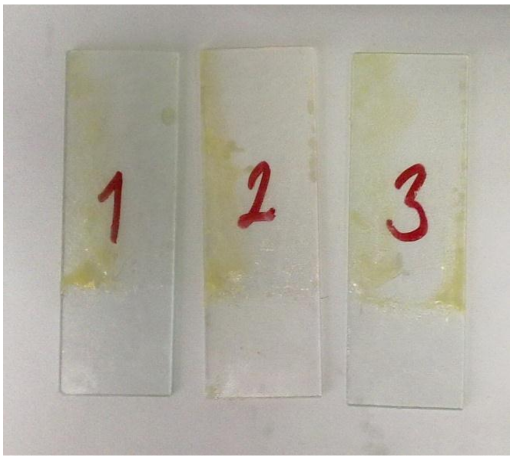
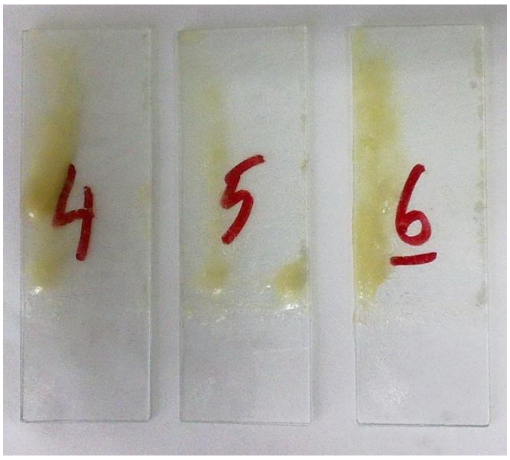
 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

Table 3.23 The images of the 0.5 % Fiber 2 reinforced lanolin based material covered glass slides at 50 ^{o}C, after 2 hours.

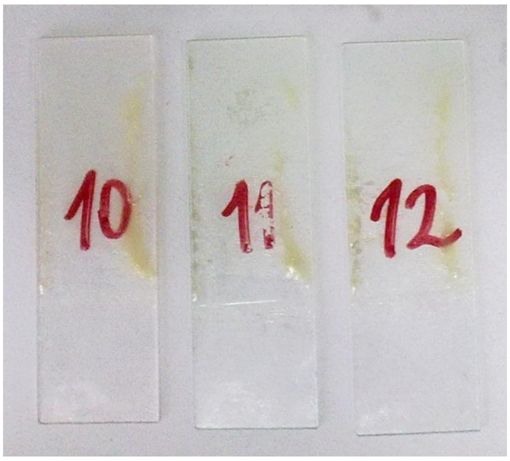


A. 250 rpm



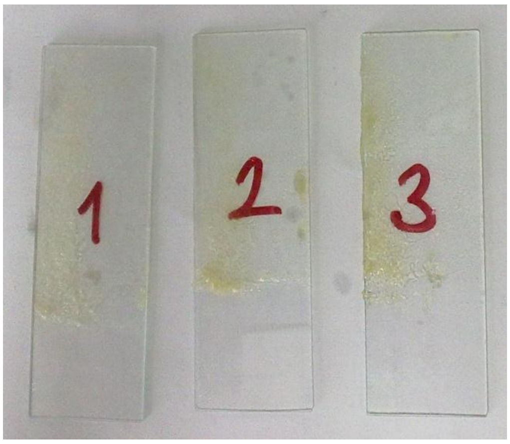
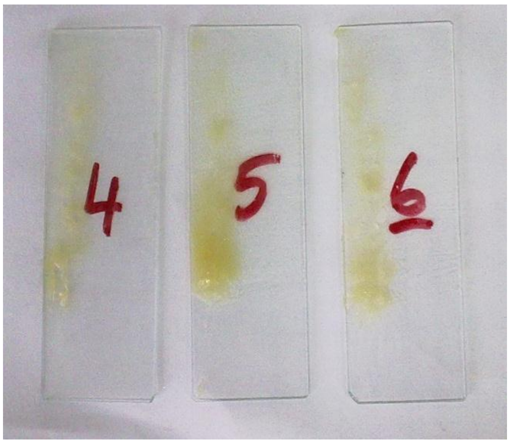
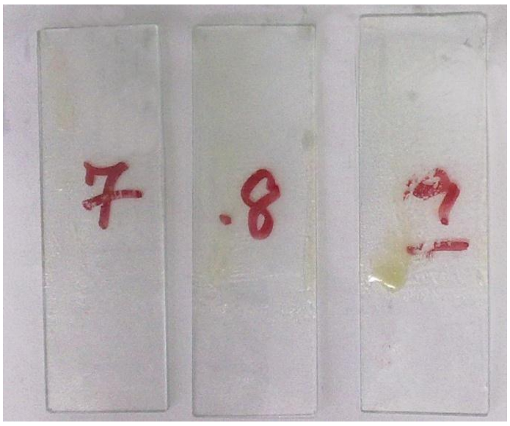
B. 500 rpm

C. 750 rpm



D. 1000 rpm

Table 3.24 The images of the 0.5 % Fiber 2 reinforced lanolin based material covered glass slides at 50 ^{o}C, after 3 hours.

 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

The self-polishing results of 1% Fibre 2 (w/w) reinforced lanolin based material were determined by rotary tests and results were depicted in Fig. 19. Results were indicated that 250 and 500 rpm rotary rate have approximately same self-polishing percentage, nevertheless, 750 and 1000 rpm have different self-polishing percentages from the other and 250, 500 and 750 rpm rotary rates have not remarkably differences ($p<0.05$). On the other hand, 1000 rpm rotary rate was statistically different from the other experimental conditions. The results of self-polishing test were presented in Table 3.25, 3.26 and 3.27. According to the these tables, the surfaces of the all the 250 and 500 rpm rotary rate results were quite smooth and have low self-polishing percentage. However, results of the other conditions which were 750 and 1000 rpm were observed highly roughness exclusive of 750 rpm 1 hour.

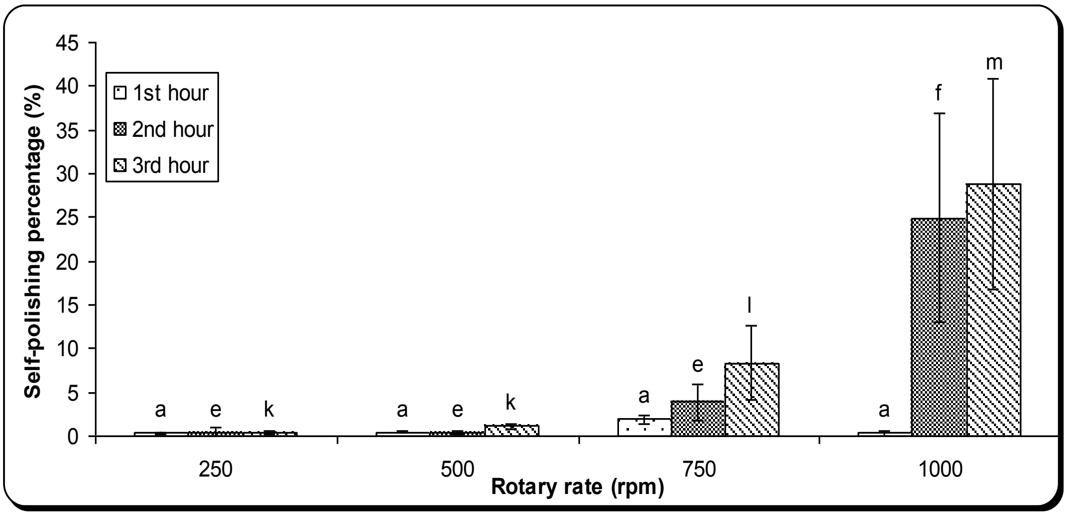


Figure 3.19 Effect of rotary rate on the self-polishing percentage of fibre reinforced lanolin based material which contains %1 fiber 2 (w/w) at 30 ^{o}C.

Table 3.25 The images of the 1% Fiber 2 reinforced lanolin based material covered glass slides at 30 ^{o}C, after 1 hour.

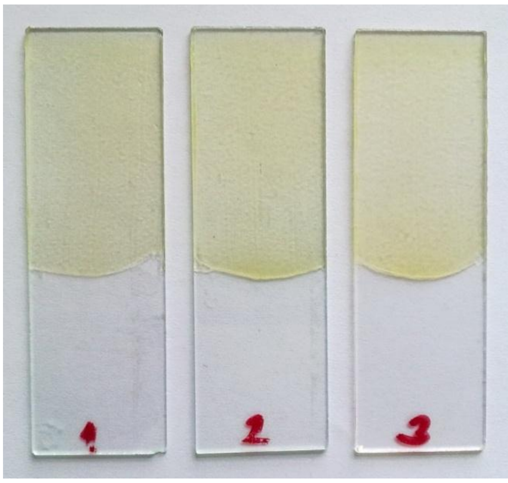
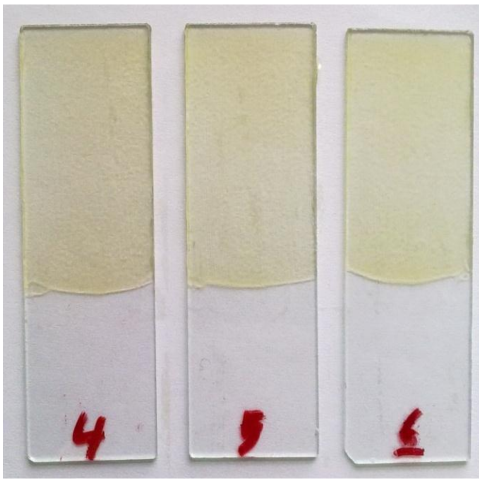
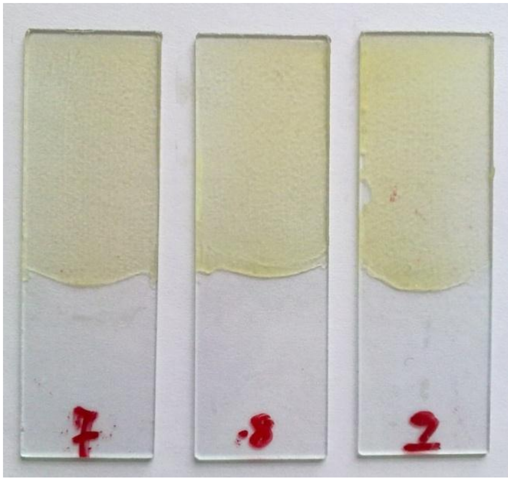
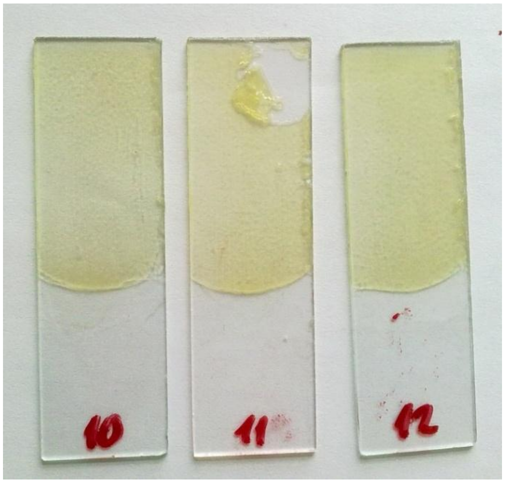
 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

Table 3.26 The images of the 1% Fiber 2 reinforced lanolin based material covered glass slides at 30 ^{o}C, after 2 hours.

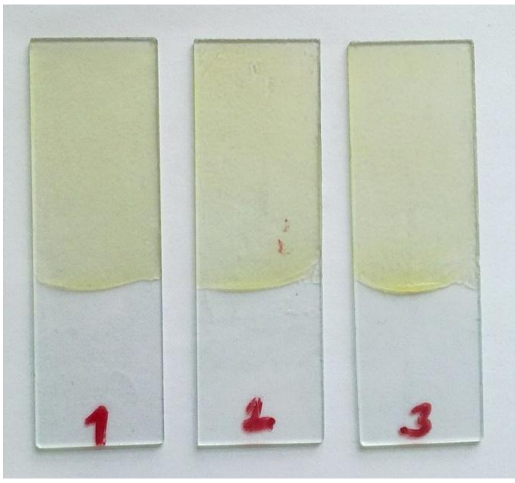
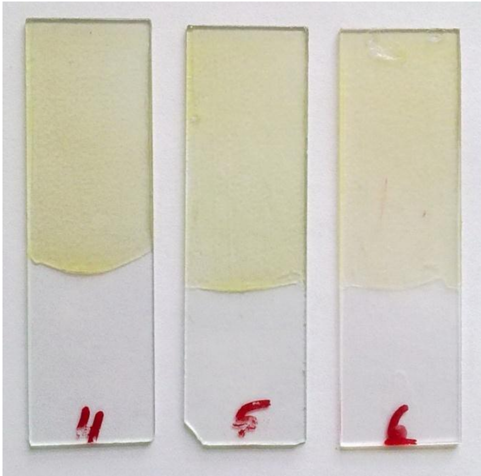
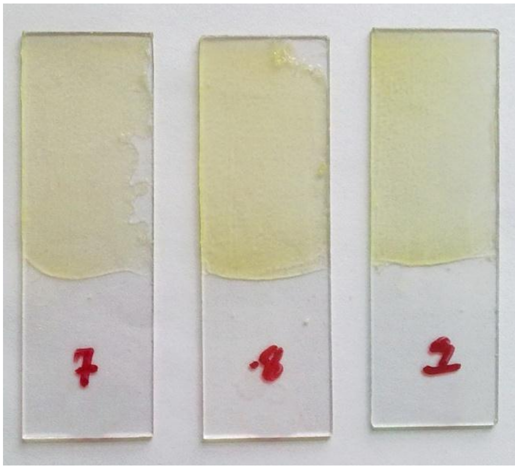
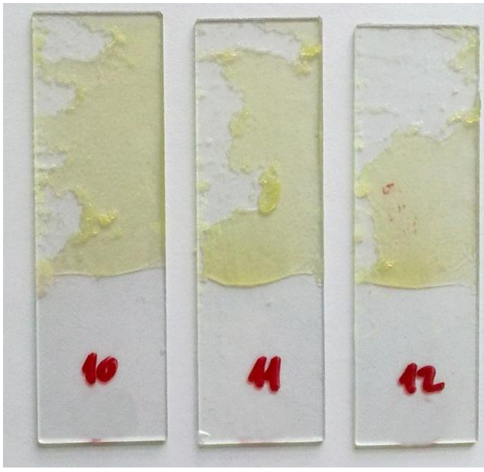
 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

Table 3.27 The images of the 1% Fiber 2 reinforced lanolin based material covered glass slides at 30 ^{o}C, after 3 hours.

<table>
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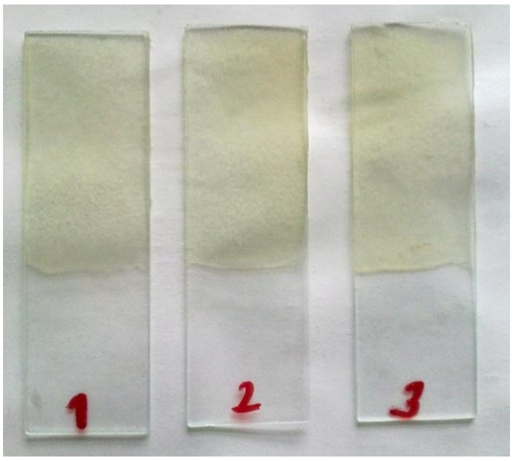
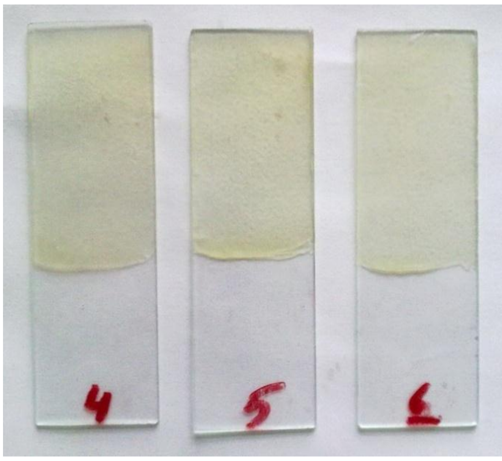
<td>

A. 250 rpm</td>
<td>

B. 500 rpm</td>
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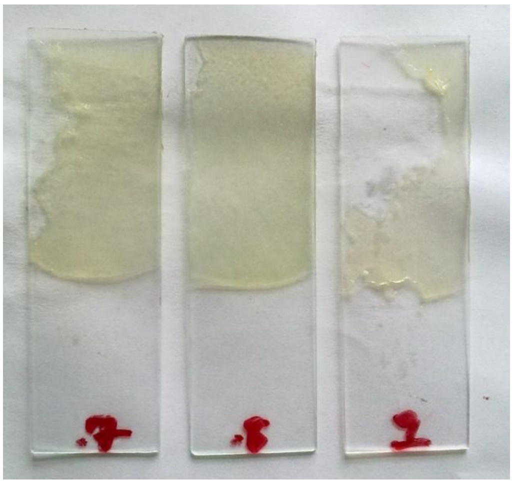
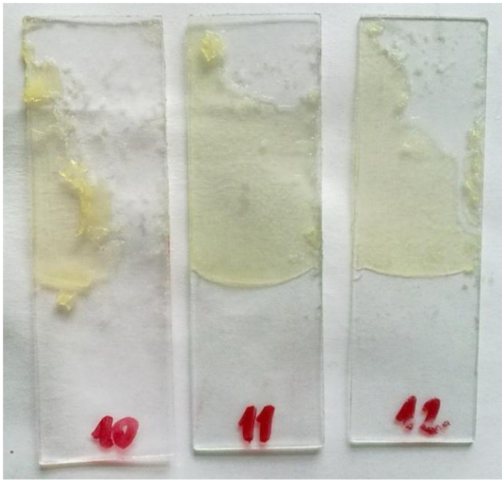
<td>

C. 750 rpm</td>
<td>

D. 1000 rpm</td>
</tr>
</table>

Fig. 3.20 depicted that the self-polishing percentage of the 1% Fibre 2 (w/w) reinforced lanolin based material covered glass slides at 40 °C artificial seawater. There is no doubt that the self-polishing percentages increased with the rotary rate effect 250-1000 rpm. However, the results of the 750 and 1000 rpm rotary rate have approximately same self-polishing percentages all of the rotary time in Fig. 3.20. The 1% Fibre 2 (w/w) reinforced lanolin based material covered glass slides also shown in Table 3.28, 3.29 and 3.30 after the self-polishing test 1-3 hour. Statistically, there were not any crucial differences among the 500, 750 and 1000 rpm in 1 hour rotary rate experiment and according to these result, 250 rpm was statistically different from them.

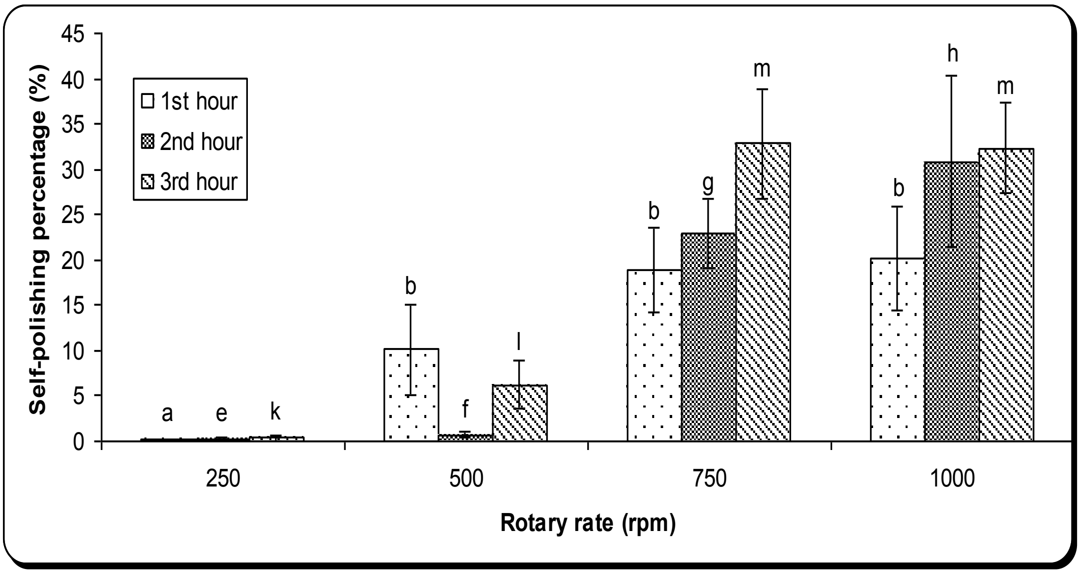


Figure 3.20 Effect of rotary rate on the self-polishing percentage of fibre reinforced lanolin based material which contains %1 fiber 2 (w/w) at 40 °C.

Table 3.28 The images of the 1% Fiber 2 reinforced lanolin based material covered glass slides at 40 ^{o}C, after 1 hour.

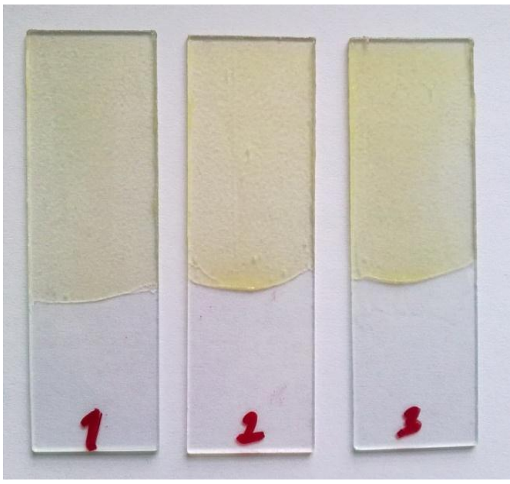
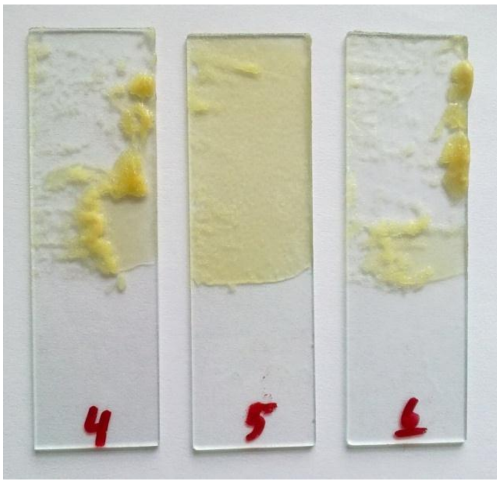
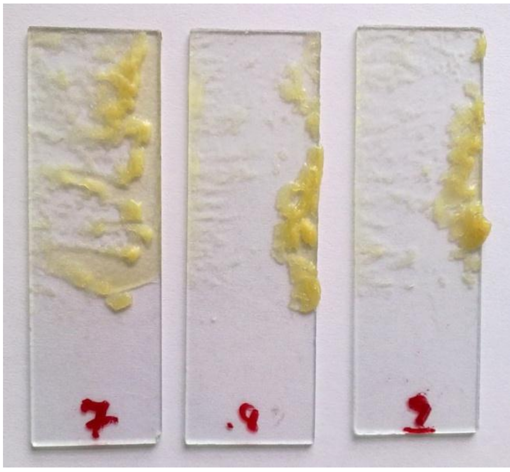
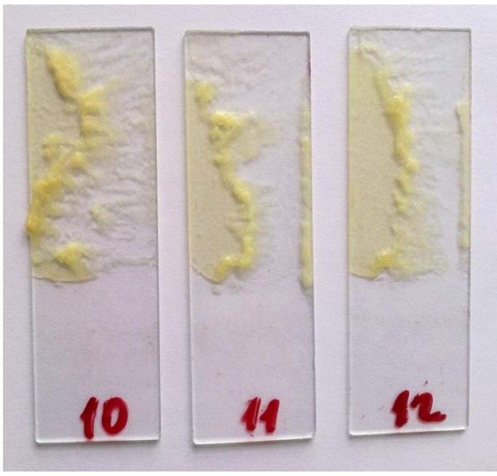
 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

Table 3.29 The images of the 1% Fiber 2 reinforced lanolin based material covered glass slides at 40 ^{o}C, after 2 hours.

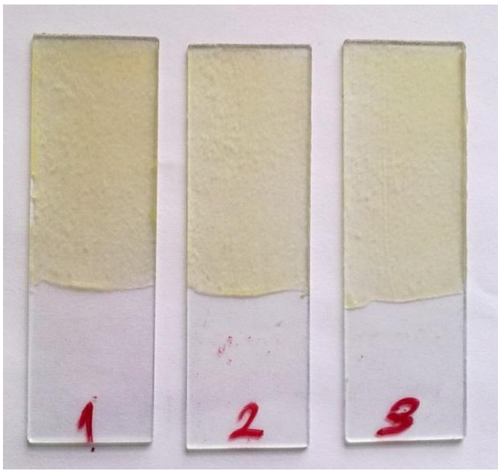
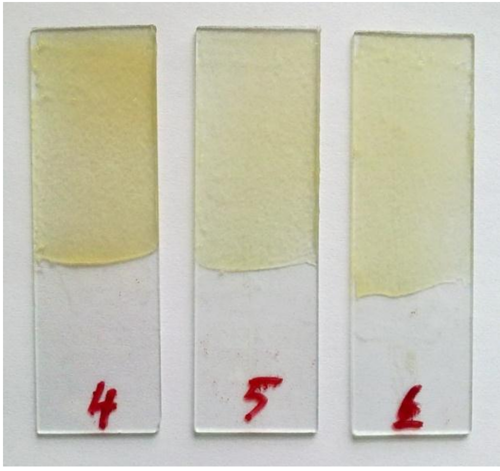
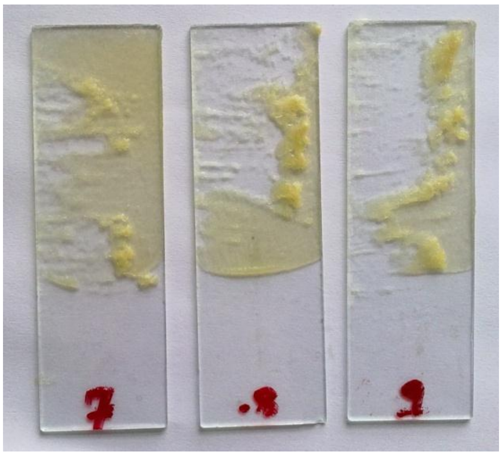
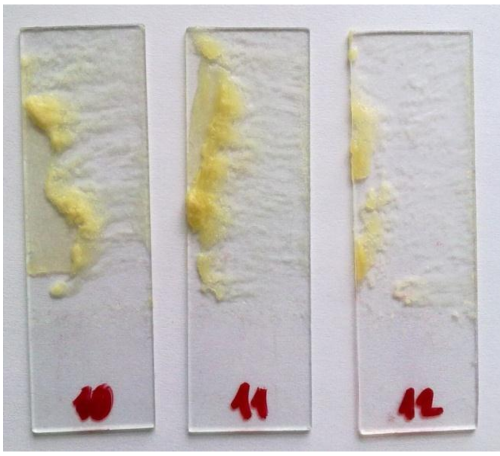
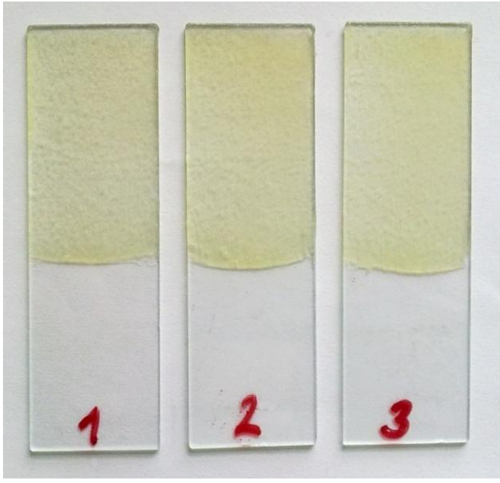
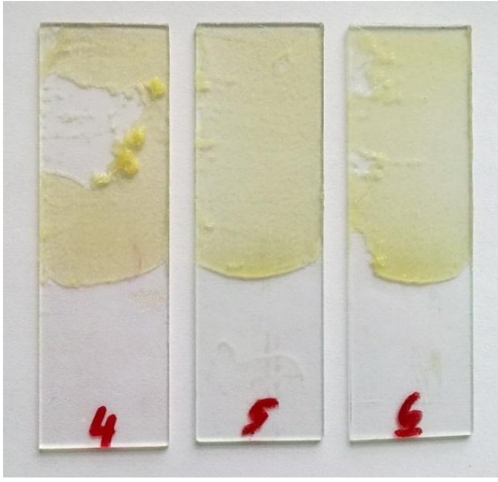
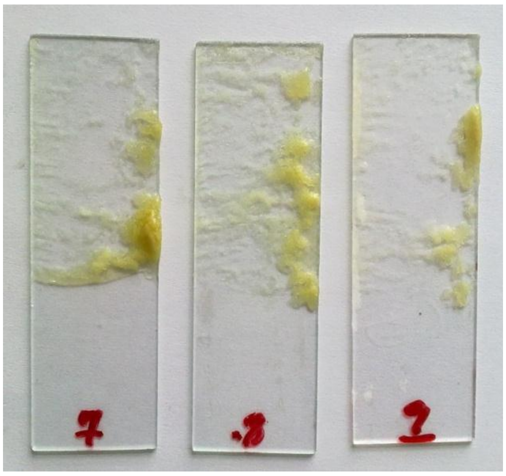
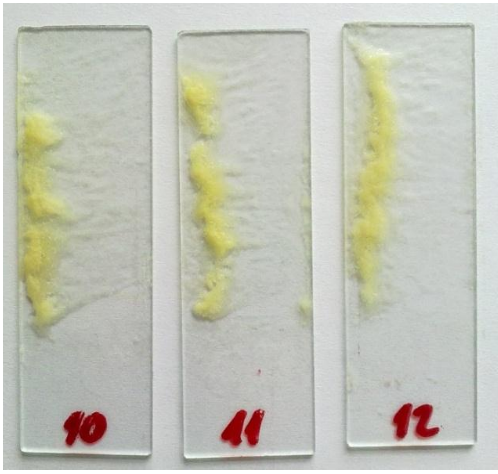
 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

Table 3.30 The images of the 1% Fiber 2 reinforced lanolin based material covered glass slides at 40 ^{o}C, after 3 hours.

 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

The self-polishing percentages of the fibre reinforced lanolin based material which contains 1% Fiber 2 (w/w) were appeared in Fig. 3.21 and the images of the 1% Fiber 2 (w/w) reinforced lanolin based material covered glass slides after the self-polishing test were presented in Table 3.28, 3.29 and 3.30. Considering the Fig. 3.21 and all of these tables, the self-polishing percentages were evaluated quite high values (50-90 %). According to the Table 3.31, 3.32 and 3.33, the results indicated that the 1% Fiber 2 (w/w) reinforced lanolin based material were melted and leaved out from the lanolin based material covered glass slides.

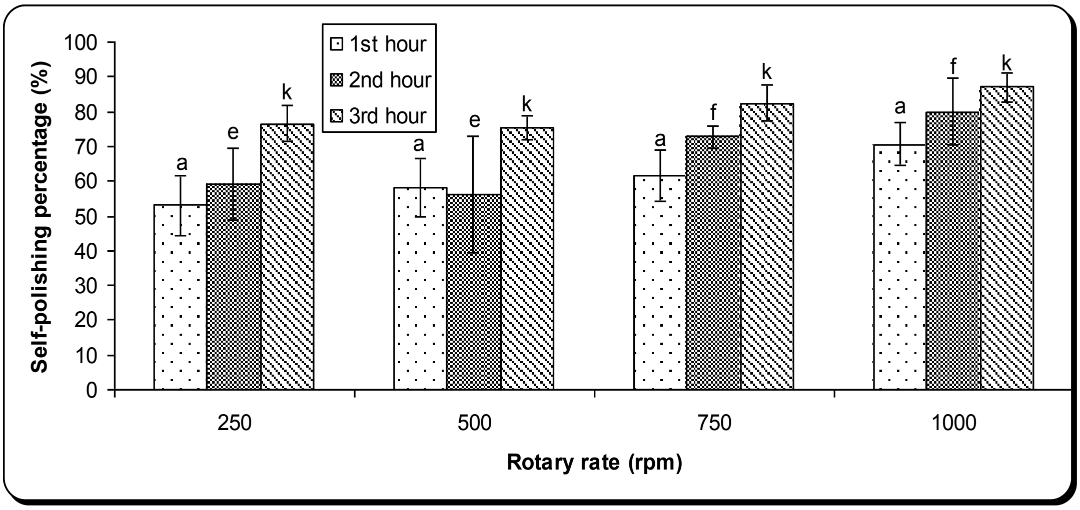
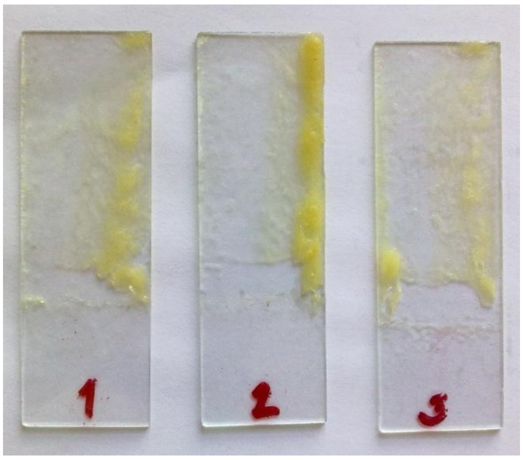
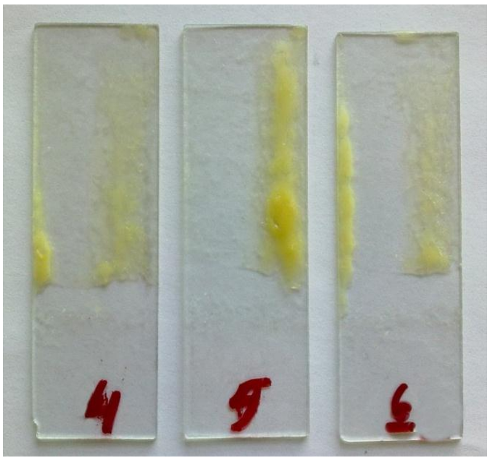


Figure 3.21 Effect of rotary rate on the self-polishing percentage of fibre reinforced lanolin based material which contains %1 fiber 2 (w/w) at 50 ^oC.

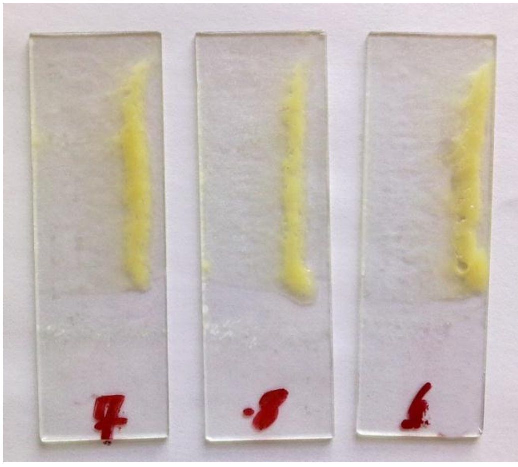
Table 3.31 The images of the 1% Fiber 2 reinforced lanolin based material covered glass slides at 50 ^{o}C, after 1 hour.



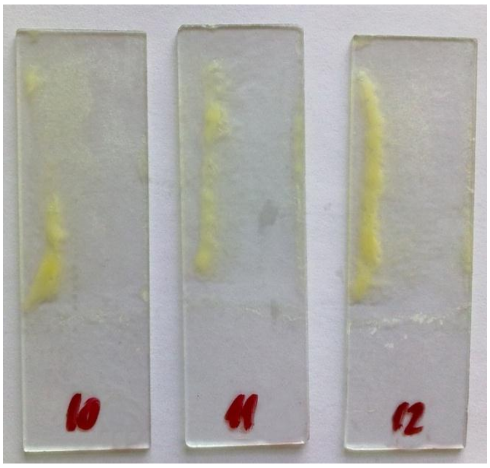
A. 250 rpm



B. 500 rpm

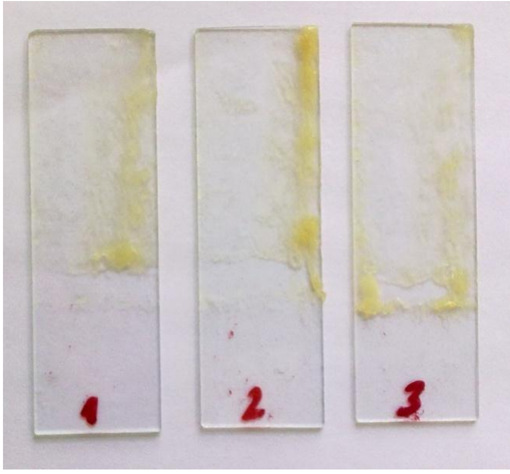


C. 750 rpm

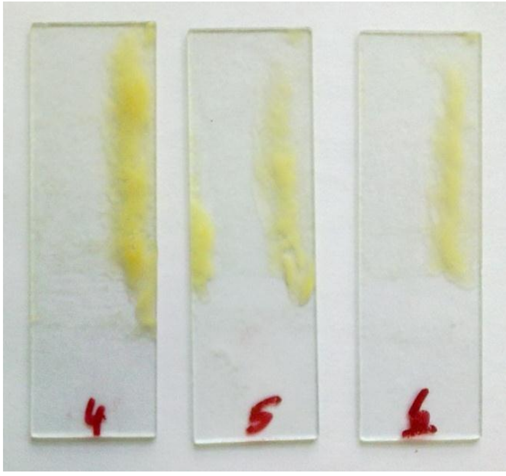


D. 1000 rpm

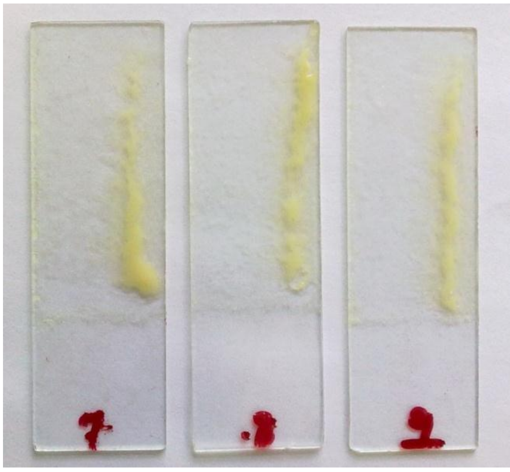
Table 3.32 The images of the 1% Fiber 2 reinforced lanolin based material covered glass slides at 50 ^{o}C, after 2 hours.



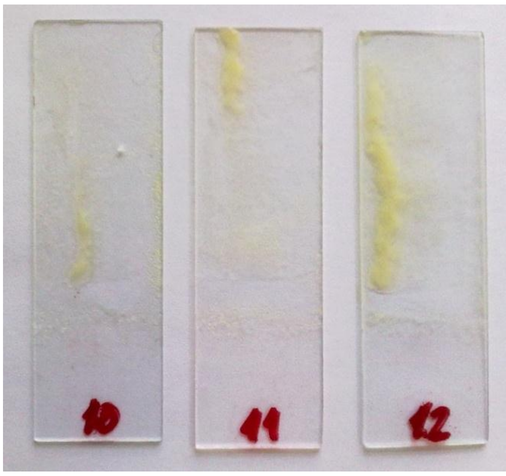
A. 250 rpm



B. 500 rpm

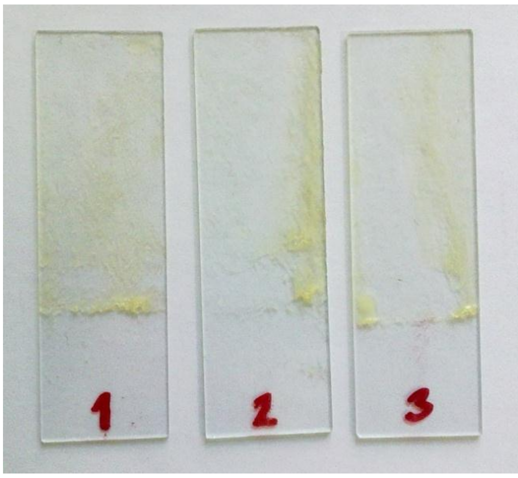
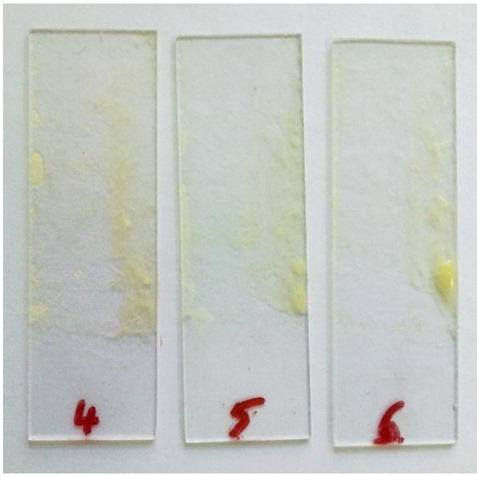
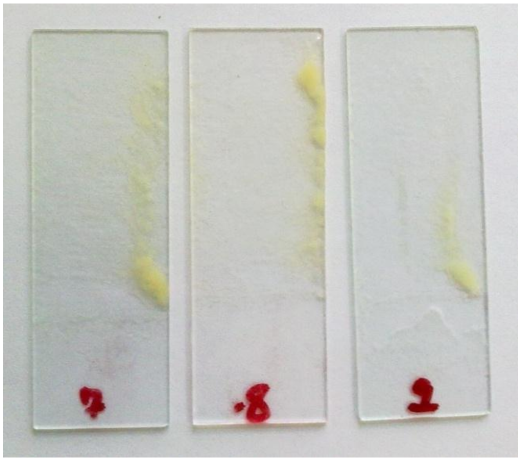
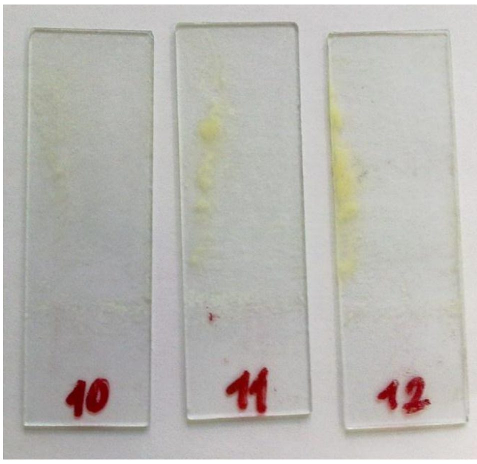


C. 750 rpm



D. 1000 rpm

Table 3.33 The images of the 1% Fiber 2 reinforced lanolin based material covered glass slides at 50 ^{o}C, after 3 hours.

 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

3.2 three-way ANOVA results

Table 3.34 and 3.35 show that the results of the three-way ANOVA statistical tests. In Table 3.34, the effect of the temperature, rotary rate and rotary time, in addition to in Table 3.35, the effect of the temperature, rotary rate and fibre ratio were analyzed by three-way ANOVA test. According to the Table 3.34 and Table 3.35, the “p” values smaller than 0.05. Furthermore, the all of the experimental conditions have a remarkable effect on the self-polishing percentages.

Table 3.34 The results of the three-way ANOVA test for Temparature, Rotary Rate and Rotary Time.

Source	DF	SS	MS	F	P
Temparature	2	31726.0	15363.0	1539.58	0.000
Rotary Rate	3	8970.3	2990.1	290.2	0.000
Rotary Time	2	1147.8	573.9	55.7	0.000
Temp.*R.Rate	6	11875.7	1979.3	192.1	0.000
Temp.*R.Time	4	2457.8	614.5	59.6	0.000
R.Rate*R.Time	6	373.3	62.2	6.0	0.000
Temp.*R.Rate*R.Time	12	630.3	52.5	5.1	0.000
Error	72	741.8	10.3		
Total	107	52923.1			

Table 3.35 The results of the three-way ANOVA test for Temparature, Rotary Rate and Fibre Ratio.

Source	DF	SS	MS	F	P
Temparature	2	571.6	285.8	16.3	0.000
Rotary Rate	2	49936.0	24968.0	1422.5	0.000
Fibre Ratio	3	10885.2	3628.4	206.7	0.000
Temp.*R.Rate	4	7122.4	1780.6	101.4	0.000
Temp.*F.Ratio	6	4345.5	724.2	41.3	0.000
R.Rate*F.Ratio	6	6802.4	1133.7	64.6	0.000
Temp.*R.Rate*F.ratio	12	2090.4	174.2	9.9	0.000
Error	72	1263.8	17.6		
Total	107	83017.2			

3.3 The effect of experimental conditions on self-polishing percentages in metal surfaces

Figure 3.22-26 shows the effects of surfaces such as metal and glass slides on the self-polishing percentages and also table 3.36-40 shows the pictures of metal and glass slides. These figures and tables respectively belong to the results of free lanolin based material, glass and metal materials covered with lanolin based material containing 1% Fiber 1, 5% Fiber 1, 1% Fiber 2 ve 5% Fiber 2. As it seen in these figures, apart from few exeptions, it was observed that self-polishing percentages of metal surfaces covered with free lonolin based material were lower than glass slides'. The percentages of lanolin based materials which is used on metal surfaces were lower because of the fact that the surfaces of glass slides are smoother than metal ones and the undercoating which is used on metal surfaces holds the lanolin based material stronger. That's why; self-polishing percentages are lower than the other.

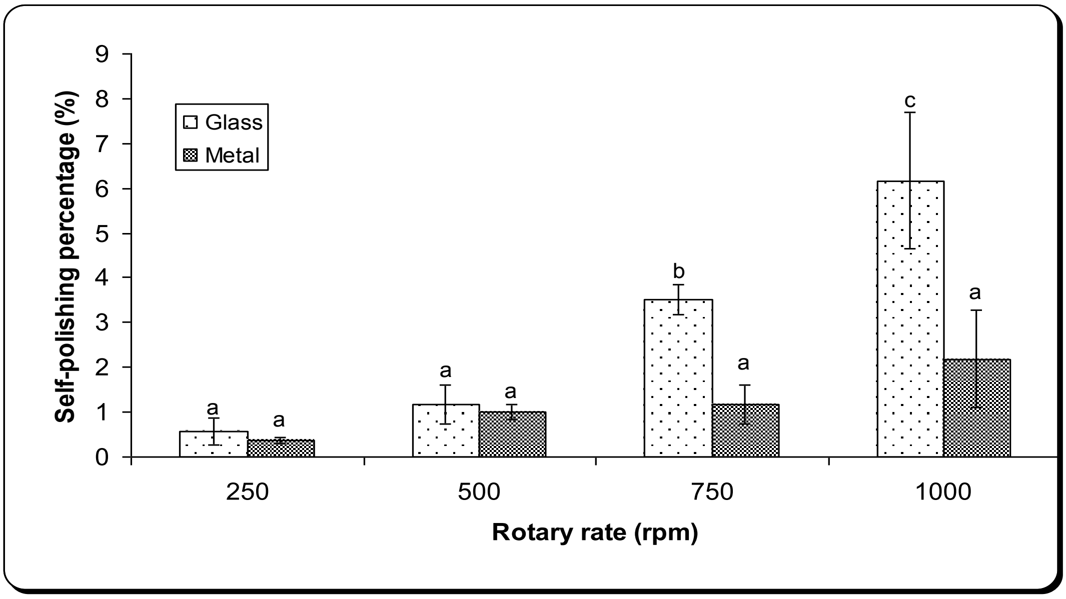


Figure 3.22 Effect of rotary rate on the self-polishing percentage of free lanolin based material which covered glass slides and metal surfaces at 30 ^oC.

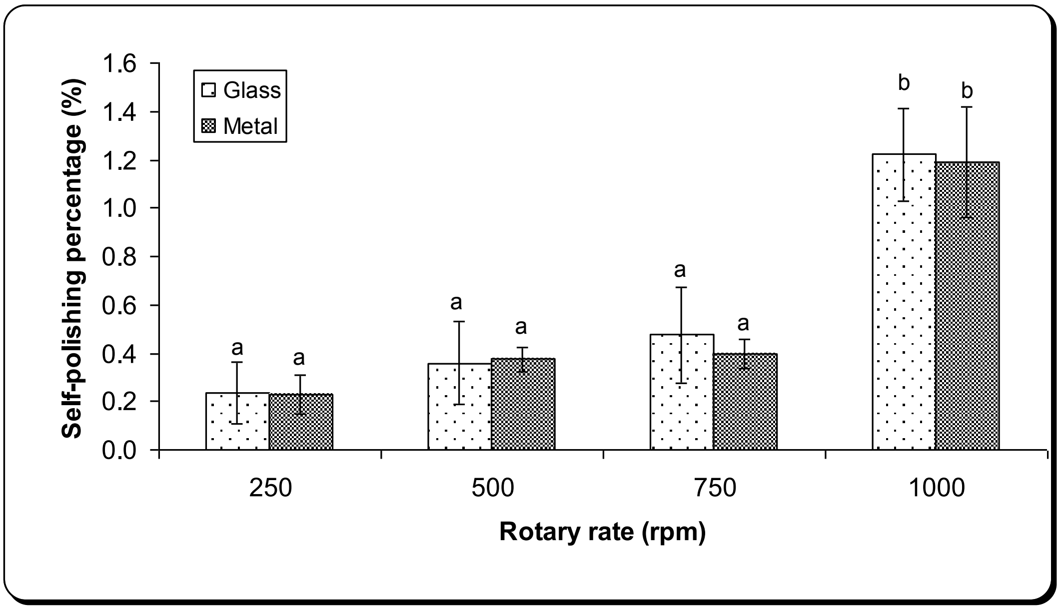


Figure 3.23 Effect of rotary rate on the self-polishing percentage of fibre reinforced lanolin based material which contains 1% Fiber 1 (w/w) at 30 ^{o}C.

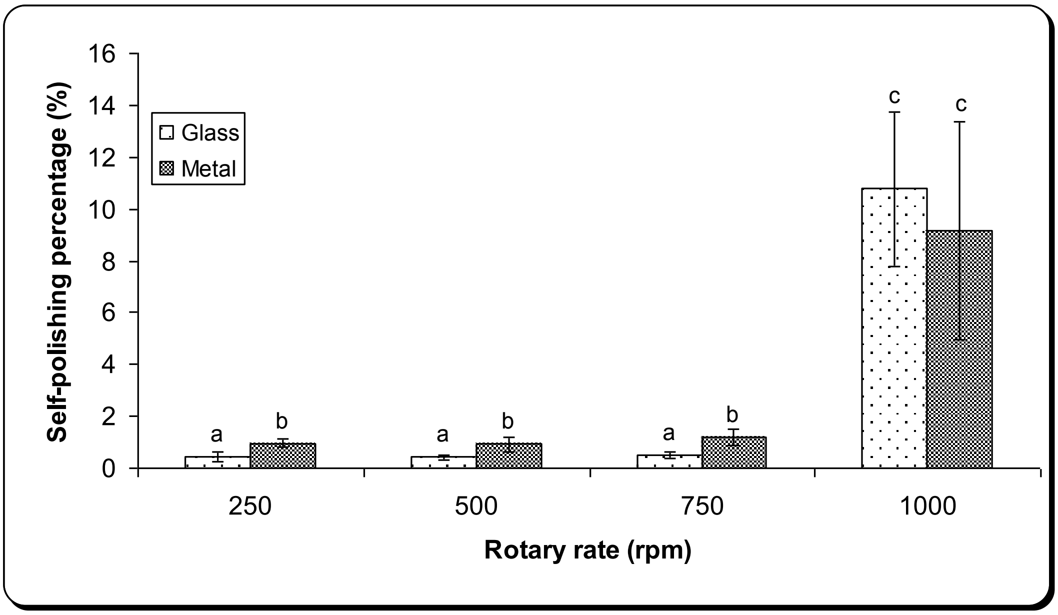


Figure 3.24 Effect of rotary rate on the self-polishing percentage of fibre reinforced lanolin based material which contains 5% Fiber 1 (w/w) at 30 ^{o}C.

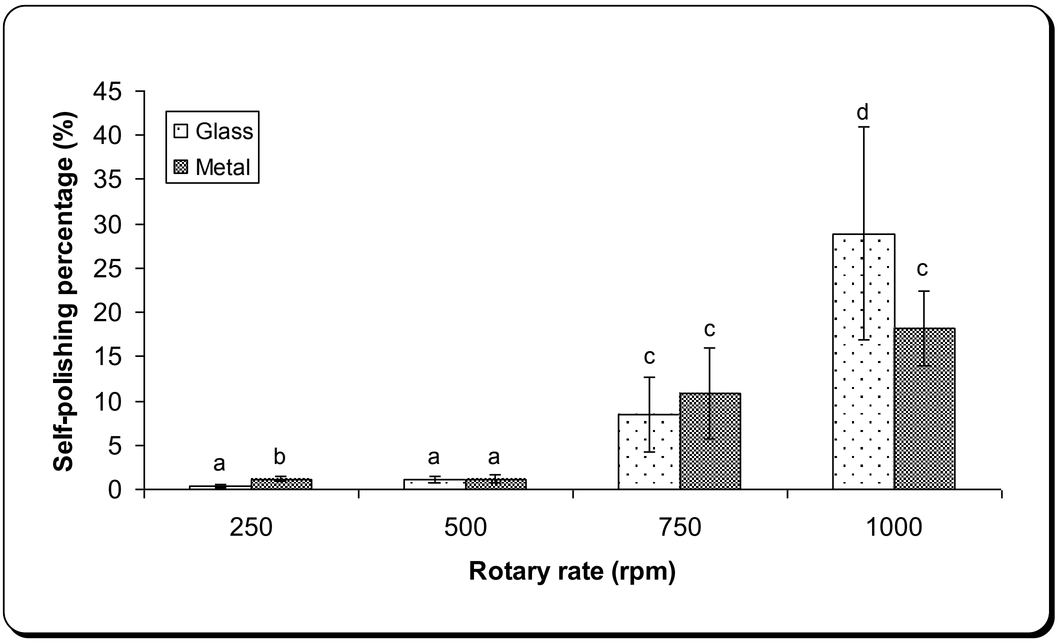


Figure 3.25 Effect of rotary rate on the self-polishing percentage of fibre reinforced lanolin based material which contains 1% Fiber 2 (w/w) at 30 ^{o}C.

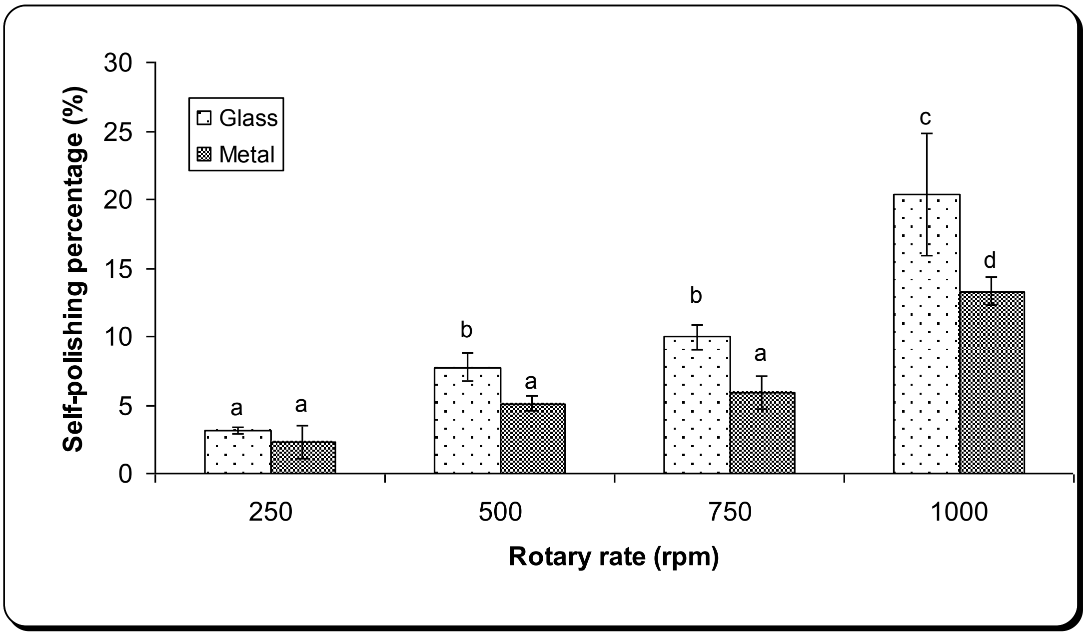


Figure 3.26 Effect of rotary rate on the self-polishing percentage of fibre reinforced lanolin based material which contains 5% Fiber 2 (w/w) at 30 ^{o}C.

Table 3.36 The images of the free lanolin based material covered metal slides at 30 ^{o}C, after 3 hours.

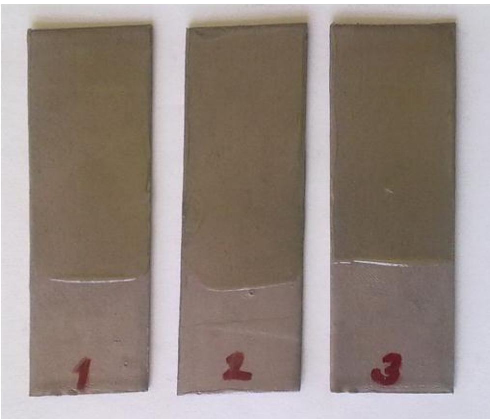
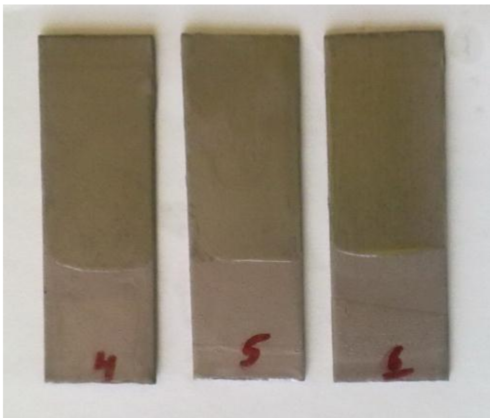
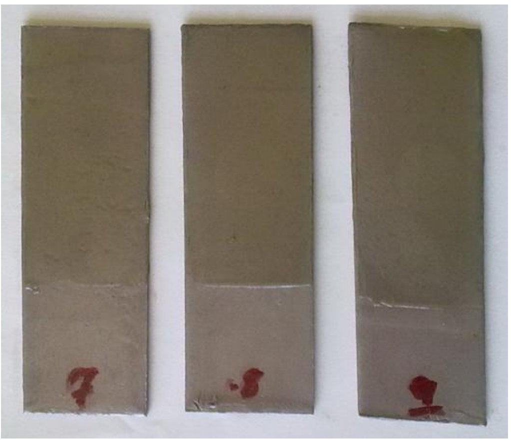
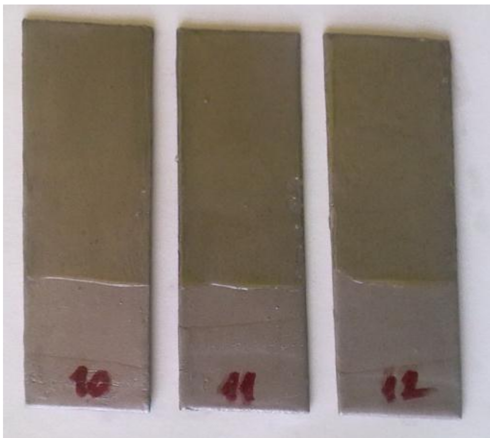
 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

Table 3.37 The images of the 1% Fiber 1 reinforced lanolin based material covered metal slides at 30 ^{o}C, after 3 hours.

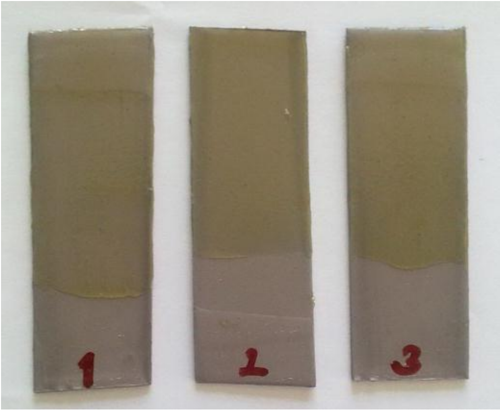
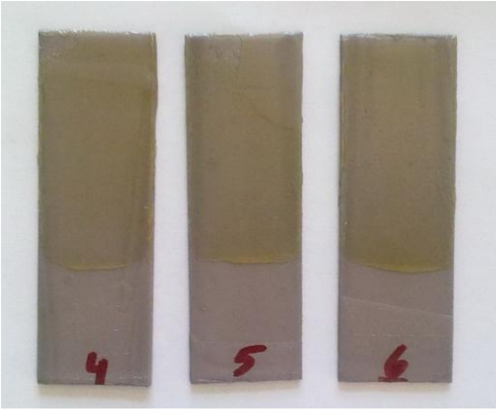
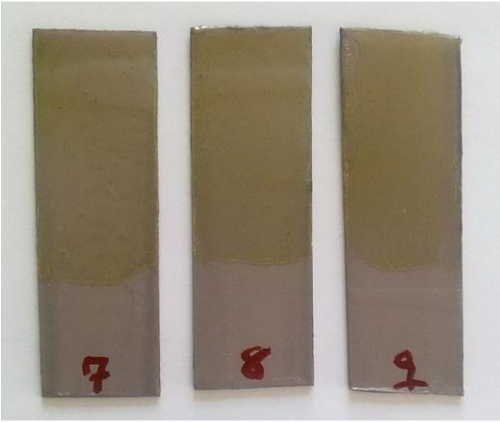
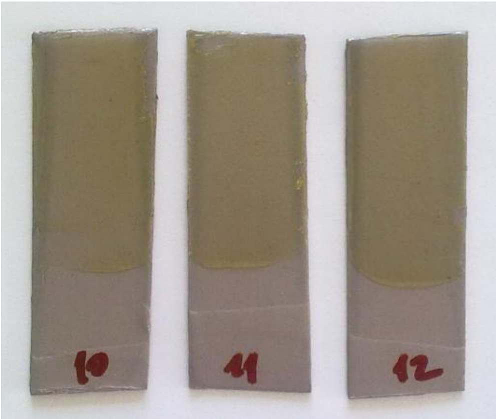
 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

Table 3.38 The images of the 5% Fiber 1 reinforced lanolin based material covered metal slides at 30 ^{o}C, after 3 hours.

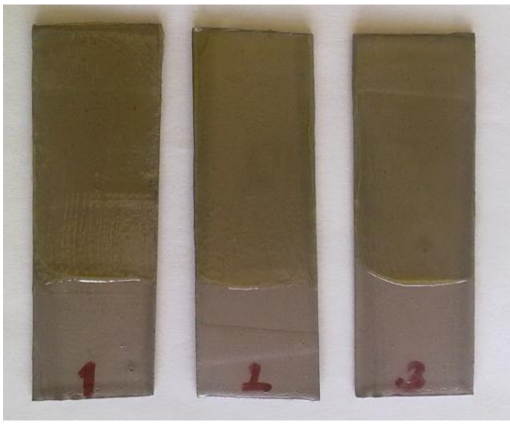
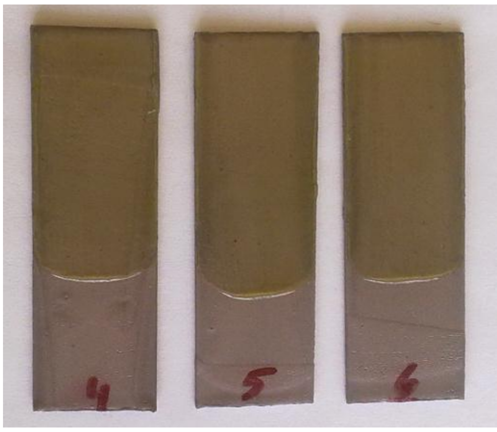
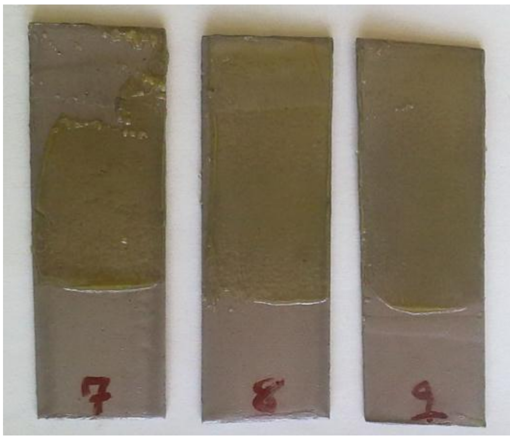
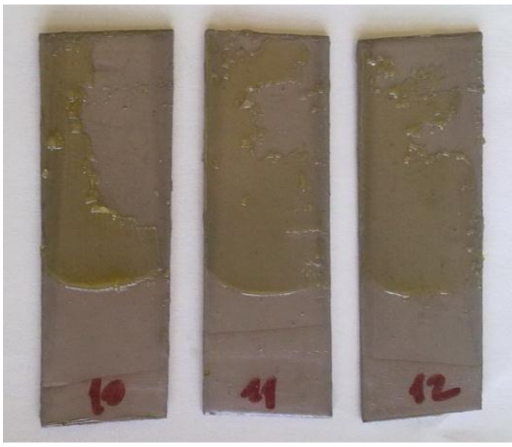
 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

Table 3.39 The images of the 1% Fiber 2 reinforced lanolin based material covered metal slides at 30 ^{o}C, after 3 hours.

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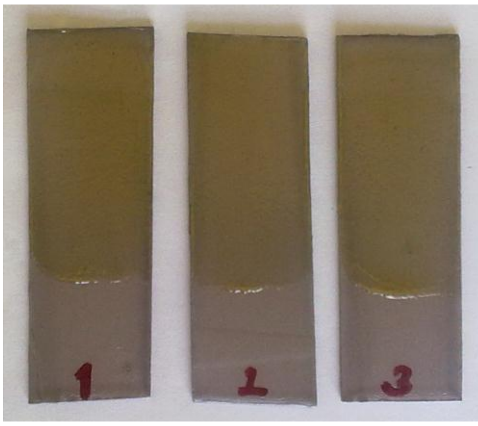
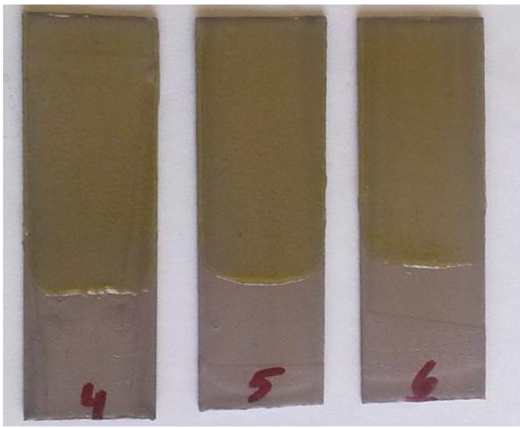
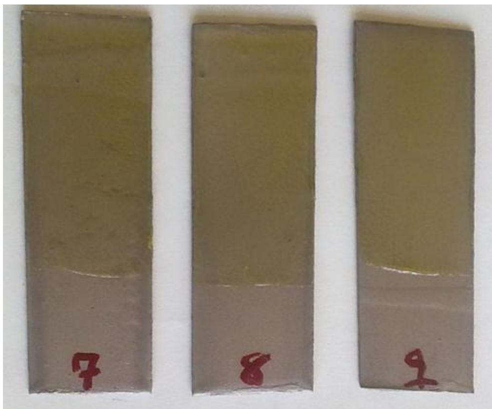
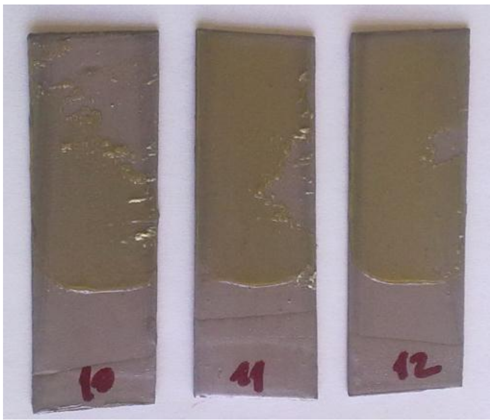
<td>

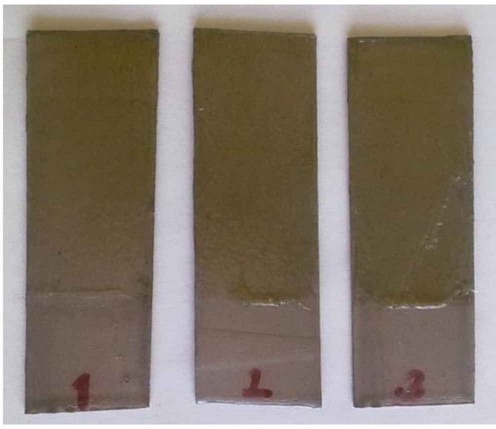
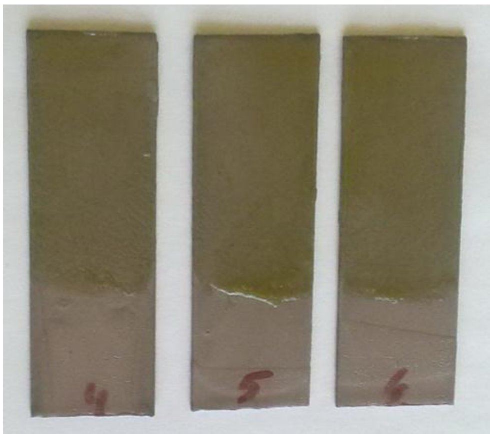
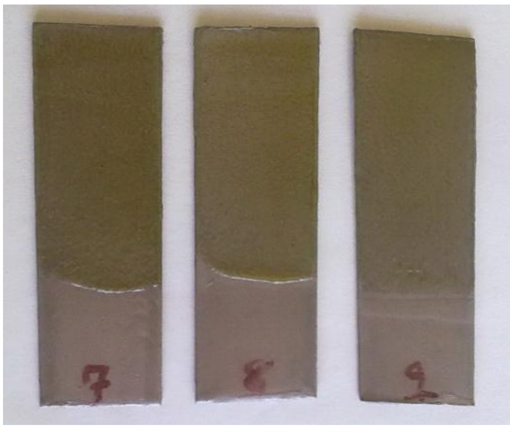
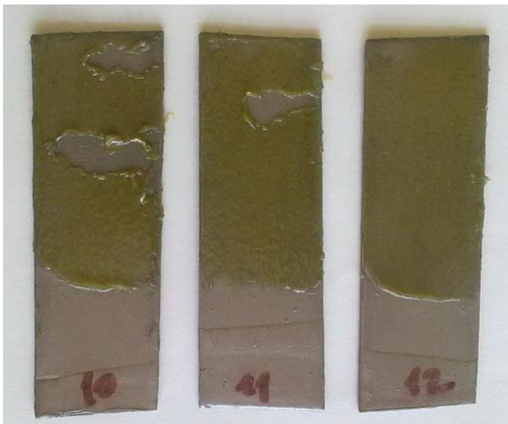
A. 250 rpm</td>
<td>

B. 500 rpm</td>
</tr>
<tr>
<td>

C. 750 rpm</td>
<td>

D. 1000 rpm</td>
</tr>
</table>

Table 3.40 The images of the 5% Fiber 2 reinforced lanolin based material covered metal slides at 30 ^{o}C, after 3 hours.

 **A.** 250 rpm	 **B.** 500 rpm
 **C.** 750 rpm	 **D.** 1000 rpm

3.4 The results of eco-toxicity tests

Eco-toxicity experiments were carried out to find the toxic effects of plant extracts. Figure 3.27-30 show that the survival percentages of *A.salina* nauplii which were exposed to *N.oleander* ve *L.nobilis* exstracts prepared in different conditions and concentrations. The results of *A.salina* nauplii which are exposed to extracts of which ethyl alcohol is vaporized and then to which water is added in the same volume of the vaporized alcohol are shown in the Figure 3.27 ve 3.29. Figure 3.28 ve 3.30 shows the results of aquous extracts of which methyl alcohol extracts were firstly prepared. Figure 3.27 belongs to *N.oleander* extracts and Figure 3.28 belongs to *L.nobilis* extracts. In Figure 3.27, it was observed that the longest life span belongs to 0.20 g/mL concentration and the shortest life span belongs to 0.50 g/mL concentration. In the Figure 3.28, the longest life span which is 140 minutes belongs to 0.17 g/mL concentration and the shortest one which is 110 minutes belongs to 0.50 g/mL concentration. In the Figure 3.29, *A.salina* deaths were observed only in 0.50 g/mL concentration. After 350 minutes, 20-40 % death rate was observed in the species exposed to other concentration. This result caused by the fact that toxic constituent existing in *L.nobilis* can not be dissolved by ethyl alcohol or with water. In Figure 3.30, the shortest life span was observed in the experiment group which was exposed to 0.50 g/mL concentration.

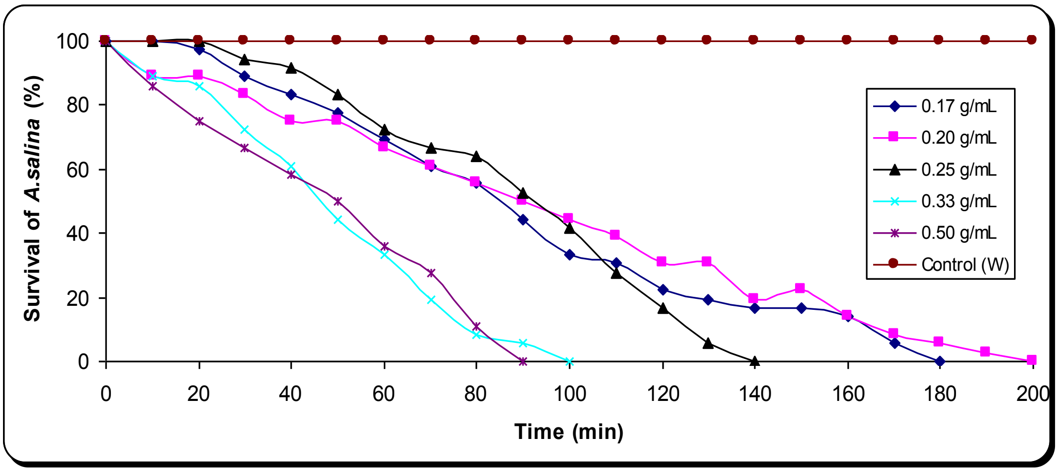


Figure 3.27 Survival percentage of *A.salina* exposured to different concentration of *N.oleander* extracts (0.17 - 0.50 g/mL).

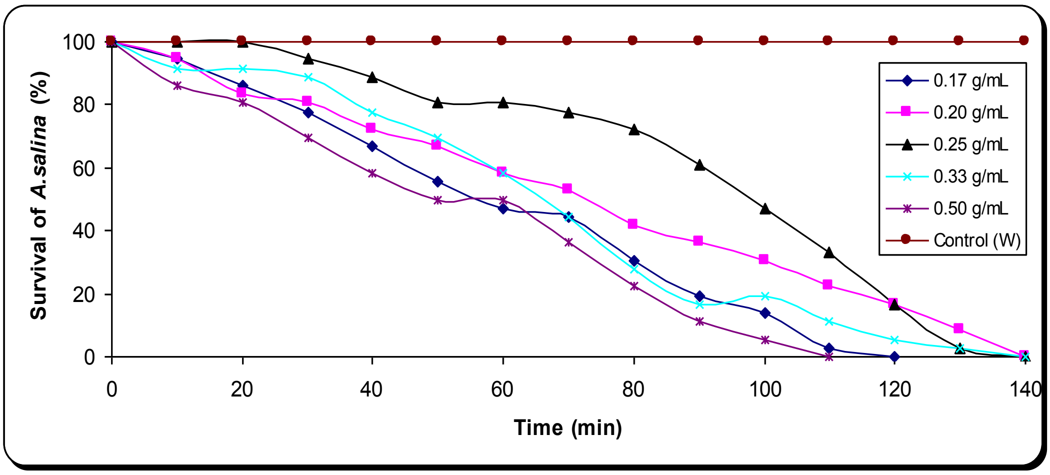


Figure 3.28 Survival percentages of *A.salina* exposured to different concentration of *N.oleander* extarcts (0.17 - 0.50 g/mL).

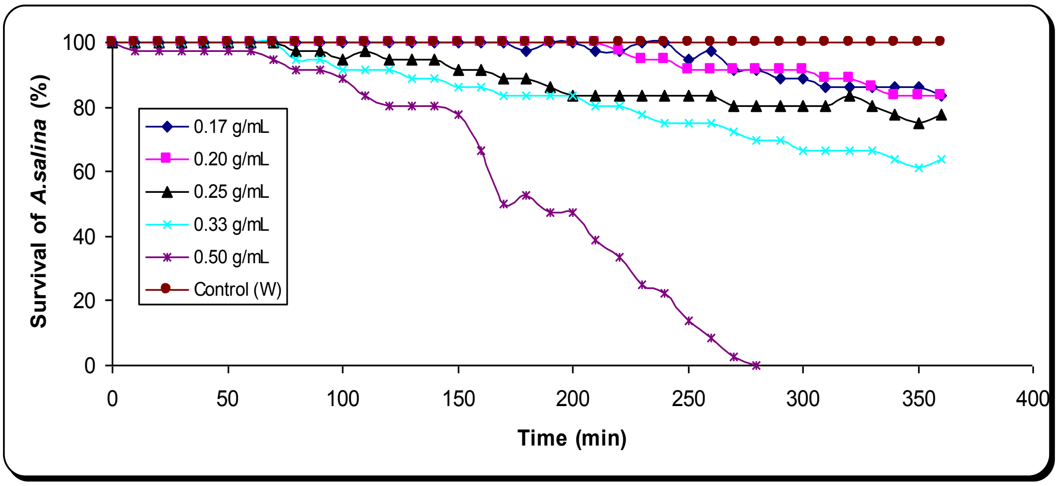


Figure 3.29 Survival percentages of *A.salina* exposured to different concentration of *L.nobilis* extarcts (0.17 - 0.50 g/mL).

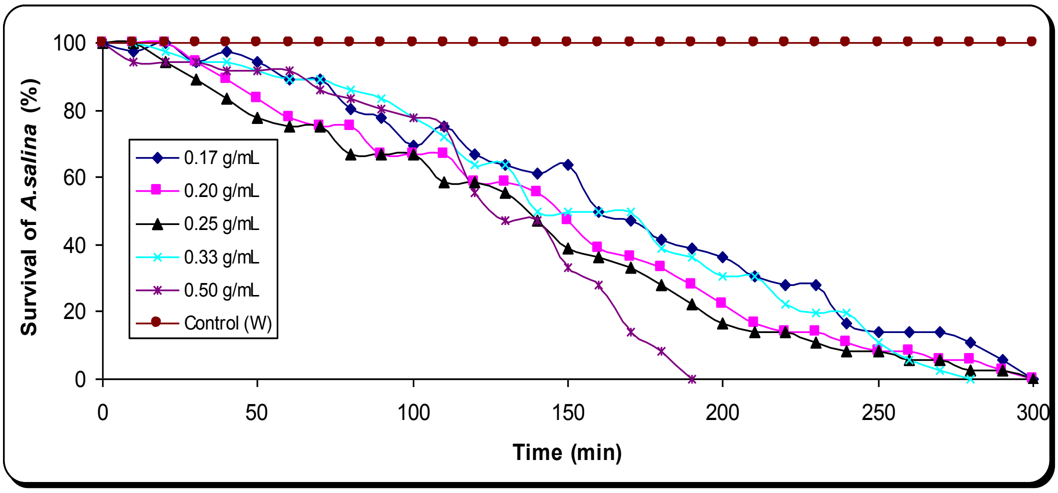


Figure 3.30 Survival percentage of *A.salina* exposured to different concentration of *L.nobilis* extarcts (0.17 - 0.50 g/mL).

3.5 Field Test Results

The field tests were carried out in Zeytinburnu coast, Istanbul for 2 months. Figure 3.31-40 show that the images of the lanolin based material covered metallic plates before and after immersion. Figure 3.31 belongs to control goup which contains any lanolin based material, fiber and plant extracts. In this figure, intensive fouling was observed in left images after 2 months immersion. According to fouling criteria, this fouling degree is Level V.

Figure 3.32 show that the images of the lanolin based material covered metallic plates. It was shown that this plate has slightly fouling organisms compared with the control group. Considering the fouling criteria this plate is Level III.

Figure 3.33 pertain to lanolin based material which contains *L.nobilis* extracts. Macroalgae and crustaceans formations were observed on the surfaces. This fouling degree is Level IV with respect to the fouling criteria.

The field test results of the lanolin based material which contains *N.oleander* extracts were seen in Figure 3.34. On this plates which exposed to seawater, some fouling organisms were appointed in some areas. In accordence with the fouling criteria this fouling scale is proper the Level III.

Figure 3.35 depicted the results of the field test which belengs to Fibre 1 reinforced lanolin based material. Fibre 1 reinforcement presents a good performances compared with the control group. The fouling level of this group is Level III.

The results of Fibre 1 reinforcement and *L.nobilis* extract added and also Fibre 1 reinforcement and N.oleander extracted added lanolin based material were presents in Figure 3.36 and Figure 3.37 respectively. There was not significant fouling on these surfaces of the metallic plates and the scale of the fouling of these groups Level III.

Figure 3.38 show that the before and after images of the Fibre 2 reinforcement lanolin based material. This group was presented a good antifouling performances. The fouling level of this group is Level II.

The field test results of the Fibre 2 reinforcemnet and *L.nobilis* extract added and Fibre 2 reinforcement and *N.oleander* extract added lanolin based material were seen in Figure 3.39 and Figure 3.40 respectively. In Figure 3.39, the metallic plates were exposed high fouling from macroalgae and crustaceans and the degree of this group Level V. Conversely, the fouling scale of the Figure 3.40 is Level III.

Figure 3.31 The metallic plates (Control group) exposed in Zeytinburnu coast 2 months immersion, left: before immersion, right: after 2 months.

Figure 3.32 The metallic plates (Free lanolin based material) exposed in Zeytinburnu coast 2 months immersion, left: before immersion, right: after 2 months.

Figure 3.33 The metallic plates (Lanolin based material and *L.nobilis* extract) exposed in Zeytinburnu coast 2 months immersion, left: before immersion, right: after 2 months.

Figure 3.34 The metallic plates (Lanolin based material and *N.oleander* extract) exposed in Zeytinburnu coast 2 months immersion, left: before immersion, right: after 2 months.

Figure 3.35 The metallic plates (Lanolin based material and Fiber 1) exposed in Zeytinburnu coast 2 months immersion, left: before immersion, right: after 2 months.

Figure 3.36 The metallic plates (Lanolin based material, Fiber 1 and *L.nobilis* extract) exposed in Zeytinburnu coast 2 months immersion, left: before immersion, right: after 2 months.

Figure 3.37 The metallic plates (Lanolin based material, Fiber 1 and *N.oleander* extract) exposed in Zeytinburnu coast 2 months immersion, left: before immersion, right: after 2 months.

Figure 3.38 The metallic plates (Lanolin based material and Fiber 2) exposed in Zeytinburnu coast 2 months immersion, left: before immersion, right: after 2 months.

Figure 3.39 The metallic plates (Lanolin based material, Fiber 2 and *L.nobilis* extract) exposed in Zeytinburnu coast 2 months immersion, left: before immersion, right: after 2 months.

Figure 3.40 The metallic plates (Lanolin based material, Fiber 2 and *N.oleander* extract) exposed in Zeytinburnu coast 2 months immersion, left: before immersion, right: after 2 months.

3.6 Corrosion Test Results

Corrosion experiments were carried out with the aim of showing hydrophobic features of lanolin based materials with using metal plates. A group of metal plates without a protective undercoating and another group completely coated with lanolin based material were immersed in artificial sea water. With the immersion of metal plates into the artificial seawater; between the 1st, 2nd, 4th and 6th hours, the changes were observed which occured in the seawater. Figure 3.41-44 show the changes occured in the 1st, 2nd, 4th and 6th hours respectively. As it is seen from the figures, while metal plates suffer from corrosion and change the color of the sea water, corrosion was not observed on the metal plates which are coated with lanolin based material.

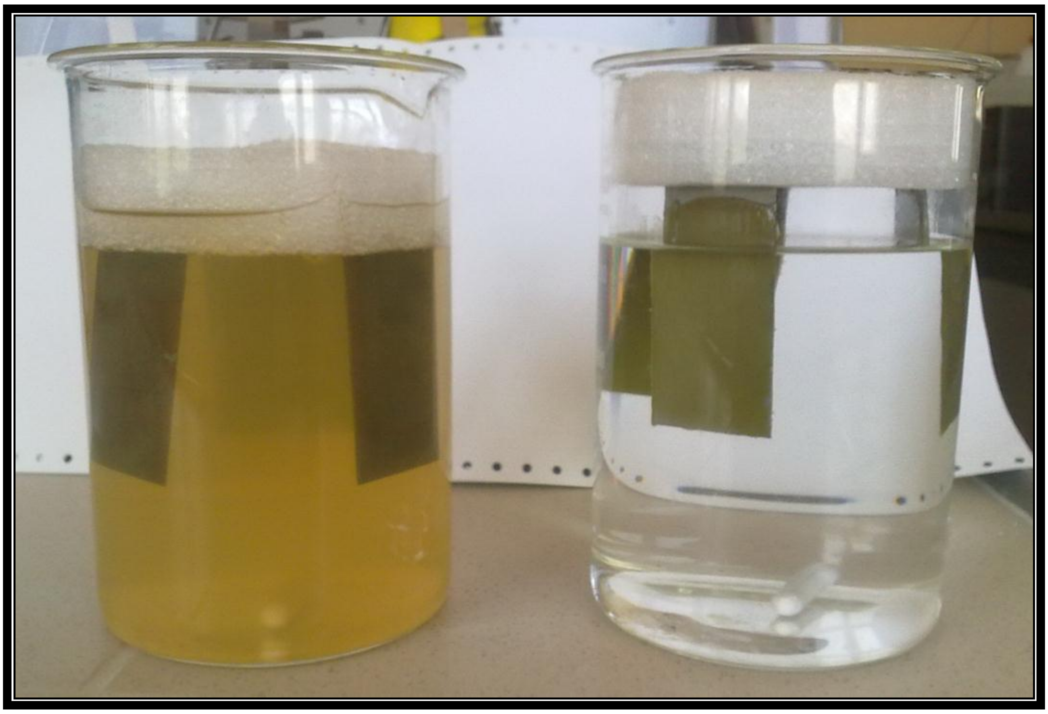


Figure 3.41 The results of the metal (left) and lanolin based material covered (right) metal surfaces which exposed to artificial seawater after the 1 hour expectation time.

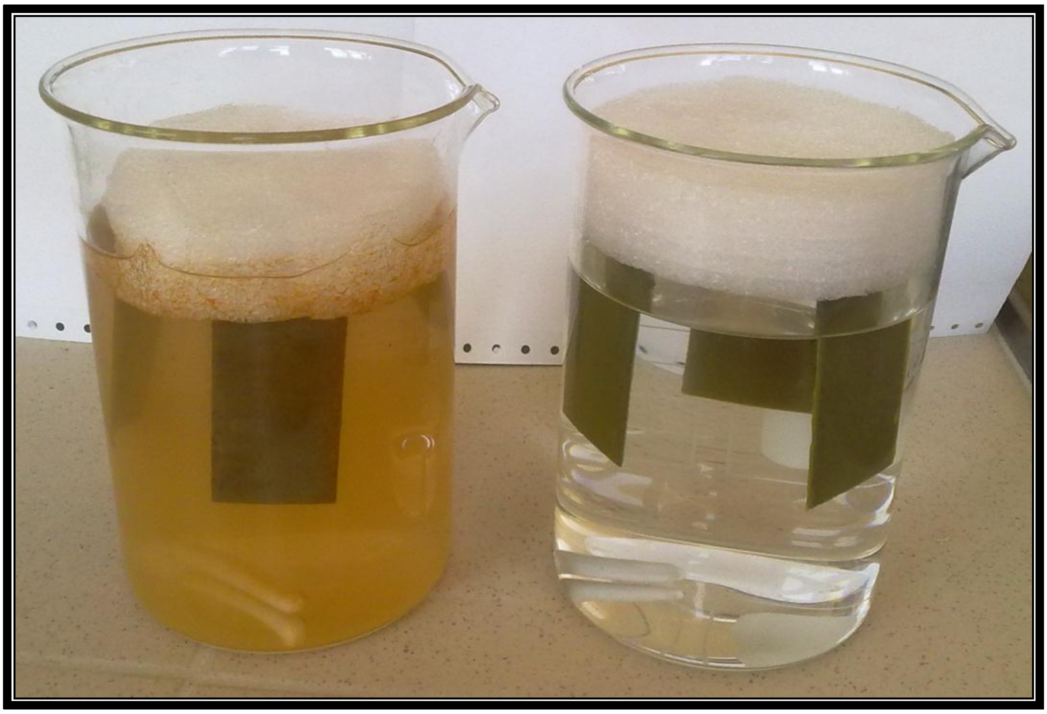


Figure 3.42 The results of the metal (left) and lanolin based material covered (right) metal surfaces which exposed to artificial seawater after the 2 hours expectation time.

Figure 3.43 The results of the metal (left) and lanolin based material covered (right) metal surfaces which exposed to artificial seawater after the 4 hours expectation time.

Figure 3.44 The image of the metal (left) and lanolin based material covered (right) metal surfaces which exposed to artificial seawater after the 6 hours expectation time.

To the best our knowledge, considering the all of the experimental data which belongs to self-polishing tests, the lowest self-polishing percentage was observed in 1% fibre, 30 ^{o}C and 250 rpm conditions in metal slides. On the other hand, the self-polishing percentages of glass slides have nearest value with the metal slides in the same experimental conditions.

There are many workouts about the evaluation of self-polishing persentages in open literature, however, there is no any study to detrmination of the self-polishing percentages of free and fibre reinforced lanolin based material. On the other hand, the application of the fibre reinforced lanolin based material to marine propellers does not exist in any scientific study. This fact is pointed out the originality of the present thesis.

Kiil et al have developed a fundamental mathematical model for self-polishing antifouling paints in 2002. The aims of the Kill et al.'s study were to show how a mathematical model can decrease the amount of the experiments needed to estimate the behavior of self-polishing paints and to suggest ways of controlling release rates of any biocides at different conditions.

Giúdice et al have investigated the dissolution rate of binders, antifouling characteristics; some rheological parameters of antifouling paints based on rosins and chlorinated rubber. Due to this purpose 3 different paint formulations were prepared and the results of initial dissolution rates of binders were found as 14.8 $\mu g/cm^2$.day, 13.6 $\mu g/cm^2$.day and 12.8 $\mu g/cm^2$.day for paints A, B and C, respectively.

In 2008, Monfared and Sharif have published a paper which name is Design guidelines for development of tin-free antifouling self-polishing coatings using simulation. They have experienced a model based on previous findings is developed and verified and then employed to obtain guidelines for the development of new TBT-free self-polishing coatings. Moreover, they have used a model to look at the polishing rate and leached layer thickness in different operational conditions of a ship and discuss the necessary response of the coating based on successful performance of TBT-SPC.

Loschau & Kratke have studied for Efficacy and toxicity of self-polishing biocide-free antifouling paints. They have examined two commercially available and self-polishing antifouling paints in order to get information on their antifouling properties and toxicological potential.

Xie et al. have prepared a coating by mixing a polyfunctional axiridine cross-linking agent and a self-polishing resin pre-synthesized via the polymerization of methyl methacrylate (MMA), acrylic acid (AA) and tributylsilyl methacrylate (TBSM) for the antifouling. In this study, besides the synthesis and preparation of this novel kind of coatings, they focused on the correlation between the TBSM content and the antifouling property by using contact angle, water-absorption, and antifouling measurements. The results of them showed that immersing different coatings in shallow submergence for two months reveal that the addition of more TBSM leads to a more hydrophilic surface and a better antifouling property.

Otherwise, in commercially, a certain number of products exist in order to use to protection of propeller. In many applications, antifouling paints and undercoating paints use for the protection of propeller.

Jotun which is the antifouling paint company produces this type paints whose commercial name is SeaLion for this purpose. SeaLion has the silicone-based elastomeric coating which provides a smooth, non-stick, water-repellant and self-cleaning surfaces. This paint is chiefly suitable for fast and high activity vessels and keeps ships' hull and propellers for attachment of foulers and corrosive effect.

PropspeedTM is the slick and non-toxic product which belongs to Oceanmax International Ltd. prevents the settlement and growing of the marine foulers to metal surfaces as the ships' hull and propeller below the waterline. PropspeedTM is an eco-friendly commercial product because of dose not contains copper, tin or any other toxic material which may cause environmental pollution

Seajet Company were developed Peller Clean, to provide protection against the marine foulers as the weed, barnacles etc. on the boat propellers, engines and stern gears. Peller Clean is the silicon based product and provides ultra slippery, non-stick surface.

Orca Slip Prop Protector Grease protects marine growth on propeller and exposed underwater metals. It is not only to protect metals from growth but is also used on rigging screws or when bolting fittings above or below the water line. It is non toxic so it can be use on hands as a barrier cream when antifouling or painting procedure. Pack into problem growth areas such as the leading edge of a rudder against the crustaceans.

CHAPTER FOUR
CONCLUSION

In the present thesis, it was aimed to increase the mechanical strength of the lanolin based propeller coatings which are applied for prevention of biofouling on propeller by adding commercial inorganic fibres to enable its use also in warmer seas. Corrosion tests were carried out to investigate its shear resistance and water repulsion ability based on hydrophobic features of the lanolin based coating improved in this thesis. Moreover; the antifouling activities of terrestrial plant extracts from *Nerium oleander* and *Laurus nobilis* and their contribution to the antifouling performance of lanolin based coating were investigated with eco-toxicity tests. All experiments were also supported with field tests.

According to the results of laboratory tests, fiber addition increased the mechanical strength and decreased the self polishing percentages of the lanolin based coating. According to field tests, fouling percentage was considerably lower on metal plates covered with lanolin based coating containing plant extracts and fiber than the control group. Self-polishing tests were only performed in the laboratory. We were not able to apply our lanolin based coatings on the propeller of a testing ship because of limited budget of the thesis. But self-polishing tests should be performed on the propellers of the ships in order to achieve more reliable results which would reflect the real behaviour of the coating.

N.oleander and *L.nobilis* extracts showed biocidal effect on *A.salina* nauplii. According to the results of toxicity tests, these extracts can be used as a potential source of eco-friendly biocide. In the subsequent studies; isolation of the active compounds could be performed to obtain an eco-friendly biocide for propeller coatings.

Field experiments were carried out in Zeytinburnu port of The Marmara Sea. In order to prepare high performance lanolin based propeller coatings, a categorization can also be made based on the characteristic properties of different sea environments.

For example, these experiments can also be performed in sea environments other than The Marmara Sea. Because three sides of our country are surrounded with seas, The Black Sea, The Aegean Sea and The Mediterranean Sea. Therefore, the mechanical strength and the antifouling performances of the lanolin based propeller coatings should also be tested in these sea environments. Furthermore, we have tested the performances of the lanolin based propeller coatings in summer. If the effect of temperature on the mechanical strength of the coatings and on the number of potential biofoulers is considered, the performance tests should also be performed in other seasons.

In conclusion, when lanolin is used as a propeller coating its mechanical strength, thermo-resistence and antifouling properties should be improved in a way that enables its worldwide use. In this thesis, above mentioned characteristics of lanolin modified with inorganic fibres and supplemented with plant extracts as a potential source of eco-friendly biocide were tested both in laboratory and field tests. It was found that lanolin can also be used in different sea environments (such as in warmer seas) when above mentioned modifications are made.

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