A SURFACE FREE ENERGY-BASED CHARACTERIZATION OF PEG-PLA COATING

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By

Beyza Özlem Yılmaz

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1 July 2021

We certify that we have read this dissertation and that in our opinion it is fully adequate, in scope and in quality, as a dissertation for the degree of Master of Science.

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Beyza Özlem Yılmaz

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LIST OF SYMBOLS

W_{ll} : Work of cohesion of liquid [mN/m or mJ/m2]
W_{sl} : Work of adhesion between solid and liquid [mN/m or mJ/m2]
W_{ss} : Work of cohesion of solid [mN/m or mJ/m2]
θ_y : Static contact angle or Young contact angle
β : Neumann's constant
γ : Surface free energy or surface tension [mN/m or mJ/m2]
γ_1 : Surface tension of material 1 [mN/m or mJ/m2]
γ_2 : Surface tension of material 2 [mN/m or mJ/m2]
γ^d : Dispersion component of surface tension [mN/m or mJ/m2]
γ^p : Polar component of surface tension [mN/m or mJ/m2]
γ_1^d : Dispersion surface tension of material 1 [mN/m or mJ/m2]
γ_2^d : Dispersion surface tension of material 2 [mN/m or mJ/m2]
γ_A^d : Surface free energy or surface tension of material A [mN/m or mJ/m2]
γ_{AB} : Interfacial surface tension between material A and material B [mN/m or mJ/m2]
γ_{Hg}^m : Surface tension of mercury [mN/m or mJ/m2]
γ_{Hg}^d : Dispersion component of surface tension of mercury [mN/m or mJ/m2]
γ_l : Surface tension of liquid [mN/m or mJ/m2]
γ_l^+ : Acidic interaction component of surface tension of liquid [mN/m or mJ/m2]
γ_l^- : Basic interaction component of surface tension of liquid [mN/m or mJ/m2]
γ_1^d : Dispersion component of surface tension of liquid [mN/m or mJ/m2]
γ_1^{LW} : Lifshitz-van der Waals component of the surface tension of a liquid [mN/m or mJ/m2]
γ_{lv} : Surface tension of liquid or interfacial surface tension between liquid and vapor [mN/m or mJ/m2]
γ_s : Surface free energy of solid [mN/m or mJ/m2]
γ_s^+ : Acidic interaction component of surface free energy of solid [mN/m or mJ/m2]
γ_s^- : Basic interaction component of surface free energy of solid [mN/m or mJ/m2]
γ_s^d : Dispersion interaction component of surface free energy of solid [mN/m or mJ/m2]
γ_s^p : Polar interaction component of surface free energy of solid [mN/m or mJ/m2]
γ_s^h : Hydrogen bonding component of surface free energy of solid [mN/m or mJ/m2]
γ_s^i : Induction interaction component of surface free energy of solid [mN/m or mJ/m2]
γ_s^{ab} : Acid-base interaction component of surface free energy of solid [mN/m or mJ/m2]
γ_s^o : Other interaction component of surface free energy of solid [mN/m or mJ/m2]
γ_s^{LW} : Lifshitz-van der Waals component of the interfacial tension between the solid and liquid [mN/m or mJ/m2]

ABBREVIATIONS

CA	: Contact Angle
CS	: Chitosan
Col	: Collagen
EQS	: Equation of State
EVA	: Ethylene-vinyl acetate
FDA	: Food and Drug Administration
HEMA	: (Hydroxyethyl)methacrylate
Mg	: Magnesium
SCA	: Static Contact Angle
SFE	: Surface Free Energy
PBS	: Polybutylene Succinate
PCLF	: Polycaprolactone Fumarate
PEC	: Poly(ethylene carbonate)
PEG	: Polyethylene Glycol
PDA	: Poly (dopamine)
PGA	: Polyglycolide
PGS	: Poly (glycerol sebacate)
PCL	: Polycaprolactone
PCT	: Percutaneous Coronary Intervention
PDA	: Polydiacetylene
PDMMLA	: Poly([R, S]-3,3-dimethylmalic acid)
PDLLA	: Poly-DL-lactic acid
PEA	: Polyethylacrylate
PEI	: Polyethyleneimine
POSS	: Polyhedral Oligomeric Silsesquioxane
PLA	: Polylactic Acid
PLCL	: Poly(lactide-co-caprolactone)
PLGA	: Poly (lactic-co-glycolic) Acid
PLLA/PAA/Col	: Poly-L-lactic acid/poly-(α,β)-DL-aspartic acid/Collagen
POSS-PCU	: Poly(carbonate-urea)urethane
PT	: Polymer Therapeutics
PTX/CS	: Paclitaxel/chitosan

PEG-PLA BAZLI KAPLAMANIN YÜZEY SERBEST ENERJİSİNE DAYALI KARAKTERİZASYONU

ÖZET

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Sağlık Sistemleri Mühendisliği, Yüksek Lisans

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Temmuz, 2021

Sağlık alanı, temel yapısı itibariyle dinamik bir yapıya sahiptir ve bu nedenle sürekli değişim ve gelişime ihtiyaç duymaktadır. Ayrıca sağlık alanında sınırlı kaynakların bulunması ve dünya genelinde artan sağlık harcamaları bu alanda yeni yaklaşımlara olan ihtiyacı artırmıştır.Polimerler, özellikle artan pazar payları ile yeni yaklaşımların geliştirilmesinde hayati bir rol oynamıştır. Başlarda, polimerlerin kullanımı, yaralanan veya parçalanan doku veya organların sorunsuz bir şekilde işlevini yerine getirmesini sağlamak, insanın yaşam koşullarını korumak ve iyileştirmek için temel olarak implant ve tıbbi cihaz olarak kullanımları sınırlıydı. Yeni kaplama teknolojileri gibi polimer mühendisliğindeki gelişmeler, polimerlerin daha geniş uygulama alanlarında kullanılmasını sağlamıştır. Polimerlerin uygulama alanları genişledikçe kullanım şekilleri de değişmiştir. Polimerlerin vücutta kullanılacak diğer malzemelerin polimer kaplanması yoluyla, hedefe yönelik tedavi veya teşhis prosedürleri geliştirmek için polimer bazlı yaklaşımlar da sunulmaktadır. Bu noktada, PEG-PLA, polimer kaplamalarda sıklıkla kullanılan FDA onaylı polimerlerdir. Bir malzemenin uygun bir kombinasyonda PEG-PLA karışımı ile kaplanması aşınma hızı, hidrofiliklik, mekanik direnç gibi farklı katkılar sağlamakla beraber birbirlerinin eksikliklerini en aza indiren umut verici yaklaşımlardan biri olarak kabul edilmektedir. Ancak yapılan kaplama uygulamalarında en önemli faktörlerden biri yüzey serbest enerjisidir. Bu noktada, bu çalışmanın temel amacı, farklı oranlarda PEG-PLA karışımları ile kaplanmış yüzeylerin statik temas ölçümleri aracılığıyla bilgisayar ortamında yüzey serbest enerjilerinin araştırılmasıdır. Çalışma sonucunda, statik temas açısı arttıkça yüzey serbest enerjisinin azaldığı gözlemlenmiştir. Yüzey serbest enerjilerinin hesaplanılmasında Neumann, Wu, Asit-Baz, Fowkes ve OWRK yöntemlerin kullanılmıştır. Neumann yöntemindeki SFE ölçümleri dikkate alınmış olup, farklı kombinasyonlardaki PEG-PLA karışımları içerisinden, yüksek yüzey serbest enerjisi nedeniyle 5 numaralı karışımının ilgili yüzeyin kaplanmasında en uygun kombinasyon olduğu sonucuna ulaşılmıştır. Bu çalışmanın, sağlık alanında kullanılacak olan bir malzemenin özelliklerinin, kaplama yöntemiyle geliştirilmesi noktasında yapılacak kaplama için uygun kombinasyonların belirlenmesi ve sınırlı kaynakların etkin bir şekilde kullanımına yönelik yapılacak çalışmaların önünü açması beklenmektedir. Böylece, yapılan kaplamaların analizlerinin gerçekleştirilerek, yüzeye uygun kaplamaların gerçekleştirilmesi ve istenen özelliklerin maliyet-etkin bir çerçevede sağlanması noktasında gelecek çalışmalara ışık tutması beklenmektedir.

Anahtar Sözcükler: Biyomalzeme, Biyouyumlu, Kaplama, PEG, PLA, Sağlık, Yüzey Serbest Enerji

A SURFACE FREE ENERGY BASED CHARACTERIZATION OF PEG-PLA COATING

ABSTRACT

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MSc in Healthcare Systems Engineering

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July, 2021

The field of health has a dynamic structure in terms of its basic structure and therefore needs constant change and development. In addition, limited resources in the field of health and increasing health expenditures around the world have increased the need for new approaches in this field. Polymers have played a vital role in the development of new approaches, especially with their increasing market shares. Initially, the use of polymers was limited mainly as implants and medical devices to ensure the smooth functioning of injured or ruptured tissues or organs, and to protect and improve human living conditions. Advances in polymer engineering, such as new coating technologies, have allowed polymers to be used in a wider range of applications. As the application areas of polymers have expanded, their usage patterns have also changed. Polymer-based approaches are also offered to develop targeted therapeutic or diagnostic procedures, through polymer coating of other materials for use in the body. At this point, PEG-PLA are FDA-approved polymers that are often used in polymer coatings. Coating a material with a PEG-PLA mixture in a suitable combination provides different contributions such as wear rate, hydrophilicity, mechanical resistance, and is accepted as one of the promising approaches that minimizes each other's deficiencies. However, one of the most important factors in coating applications is the surface free energy. At this point, the main purpose of this study is to investigate the surface free energies in computer environment by means of static contact measurements of surfaces coated with PEG-PLA mixtures at different rates. As a result of the study, it was observed that the surface free energy decreased as the static contact angle increased. Neumann, Wu, Acid-Base, Fowkes and OWRK methods were used to calculate the surface free energies. SFE measurements in the Neumann method were taken into account, and it was concluded that among the PEG-PLA mixtures in different combinations, the mixture number 5 was the most suitable combination for coating the relevant surface due to its high surface free energy. It is expected that this study will pave the way for the determination of the appropriate combinations for the coating to be made at the point of improving the properties of a material to be used in the field of health, and the effective use of limited resources. Thus, it is expected that the analysis of the coatings made will shed light on future studies on realizing coatings suitable for the surface and providing the desired properties in a cost-effective framework.

Keywords: Biocompatible, Biomaterial, Coating, Healthcare, PEG, PLA, SFE

CHAPTER 1

1. INTRODUCTION

The field of health is constantly undergoing development and change to meet the needs and maintain the well-being of the individuals in all the processes it encounters. Maintaining an individual's well-being has become even more critical due to changing demographic properties of the society such as the aging population around the world [1]. Aging is a complicated process in which the functioning of all body functions from cells to organs is impaired and functional capabilities of the body are reduced [2]. When the body cannot perform its functions properly, the person's complete well-being deteriorates. Therefore, new approaches/studies are needed in the field of health, not only because of the differentiation of aging community-borne diseases but also due to various situations such as some inevitable accidents, inadequate treatments despite developing technology. The common crucial purpose of these studies is to eliminate the drawbacks in the body functions through medical equipment, materials, and devices used to perform functions like before or improve the existing system. At this point, the biocompatibility feature which is defined as the physical, chemical and biological compatibility of materials to be used in the body in contact with the body, to body tissues and optimum adaptation to body behavior has a critical role [3]. Moreover, the need for the new material to be used to be safe and effective is increasing from day to day but at the same time, health expenditure has been gradually increasing over the last decade and is assumed to continue to increase in the coming years. Therefore, cost-effectively maintaining an individual's well-being against limited resources in the field of health has become a top priority around the world [4]. Hence, cost-effective approaches take a significant role in the advancement of materials that are both intended to be used as a new approach and expected to show biocompatibility property. Although the materials can provide this property concerning their bulk characteristics, surface properties are another significantly important concern [5].

The surface is defined as the region where the structure and composition affected by the interface differ from the bulk composition and structure [6]. In other words, since the top layer of surface atoms is in direct contact with solid, liquid, or gas phases, this top layer of surface atoms can be regarded as the surface [7]. Surface characteristics can be investigated into three groups: surface morphology, surface structure, and surface properties. Surface properties have a tremendous impact on the success or failure of the material to be used for the related application in the health field since the surface comes into first contact with the environment. Therefore, surface properties provide information about the behavior and suitability of the material. For this reason, the need for determination and research of surface properties is obvious for the effective and true application of the material, both in the past and today. The surface properties of most of the materials used in the health field cannot meet the required demands in various applications and not be sufficient anymore in the face of developments and changes experienced. Namely, the surface may need to be adjusted and engineered in line with the desired condition. Moreover, the availability of limited resources in the field of health requires a cost-effective approach. Surface modification to adjust surface properties has become one of the most interesting and cost-effective approach in the biomaterial research field, proving to be very effective in ameliorating the biocompatibility and corrosion resistance of the material. It enables modification of the material surface with superior biofunctionality and bulk characteristics [8]-[12]. Various studies have focused on advancing the "biocompatibility" of biomaterials through a variety of surface modification and thin-film coating applications.

Medical coatings take critical role in meeting the relevant usage requirements of biomaterials [13]. Biocompatibility can be importantly improved and adverse effects such as physical irritation, inflammation, infection, toxicity, or carcinogenic effect can be avoided by coating application on the surfaces of the biomaterials. The application of a coating on the surface makes biomedical devices and biomaterials much more qualified to meet clinical requirements and to provide targeted properties [14]. At this point, polymer-based coatings continue to be utilized in more diverse applications and sectors than ever before due to the advantages offered by medical polymers. Polymers offer the advantage of enhancing a range of functional properties for their underlying hosts, from barrier coatings in a simple way to elaborate nanotechnology-based composites [15].

The widespread use of polymers in the field of biomedical research and medical applications, and their becoming a basic workforce in biomaterials, emphasize the importance of polymers in the field of health [16]. The surprising market size of medical polymers is expected to exceed $24 billion by 2024 and reach a CAGR of 9% is another phenomenon that supports the importance of polymers in the health field. Moreover, the increasing elderly population and increasing medical needs are expected to direct the market share of medical polymers in near future and to become prominent in the field of health [17]. For example, the elderly population, which is the population aged 65 and over, was 6 million 495 thousand 239 people in 2015. However, it increased by 22.5% in the last five years and achieved 7 million 953 thousand 555 people in 2020 in Turkey. While the proportion of the elderly population in all population was 8.2% in 2015, it increased to 9.5% in 2020 [18]. Related changes in population are demonstrated in **Figure 1.1.**

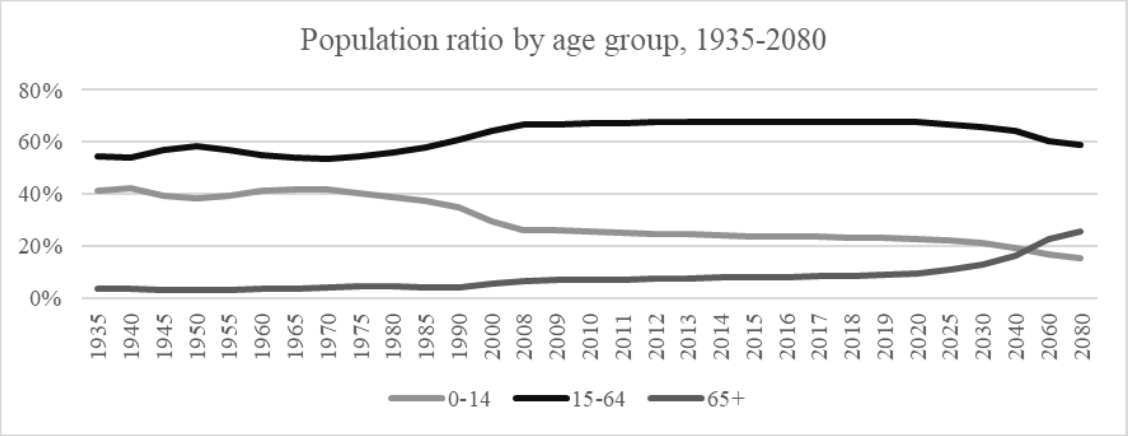

Figure 1.1: Population distribution and rate by age group [18].

Instead of limiting the use of polymers directly as biomaterials, polymer-based approaches are also provided where targeted treatment or diagnostic procedures can be performed using the coating of materials to be used within the body. Since polymers are outstanding candidates in healthcare because of their substrate-independent properties and adaptable surface functions, polymeric coatings are increasingly used in a diversity of applications in different biomedical fields [19].

The surface characteristics/properties of a material can be determined by different parameters. The SFE is a key parameter among these parameters, which characterizes the solid surface and its interaction with other surfaces. This parameter is associated not only with the wettability of the material but also with many other substantial properties at the

surface/interface [5],[20]-[21]. Moreover, biocompatibility is affected mainly by the surface properties of the biomaterials, especially wettability, SFE since the surface of the biomaterial is in direct contact with biological cells or fluids. For this reason, the causes and consequences of surface coating applications are directly related to SFE [22].

The main objective of the study is to conduct a study on the SFE of the surface coated with different PEG-PLA combinations. SFE measurement will be performed on the surfaces coated with mixtures containing PEG-PLA in different ratios. The surface characteristics of the materials used in the health field, especially a material to be used in the body, play a key role in whether they are suitable for relevant use. Therefore, it is aimed to guide the development of the surface properties of the material to be used at the desired level with this study. Consequently, the results of this study will play a role in examining the surface properties and determining the appropriate coating ratio/model for a material to be used in the health field to show a suitable and targeted fit.

1.1. Polymer-Based Coating Applications

1.1.1. General information about polymer

The polymer-based approach in healthcare is being investigated, but at this point, it is essential to comprehend basic concepts and types of the polymer. The word "polymer" consists of two main words, meaning "poly" and "mers" parts or units "in Greek. “Polymers are defined as long-chain high molecular weight compounds where each molecule is more or less specifically arranged”. The small molecular weight units used when starting the synthesis are called "monomers" [23]-[24].

Polymers that have an extensive scope of application as biomaterials are classified into two groups as natural and synthetic. Natural polymers have many advantages when compared to synthetic polymers due to the utilization of natural resources, cheapness, and chemically replaceable reasons. Collagen, gelatin, elastin, silk, polysaccharides are commonly used natural polymer types.

Synthetic polymers contribute to chemical changes and are relatively versatile and customizable to specific needs. However, they are found in abundant amounts when compared to natural polymer types [25]. Frequently used synthetic polymer types can be listed as poly (lactic acid), poly (glycolic acid) and their copolymers, poly (ethylene oxide, poly (hydroxyethyl methacrylate), Polyanhydrides, polyphosphazene, poly

(orthoesters), silicone, poly (ethylene), polyethylene (PE), polyvinyl chloride, polyurethane (PU), polycaprolactone [26]. Synthetic polymer coatings are widely applied in biomedical applications thanks to their material versatility and workability. By controlling its composition, physical and chemical properties, these coatings can be utilized for different applications, and they can be modified to suit various complex structures and shapes [27].

1.1.1.1. Polyethylene glycol (PEG)

PEG is a polyether involving repeated units of ethylene glycol. It is a synthetic polymer that is soluble in water, biocompatible and non-immunogenic and has low cost, high permeability, solubility, structure flexibility and hydration capacity[28]. The chemical structure of PEG is demonstrated in **Figure 1.2.**

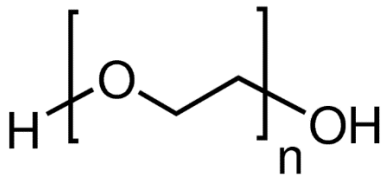

Figure 1.2: The chemical structure of PEG [29].

PEG derivatives are neutral polyethers in linear or branched structures with extraordinary biological properties. Although its chemical structure looks like a very simple molecule, it comes into prominence in biotechnical and biomedical applications. They are materials that are compatible with biological materials, non-toxic, can provide cell combinations at high concentrations, and can form complexes with metal cations. It is suitable for chemical modification or bonding with other molecules or surfaces. When it interacts with other molecules, it does not cause much chemical change, but it can affect their solubility [30].

PEG is approved by FDA. PEG-based materials are the most widely used polyether in biomaterial utilization thanks to their superior biocompatibility, structural advantages, and ability to reduce protein adsorption on a type of hydrophobic material [31].

1.1.1.2. Polylactic acid (PLA)

PLA is rigid thermoplastic polymers in semi-crystalline or amorphous form. PLA polymer has the characteristics of PET and also features PP [32]. Polylactic acid, which is produced by making use of plants rich in starch such as corn, sugar cane and wheat, is

biocompatible and biodegradable [33]. Moreover, it is a very useful polyester due to its great mechanical properties and well machinability. Additionally, in regard of biodegradable polyesters, PLA is considered to be the biopolymer with the highest potential because of its easy availability and low-cost advantages [34]. It has been approved by the FDA for use in many biomedical applications and is currently used mainly for drug delivery systems and tissue engineering [35]. The chemical structure of PLA is demonstrated in **Figure 1.3.**

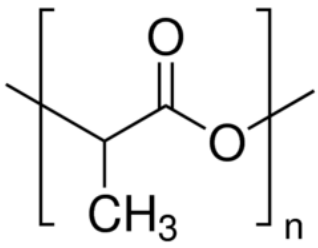

Figure 1.3: The chemical structure of PLA [36].

Various findings have been made about PLA from past to present. Especially in recent years, studies involving PLA have been increasing. However, despite all the advantages of PLA, it suffers from the most critical disadvantage of its fragile structure, which limits its usage areas [37].

1.1.2. Polymeric-based coating applications in health field

A coating can be defined as a layer applied to the surface of an object or material that is sometimes called substrate for protection, decoration to affect, or change surface functionality [38]. The coating is an effective method that is utilized in many different biomedical applications and provides the desired properties by changing the surface properties of any substrate biomaterial, therefore, changing the response with the surface, when the desired properties are not achieved due to the essence of a biomaterial. In the biomedicine field, the coating of materials is an application that is used frequently to eliminate missing or insufficient properties due to the nature of the material and to adapt the materials to the desired properties. Covering the surfaces of the related materials with polymer has gained global attraction due to the various advantages of the polymers, the developments and changes observed especially in the biomedicine field. The coating can be carried out chemically, mechanically or physically to produce materials with the desired combination of properties which are wear resistance, improved mechanical strength, improved biocompatibility, nontoxicity, special surface chemistry and corrosion

protection. Therefore, they are widely applied for non-thrombogenic, slippery, antimicrobial, protective and many other purposes in biomedicine. Polymer coatings can be made in a single polymer type or composite form. As a result, the polymeric coating provides a large market for medical materials implanted into the human body [39-40]. For this reason, the studies in the literature are guiding further studies and stakeholders in the field of health as this area is promising and continues to develop. All this has led to the need to focus on polymer-based coating studies in the field of health in this study. In this context, a general literature review including the last decade has been carried out with the keywords "polymer coating", "biomedical" and "healthcare". A classification has been made within the scope of the fields where the studies have shown the most intensity, and therefore the classification of the study has been determined as "cardiovascular implants, "drug delivery", "tissue engineering and regenerate medicine" and "orthopedic implants" in a detailed manner. The classification made to analyze polymer-based coating studies is given in **Figure 1.4.**

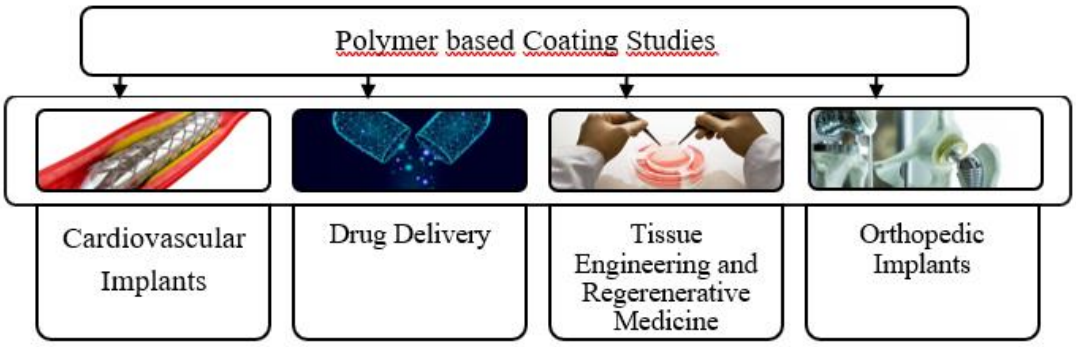

Figure 1.4: Classification of polymer-based coating studies.

1.1.2.1. Cardiovascular implants

In this section, polymer-based coating studies in cardiovascular implant application will be summarized to explain its role and development.

Providing degradation and releasing of drugs, mimicking biological functionality are the main capabilities of polymers in cardiovascular implants. Therefore, polymer-coated and polymer-based implants are essential components and revolutionary advances in diagnosing and treatment of cardiovascular diseases [41].

Cardiovascular implants commonly involve heart valve frames, stent, stent graft, and permanent vena cava filters [42]. Stents are implants that are frequently used in the treatment of cardiovascular patients to provide sufficient blood flow to the heart by re-

expanding the narrowed cardiovascular vessels and prevent reclosing. Stents are manufactured from different biomaterials. The main material of the stents available on the market is generally stainless steel. Moreover, gold, a biocompatible material, is suitable to use but is expensive. Although there are stents made from cobalt-chrome-nickel alloys or tantalum, metal stent problems persist. In other words, an inflammatory reaction arising from the stent implantation causes neointimal hyperplasia in 10-30% of cases which is called restenosis, ends up with insufficient treatment results. To overcome relevant restrictions and problems, new solution approaches are required. At this point, studies on the coating of stents with polymeric materials have been initiated as a new approach due to the substantial properties of polymers such as hemocompatibility and biodegradability [43]-[44].

Drug-releasing stents contain drugs that are released for a certain period in the region where they are placed and that reduces the narrowing of the vascular. After the stent has been placed in the body, drugs are used to prevent inflammation and clotting, and any reactions by the immune system. The main issue is to keep the drug dose constant. For this reason, drugs are absorbed into polymers, covered on the stent and placed inside the body. Compared with bare-metal stents, drug-releasing stent placement has been proven by numerous studies to significantly reduce re-narrowing and re-vascularization.

When the literature is examined, it is barely visible that the interest of the polymer-based coating applications in the cardiovascular implant so that the studies in this area have increased during the last decade. Moreover, several review studies are available to emphasize advances and future directions of the role of polymer coating in cardiovascular implants especially stents. For example, Strohbach and Busch indicated that polymers are utilized for different implementations in cardiology, especially in coronary vascular interventions as stent platforms, and in coating matrices for drug-releasing stents. They emphasized that especially biodegradable polymer coating can contribute to the reduction of undesired results such as intrastent restenosis, late stent thrombosis and hypersensitivity reactions, especially since they deteriorate after their functions are fulfilled [41]. Li and his friends stated that although Mg and its alloys are preferred in the first places for stent applications due to their great biomechanical property and biocompatibility, their high degradation rate in the physiological condition cause a problem in clinical applications. Therefore, they summarized the recent advances in polymeric coatings onto the surface of the biodegradable Mg and its alloys, related

preparation strategies for PLA, PLGA PCL, PDA, CS, Col and their composite, and their performance with regards to corrosion resistance and biocompatibility. As a result, they emphasized that controllable degradation rate and multifunctional polymer coatings are a promising solution for Mg-based implants and will gain more attention in the following year's clinical results, as verified by low MACE and ST ratios for f the stent coated with NFs was that the sheath of the NFs allowed [45]. The summary table of the studies discussed is given in **Table 1.1** based on polymer type and the aim of the study.

Table 1.1: Polymer-based coating studies for cardiovascular implants [46]-[60].

Author	Polymer Type	Aim of the Study
Bakhshi et al. (2011)	POSS–PCU	To analyze surface resistance and improve biocompatibility
Liu et al. (2011)	EVA/PLA and EVA/PEG	To improve the release profiles and mechanical performance
Bege et al. (2012)	PEC	To obtain biocompatible, and favorable mechanical properties
Acharya et al. (2012)	PLGA, PEG and PCL	To improve the surface morphology and the drug release duration
Kimble et al. (2015)	PLA/PGA	To assess mechanical properties and viscoelastic behavior
Park et al. (2015)	PLGA and PEG	Reducing restenosis and improving deterioration over time
Farhatnia et al. (2016)	POSS–PCU	Biocompatible and hemocompatible nanocomposite polymer
Nishimiya et al. (2016)	PDLLA-PCL and PLA	Enhanced coronary vasoconstricting responses through inflammatory changes
Belibel et al. (2016)	PDMMLA	To provide biodegradability and biocompatibility properties
Tang et al. (2017)	PTX/CS	Higher drug loading content
Abhyankar et al. (2018)	All biodegradable stent	Lower major adverse cardiac events and very late stent thrombosis
Baikin et al. (2019)	PLA	To improve mechanical properties and oscillations of prourokinase macromolecules
Lee et al. (2019)	PDA, PEI and Heparin	To prevent restenosis and thrombosis
Yang et al. (2020)	PEA	To prevent the thrombosis and coagulation of platelets
Kersani et al. (2020)	Chitosan/poly-cyclodextrin	To improve drug solubility, release and antibacterial property
Li et al. (2020)	PLA	Long-term efficacy of biodegradable stents

Sevostyanov et al. (2020)	PLGA	To improve mechanical properties and release ability of biological compounds
Mckittrick et al. (2020)	Unspecified	To improve bioactive response

It is concluded that polymer coatings are mostly performed in the cardiovascular field for stent applications and in-stent types, mostly in drug-releasing stents with the studies examined in this section. The common aim is generally to reduce the undesired responses that occur after the drug-released stent is placed inside the body. In this context, different types of polymers, especially PCL, PLA and PLGA, have been utilized in the coating of stent surfaces.

1.1.2.2. Drug delivery

In this section, polymer-based coating studies in drug delivery application is analyzed. Polymers first served as a carrier in drug delivery systems by Ringsdorf in 1975. Then, in 1984, it became a biological rationale with the progress of Duncan and Kopecek, 1984 [61]. Polymers and related nanotech technologies are defined as Polymer Therapeutics (PT) and these macromolecules are conjugated to therapeutic agents (5-100 nm). The design of a regular polymer therapeutic system includes a biocompatible and preferably biodegradable polymeric support in which bioactive compounds are conjugated with biodegradable covalent binders or supramolecular interactions. Both natural and synthetic polymers can be utilized as suitable platforms for therapeutic delivery [62].

The main duties of drug delivery within the body are to improve the bioavailability of drugs, reduce therapeutic doses and possible side effects, thereby increasing safety, ensuring targeted drug delivery and providing a personalized drug system for the long-term future. Drug delivery systems have become a multi-billion-dollar industry today with various applications carried out by many interdisciplinary sciences, and it is undoubtedly a research area that growing in importance day by day. Therefore, workers in this field are looking for new approaches. To obtain an enhanced pharmacological response and to release and control drug molecules; they are investigated with various types of polymers with various physicochemical properties [63]-[64]. Therefore, polymer structures have been benefited from various applications for this drug release.

In recent times, studies that have targeted drugs to specific organs or tissues, thus preventing them from spreading outside of the target area, have come into prominence. Such systems, which are defined as the controlled release or delivery systems, are the

systems that allow the drug to be released at the desired speed and time. Polymer-based drug delivery systems constitute a major part of controlled release studies [65]. Several studies mentioned the importance of polymers in drug deliveries in recent years. For example, Liechty et al. (2010) emphasized that polymer therapeutics has been successful in mediating by providing safe and effective delivery of a several variety of medical conditions in the past few decades. The research interventions highlighted in this review show that the delivery of the drug only to the places where it is needed in therapeutically relevant amounts, and the recent advances in polymers that can direct molecular recognition or intracellular transmission will be at the forefront as promising studies in drug delivery of polymers in the future [66]. Recently, Prajapati et al. (2019) reported that the mechanical properties, minimal cytotoxicity and biocompatibility of polymers offer outstanding advantages to develop the possible drug/gene delivery systems. For this reason, polymers continue to be of interest as encouraging materials to conduct the study related to new drug delivery systems [67]. Calzoni et al. (2019) investigated different types of polymer nanoparticles (NPs) and emphasized their substantial role in drug delivery. They pointed out that the engineering of polymer NPs is a milestone shortly that can lead to the effective use of these versatile systems in large-scale therapeutic applications [68]. Alsehli (2020) emphasized that polymeric nano-carriers promise tremendous hope in drug delivery applications as they increase the bioavailability of drugs at site of disease [69].

When the studies in the related field are examined, it is observed that it is an application that is frequently used especially in cancer disease. For this reason, related studies are classified as cancer diseases and other diseases. The classification of polymer-based coating studies in the drug delivery section is given in **Figure 1.5.**

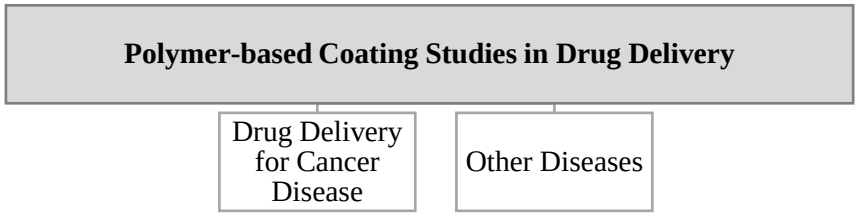

Figure 1.5: The classification of polymer-based coating studies in drug delivery.

1.1.2.3. Tissue engineering and regenerative medicine

Tissue engineering is known as a new and promising field in interdisciplinary science, which jointly utilizes the values of engineering and life sciences to provide continuity of

life processes and to develop biological substitution. Polymers are the most preferred biomaterials in tissue engineering thanks to their flexibility in mechanical manner and similarity to the essential characteristics of tissue [70]. Biodegradability is a critical issue for polymer-based coating in both tissue engineering and regenerative medicine. Most commonly synthetic degradable polymers used in tissue engineering can be listed as PGA, PCL, PLA, polyurethanes, PGS, PEG, polypyrrole, and so on. Moreover, not only synthetic polymers but also natural polymers are widely utilized in tissue engineering. Collagen, fibrin, hyaluronic acid, alginic acid, and chitosan are the commonly utilized biodegradable natural polymers in tissue engineering [71].

Regenerative medicine has become a broad and modern research field, covering numerous parts of materials science, biomedicine, tissue engineering and so on. It offers many furthered applications such as stem cell therapy, fabrication of artificial transplantable organs and plays a role in the curing of various terrible diseases. Polymers play a crucial role in regenerative medicine with various applications from scaffold synthesis to self-assembled material production and nanomedicine. They can be converted to the desired shape and consistency due to the designed polymers. For example, PGA, PLA and PCL-PLA copolymers appear to be effectively integrated into the restoration of organs for example blood vessels, skin and the bladder. Shortly, polymer coatings have become a significant tool for both tissue engineering and regenerative medicine, as the polymer can enable specially designed and multi-functional features. Polymeric coatings offer several advantages such as, cell adhesion which includes proliferation and differentiation, biofilm formation, reducing toxicity, oxidation and inflammation [71]-[73]. A scaffold used in tissue engineering should have critical characteristics such as biocompatibility, biodegradability, required mechanical strength, non-toxic for cellular activities to continue. The summary table of the studies discussed is given in **Table 1.2** concerning the specific application field.

Table 1.2: Polymer-based coating applications in tissue engineering [74]-[83].

Author	Polymer Type	Specific Application
Tsai et al. (2011)	Poly (dopamine)	Cartilage tissue engineering
Radhakumary et al. (2011)	HEMA	Lung tissue engineering
Ravichandran et al. (2011)	PLA/PAA/Col I&III	Dermal tissue regeneration

Haaparanta et al. (2014)	Collagen/PLA, CS/PLA, and Collagen/CS/PLA	Cartilage tissue engineering
Kao et al. (2015)	PDA	Bone tissue engineering
Kanneci Altınışık et al. (2017)	PLA and PBS blend	Neural tissue engineering
Kim et al. (2018)	PCL	Bone tissue engineering
Araque-Monro´s et al. (2019)	PLA-PEG	Tendon/Ligament tissue engineering
Guo et al. (2020)	PLA, PCL, PLGA, PLCL and gelatin	Bone tissue engineering
Sadeghzade et al. (2020)	PCLF	Bone tissue engineering

It can be concluded that PLA is the most used polymer type within the scope of tissue engineering application due to its biodegradability, favorable mechanical strength, and low immunity. Furthermore, it can be emphasized that the main objective is the polymer coating in tissue engineering and regenerative medicine is to mimic the tissue by providing longer time degradation.

1.1.2.4. Orthopedic implants

The utilization of metals and metal alloys as biological implant material has increased due to their strength/weight ratio, biocompatibility, mechanical properties and corrosion resistance. However, since the stable oxide layer of metal-based orthopedic implants gets rough, they restrict the lifespan of implants in biological fluids that results in infections and diseased conditions. At this point, the fact that metal implants are not suitable for use in the joint areas of the body. This situation creates a need for new approaches. At this point, polymeric coatings provide a great advantage in the provision of orthopedic implants with the desired properties. Polymers to be used in orthopedic applications should have features such as not to produce a disproportionate inflammatory/toxic response, to be able to be metabolized in the body, to be simply processed into the last product form, to have a suitable shelf life, to be straightforwardly sterilized, without leaving any trace components [84].

The summary table of the studies discussed is given in **Table 1.3** concerning its acquisitions and polymer type.

Table 1.3: Polymer-based coating studies conducted in orthopedic implants [85]-[93].

Author	Polymer Type	Acquisition
Wong et al. (2010)	PCL	Higher corrosion resistance
Kim et al. (2013)	PEI	Higher corrosion resistance
Kahraman (2013)	poly (HEMA-GDMA)	Higher polarization resistance and lower corrosion rate
Mishra and Kannan (2014)	CS/PVA	Better corrosion protection and improved biocompatibility
Chen et al. (2016)	poly (γ-glutamic acid)-g-7-amino-4-methylcoumarin/	Improved the degradation period and better histocompatibility
Neacsu et al. (2017)	CA	Higher corrosion resistance
Abdal-hay et al. (2019)	PU	Improved surface bioactivity performance
Mathi et al. (2019)	hydroxyapatite/poly(N-methyl pyrrole)	Improved mechanical and antimicrobial properties
Kumar et al.(2020)	PC / PPy	Improved biocompatibility and corrosion protection

The common purpose of utilizing from polymer coating applications in orthopedic implants is to obtain longer degradation time or lower degradation rate and improving corrosion resistance according to studies conducted in this field. Despite these promising purposes, the number of studies conducted in this category is in a minority when compared with the other categories. Hence, it can be emphasized that the next studies should be focused on this category.

When the literature review is completed, it can be inferred that polymer coatings are being applied in many areas in the healthcare field and will continue to be at the forefront in the near future. However, it has been observed that PEG and PLA are used separately in many different studies. However, although the use of PEG-PLA together eliminates the disadvantages of using each other separately, it has been concluded that the studies on this subject are in a minority. This situation has been a source of motivation for this study.

1.1.2.5. PEG-PLA coating applications

PLA is biodegradable, has good reliability, poor immunity and provides great mechanical strength. Therefore, it has been approved by the FDA for utilization in different medical systems and equipment such as tissue engineering, medical supplies, drug carriers [94]. However, the desired improvement might not be obtained when PLA is used alone. Namely, its poor hydrophilicity and drug loading of polar drugs and extremely long degradation time cause its use to be restricted. On the other side, PEG's good water

solubility, flexibility, antifagocytosis against macrophages, resistance to immunological recognition, and biocompatibility can be listed as some of the various advantages [95]. Hence, coating the material through the mixture of PEG and PLA can provide different contributions such as degradation rate, hydrophilicity, mechanical strength in an appropriate component composition and is accepted as one of the promising approaches to improve characteristics of the system in accordance with the objective by minimizing each other's shortcomings. For example, when a material is coated only with PEG, PEG wears off with water and disappears in the progress of time due to its solubility in water. While the material is coated with a combination of PLA and PEG, PLA can provide mechanical strength due to its hydrophobicity property that can minimize the wear of PEG to the system. In this context, it is emphasized that especially the advantages of PEG and PLA in their use together and that they minimize the disadvantages of each other according to the situation in which they are used separately, and for this reason, it is frequently used in different studies under polymer coating in the health field. Some examples selected from the literature are as follows.

Vila et al.(2004) investigated the efficacy of PLA nanoparticles coated with PEG as a carrier for nasal delivery of bioactive compounds. As a result, PEG-PLA nanoparticles exhibited improved responses. These studies demonstrated the important role of the PEG coating around the particles in the stabilization of PLA particles in the mucosal environment and facilitated antigen transport to nanoencapsulation, suggesting a long-term drug/vaccine delivery enhanced use response. The working life and efficacy of polylactic acid nanoparticles coated with a hydrophilic polyethylene glycol coating which is PEG-PLA nanoparticles as a carrier for nasal delivery of bioactive compounds were emphasized. [96].

Chen and He (2014) examined PLA-PEG-coated hollow X-ray and upconversion nanophosphorus which includes folic acid as tumor targeting ligand for a novel drug delivery system. Among various nanomaterials, the biocompatible block-copolymer consisting of poly (lactide) - poly (ethylene glycol) (PLA - PEG) is expected to led to critically important developments for drug carrier utilization due to its important advantages such as improved biocompatibility, lack of intrinsic immunogenicity and biodegradability is expected [97].

Li et al. (2017) focused on the problem of high restricted restenosis rate, usually after bare-metal stent placement for the curing of coronary heart disease with PCT. The use of

a PEGylated stereocomplex poly (L lactide) (PEG - scPLA) coating in the surface modification of the stainless steel (SS) plate was studied to create a solution for the problem. As a result of the study, it was emphasized that PEG - scPLA can increase comprehensive performances such as surface modification of the SS layer, biocompatibility and drug loading capacity, and PEG - scPLA is an outstanding coronary stent coating for PCT [98].

Amani et al.(2019) stated that surface modification by hydrophobic polymers such as PLA and hydrophilic polyethylene glycol and the production of the amphiphilic polymer PLA-PEG polymer increases DNA encapsulation and circulation time in blood compared to nanoparticles made from PLA alone, and this coating approach increases hydrophilicity [99].

In all these approaches to improve surface properties, determination and investigation of surface properties is the crucial point to ensure successful control of the polymer coating. The energy state of the surface layer, the surface free energy, plays a critical role in approaches such as coating, where adhesion is an important property that conditions the effects of the process [100].

CHAPTER 2

2. THEORETICAL PART

2.1. Surface Free Energy (SFE)

Molecules on the boundary surface have less stabilizing interaction compared to the bulk phase, as there are fewer neighboring molecules on the surface. Therefore, excessive energy occurs. This excess energy is called SFE (J/m2 or ergs/cm2). Moreover, the created inward tension at the surface is called surface tension (N/m or dyne/cm) [101]. Generally, SFE is utilized for solids while surface tension is utilized for liquids [102]. Schematic representation of intermolecular interactions, SFE, and surface tension is included in **Figure 2.1.**

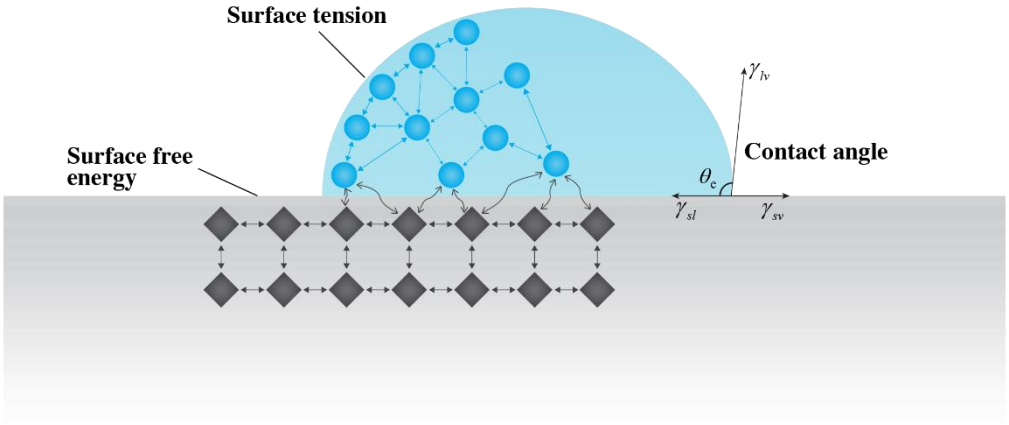

Figure 2.1: Surface tension, contact angle and surface free energy.

2.2. Contact Angle

When a liquid dropped onto a solid surface does not completely spread to the surface, the angle resulted between the liquid and the solid surface is known as the contact angle(θ). The force that occurs between two different substances is called the adhesion forces, while the internal forces that arise due to the attraction of the molecules of an object are

called cohesive forces. Cohesive forces cause the water droplet to have a spherical shape and avoid contact with the surface. Namely, the formation of the contact angle of a droplet dropped onto the solid surface can be explained due to adhesive and cohesive forces [103]. The schematic representation of the contact angle is shown in **Figure 2.2.**

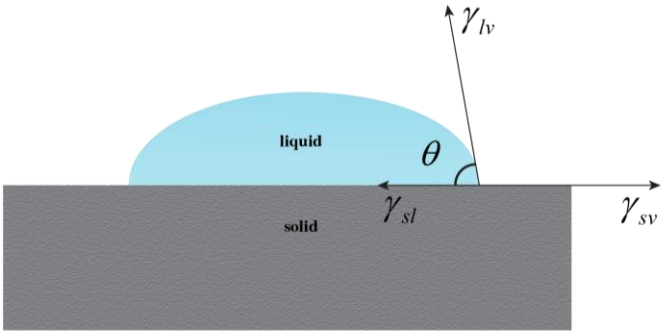

Figure 2.2: Schematic representation of contact angle.

The wettability property of the surface can be determined based on the degree of the contact angle. To interpret the wettability property, the priority limit has been determined as 90 degrees. For low contact angles, which are less than 90°, the droplet dropped onto the solid surface spreads over most of the surface and wetting occurs. At high contact angles, which are greater than 90°, the droplet does not spread over the solid surface, no wetting happens, and contact minimizes. As a result of all these situations, if the surface can get wet, the surface is called 'hydrophilic', while the condition in which the surface is not wet is called 'hydrophobic' [104]. The relation between contact angle and wettability relation is demonstrated in **Figure 2.3.**

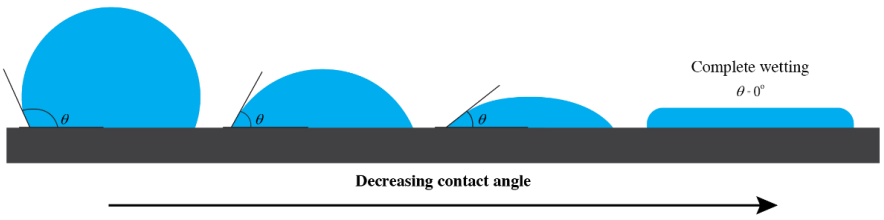

Figure 2.3: Contact angle and wettability.

Contact angle types are generally divided into two as SCA and DCA. SCA and DCA can be measured by various measurement methods. Among this variety, the sessile drop method is a frequently preferred SCA measurement technique since it provides accurate SFE measurement, and it is easy to apply and cost-effective method [105],[106]. The

sessile drop method can be explained as the measurement of the tangent angle from three-phase equilibrium interface point directly. The contact angle can be measured directly by analyzing the drop profile. A drop image is visualized on a screen and main lines are obtained after measuring the angle [107].

2.3. SFE Determination Methods

Determination of SFE has been one of the leading remarkable topics for many years. Despite of the significance of the topic for various industries, a definitive decision on the measurement of free energies could not be reached, as no method has been defined worldwide to determine solid surface SFE [108].

The contact angle measurement method for determining the SFE of solid material is a quantifiable and frequently used measurement method to investigate interfacial phenomena. SFE of solids can be computed by measuring contact angles through the measurement liquid with known SFE [109]. The most preferred SFE methods can be listed as Neumann Method, Fowkes Method, Owens-Wendt Method, Wu Method and Van Oss-Chaudhury-Good Method.

The relationship defined by Young in 1805 is the basis for the determination of the surface measure from contact angles, and therefore of all SFE measurement methods. He stated that the contact angle (θ_y) of a liquid droplet on a solid surface can be determined by the mechanical balance of the drop under the influence of its three interfaces which are solid-vapor, γ_{sv}, solid-liquid, γ_{sl}, and liquid-vapor, γ_{lv} by this relationship. The Equation 2.1 that examines this relationship is defined as follows, and its name is called the Young Equation [110].

$$\gamma_{lv} \cos\theta\gamma = \gamma_{sv} - \gamma_{sl} \qquad \textbf{(2.1)}$$

The relationship between these three and contact angle is demonstrated in **Figure 2.2** Determining the SFE for solids would become very easy once the relevant parameters in Young's Equation were measured. However, only two parameters of the Young Equation, namely contact angle (θ_y) and liquid-vapor surface tension (γ_{lv}), can be measured experimentally. Measurement of surface tension between the liquid and solid surface (γ_{sl}) cannot be carried out experimentally directly. For this reason, SFE measurement for solids via Young Equation is thus become inconvenient and the need to develop this

equation with new approaches arises. In this context, various studies focused on some assumptions to develop methodologies to determine surface tension between the liquid and solid [110]-[112]. The approach that γ_{sl} value is a parameter that depends on the properties of the solid and the measuring fluid is accepted as the basis of these approaches, and many studies, especially the studies of Neuman et al., have focused on this assumption [110],[113]-[119]. This assumption can be presented with the known equation of state (EQS) Equation 2.2.

$$F(\gamma_s, \gamma_l, \gamma_{sl}) = 0 \quad \textbf{(2.2)}$$

This equation 2.2 can also be demonstrated with the following Equation 2.3

$$\gamma_{sl} = f(\gamma_s, \gamma_l) \quad \textbf{(2.3)}$$

Taking this basic approach and studies into consideration, Berthelot started related studies towards the end of the 19th century. He proposed a hypothesis that is based on interfacial adhesion work (W_{sl}) between liquid and solid is equal to the cohesion work of a measuring liquid (W_{ll}) and the geometric mean of the cohesion work of a solid (W_{ss}). The related equation is given in Equation 2.4.

$$W_{sl} = \sqrt{(W_{ss} W_{ll})} \quad \textbf{(2.4)}$$

Considering that two different surfaces in contact are accepted as a single surface, the work that needs to be done to separate these two different surfaces within a single surface is called the work of adhesion. In other words, the work required for the separation of the contacting surfaces is called as the work of adhesion. The related equation which is associated with the work of adhesion is given in Equation 2.5 [120]-[121].

$$W_{adhesion} = \gamma_A + \gamma_B - \gamma_{AB} \quad \textbf{(2.5)}$$

In this equation, γ_{AB} demonstrates the interfacial tension between A and B materials while γ_A demonstrates the surface tension for material A and γ_B is the surface tension for material B.

When it is accepted that material A is solid and material B is a liquid, the equation for work of adhesion can be explained with Equation 2.6.

$$W_{sl} = \gamma_s + \gamma_l - \gamma_{sl} \quad \textbf{(2.6)}$$

When Young Equation and Equation 2.6 are merged, a new equation is called as Young-Dupre Equation and can be demonstrated as in Equation 2.7.

$$W_{sl} = \gamma_l(1+\cos\theta_Y) \quad \textbf{(2.7)}$$

The equation related to the work of adhesion can be explained with the following equation:

$$Wcohesion = \gamma_A + \gamma_B - \gamma_{AB} \quad \textbf{(2.8)}$$

When Equation 2.7 is adjusted for solid and liquid, the equation becomes shown in Equation 2.9 and 2.10

$$Wss = \gamma_s + \gamma_s - 0 = 2\gamma_s \quad \textbf{(2.9)}$$

$$W_{ll} = \gamma_l + \gamma_l - 0 = 2\gamma_l \quad \textbf{(2.10)}$$

Berthelot provides the equation in 2.11 by combining Equations 2.4, 2.7, 2.9 and 2.10, and this equation is called the Berthelot hypothesis, and this hypothesis is considered another most important basis of SFE calculation methods.

$$\gamma_{sl} = \gamma_s - \gamma_l - 2\sqrt{\gamma_s\gamma_l} = (\sqrt{\gamma_l} - \sqrt{\gamma_s})^2 \quad \textbf{(2.11)}$$

There are also different hypotheses based on the hypothesis developed by Berthelot. However, it is not widely used because it is not based on an adequate scientific approach compared to the one developed by Berthelot. Antonow's hypothesis which is explained with the Equation 2.12 is one of these approaches [122].

$$\gamma_{sl} = |\gamma_l - \gamma_s| \quad \textbf{(2.12)}$$

2.3.1. Fowkes approach to determine SFE of solids

Fowkes stated that the intermolecular attractions that cause surface tension are due to various prominent intermolecular forces. In his approach, most of these forces, such as metallic bonds or hydrogen bonds, are a function of a certain chemical structure, and these are different kinds of parameters that contribute to the measurement of SFE. For this reason, he emphasized that SFE is composed of the sum of all these parameters, and it can be expressed with the following equation:

$$\gamma_s = \gamma_s^{\,d} + \gamma_s^{\,p} + \gamma_s^{\,h} + \gamma_s^{\,i} + \gamma_s^{\,ab}\gamma_s^{\,0} \qquad \textbf{(2.13)}$$

While γ_s^d, γ_s^p, γ_s^h, γ_s^i , γ_s^{ab} represent dispersion, polar, hydrogen, induction and acid-base components respectively, γ_s^0 represents the contributions of all residual component forces. In addition, he emphasized that London dispersion forces, which always create an attractive force between adjacent atoms or molecules, are present in all kinds of matter, no matter how different their chemical structures are. London dispersion forces are generated through the interaction of fluctuating electronic dipoles with induced dipoles in neighboring atoms or molecules. These forces, which are independent of temperature, are related to the electrical properties of the respective volume elements and the distance between them. He used mercury to explain this situation and stated that the two main interatomic forces, metallic bonding and London dispersion forces are effective in a liquid such as mercury. As a result, he proposed that the surface tension of mercury is due to two different forces, the part caused by dispersion forces and the part caused by metallic bonds. Therefore, he expressed the relevant equation as follows:

$$\gamma_{Hg} = \gamma_{Hg}^{\,d} + \gamma_{Hg}^{\,m} \qquad \textbf{(2.14)}$$

Fowkes analyzed two-phase systems in which dispersion forces are generated. He took into consideration a system consisting of two liquids, mercury and a saturated liquid hydrocarbon. It has been emphasized that the intermolecular attraction in saturated liquid hydrocarbons is directly related to London dispersion forces. In this context, it can be inferred that the only significant interfacial interactions between a saturated hydrocarbon and any other substance will be London dispersion forces. Since the interface of two liquids consists of adjacent interfacial regions of each liquid, the interfacial tension is expressed as the sum of the stresses at the interfacial regions of each fluid. Molecules in the interface region of the hydrocarbon are under the effect of both intermolecular forces which create a tension equal to the surface tension of the hydrocarbon and the London dispersion forces of mercury. Thus, the tension in the interface region layer can be defined as a function of the difference between the surface tension of the hydrocarbon and the London dispersion forces between hydrocarbon and mercury. Considering Berthelot's geometric mean hypothesis, it is deduced that the London dispersion forces between hydrocarbon and mercury can be calculated by taking the geometric mean of the dispersion surface tension, γ^d, of both hydrocarbon and mercury which can be calculated with the Equation 2.15.

$$\sqrt{\gamma_1^{\,d} - \gamma_2^{\,d}} \qquad \textbf{(2.15)}$$

Since the geometric mean of the dispersion surface tension, γ^d, of both hydrocarbon and mercury is equal to Equation 2.16.

$$\sqrt{\gamma_1^{\,d}\gamma_2^{\,d}} \qquad \textbf{(2.16)}$$

the tension in the interface region of hydrocarbon can be calculated with Equation 2.17.

$$\gamma_1 - \sqrt{\gamma_1^{\,d}\gamma_2^{\,d}} \qquad \textbf{(2.17)}$$

The tension in the interface region of mercury can be calculated with $\gamma_2 - \sqrt{\gamma_1^{\,d}\gamma_2^{\,d}}$ with the same logic. In this regard, it can be stated that the interfacial tension between hydrocarbon and mercury, γ_{12}, can be calculated with the following equation:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^{\,d}\gamma_2^{\,d}} \qquad \textbf{(2.18)}$$

Then, Fowkes demonstrated the whole system in Figure 2.4.

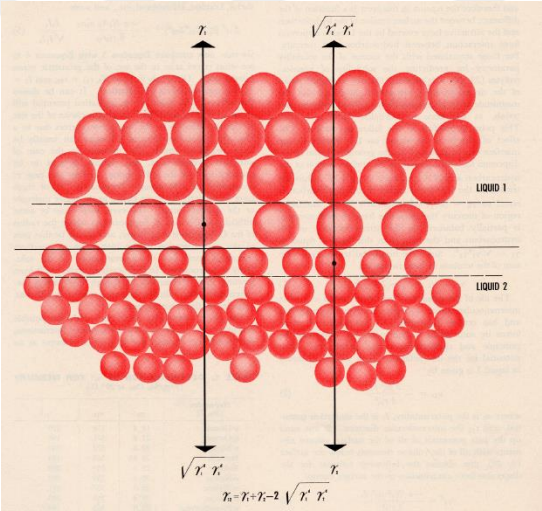

Figure 2.4: The interface and interfacial interactions between hydrocarbon and mercury [123].

Considered like the hydrocarbon and mercury system, Fowkes indicates that the interfacial tension between a solid and a liquid can be determined by the following equation for a solid and a liquid system where only dispersion forces take place:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\sqrt{\gamma_s{}^d \gamma_l{}^d} \quad \textbf{(2.19)}$$

Since the SFE of the multiple of Equation 2.19 is equal to the distribution component of the SFE of the solid, the combination with Equation 2.1 provides the SFE formula for a non-polar solid.

$$\gamma_s = \gamma_s{}^d = \frac{\gamma_l{}^2 (1+\cos\theta y)^2}{4\gamma_l{}^d} \quad \textbf{(2.20)}$$

When the liquid is selected only when it is a liquid with dispersion interactions the Equation 2.20 transforms into:

$$\gamma_s = \gamma_s{}^d = 0.25\gamma_l (1+\cos\theta_y)^2 \quad \textbf{(2.21)}$$

If two liquids which one has only dispersion interaction and one has only polar interaction with known surface tension are used, the Fowkes method also be utilized to determine the solid SFE (s) by assuming that SFE is expressed as two components, dispersion and polar. However, it should be noted that polar interactions will also take place on the molecules in the interfacial region, then Equation 2.21 transform into:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\sqrt{\gamma_s{}^d \gamma_l{}^d} - 2\sqrt{\gamma_s{}^p \gamma_l{}^p} \quad \textbf{(2.22)}$$

Then, the formula for calculating the polar component of the SFE of the solid is obtained by combining Equation 2.1 with Equation 2.22:

$$\gamma_s{}^p = \left[0.5\gamma_l (1+\cos\theta_y - \sqrt{\gamma_s{}^d \gamma_l{}^d} \right]^2 / \gamma_l{}^p \quad \textbf{(2.23)}$$

As a result, the SFE of the solid is equal to the sum of the dispersion and polar components of the SFE, and this method is called as Extended Fowkes Method. The Fowkes Method is generally used to determine the SFE of polymeric non-polar materials. It is emphasized that, for measuring liquids, it is often convenient to use water and diiodomethane in most applications.[123]-[126]

2.3.2. Owens-Wendt approach to determine SFE of solids

Owens and Wendt have been presented a method to determine the SFE of solids by benefiting from the contribution of two different parameters which are the dispersion and the dipole-hydrogen bonding forces. This relationship can be explained as Equation 2.24.

$$\gamma_s = \gamma_s^{\,d} - \gamma_s^{\,h} \tag{2.24}$$

In Equation 2.24, the superscripts h and d address to the hydrogen bonding and dispersion force components, respectively. This equation is enhanced as the following equation:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\sqrt{\gamma_s^{\,d}\gamma_l^{\,d}} - 2\sqrt{\gamma_s^{\,h}\gamma_l^{\,h}} \tag{2.25}$$

Considering Owens and Wendt's approach that SFE consists of dispersed and polar components, the following equation is expressed.

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\sqrt{\gamma_s^{\,d}\gamma_l^{\,d}} - 2\sqrt{\gamma_s^{\,p}\gamma_l^{\,p}} \tag{2.26}$$

It should be stated that since Owens and Wendt's polar interaction definition is different from Fowkes's polar interaction definition, $\gamma_s^{\,p}$ and $\gamma_l^{\,p}$ Equation 2.26 is different than those used in Equation 2.12.

Fowkes put forward another equation by combining Young's equation and Equation 2.26 to explain the contact angle of a liquid at the solid surface, considering the dispersion strength contributions of each. The equation is demonstrated below.

$$1 + \cos\theta_y = 2\frac{\sqrt{\gamma_l^{\,d}\gamma_s^{\,d}} + \sqrt{\gamma_l^{\,p}\gamma_s^{\,p}}}{\gamma_l} \tag{2.27}$$

Values of γ_l^d have been published for many liquids. Therefore, γ_s^d can be approximated through a single measurement of θ by eq. in which only dispersion forces perform. Therefore, it is inferred that there are two unknowns in the equation, $y_s^{\,d}$ and $y_s^{\,p}$. Hence, to solve the equation, two contact angle measurements through two different measuring liquids with known dispersive and polar components are needed. At this point, it should be taken that at least one of the measured liquids is a predominantly polar interacting liquid. In determining the SFE of a solid by the Owens-Wendt Method, water, glycerol or formamide polarly and diiodomethane, tetradecane or heptane as a dispersing measurement liquid can be utilized [126]-[127].

2.3.3. Wu's approach to determine SFE of solids

Wu conducted the study to put forward polar and nonpolar (dispersion) interactions of interface energies equations by utilizing the energy additivity approach in a semi-

continuum model. In this context, the assumption that the interfacial energies can be decomposed into nonpolar (dispersion) and polar components are taken into account.

He proposed three different formulas on which different approaches are based.

The first one is an equation based on the harmonic mean and for this reason, it is called a harmonic mean equation that can be utilized in low energy systems such as organic liquids, water, polymers and organic pigments:

$$\gamma_{sl} = \gamma_s + \gamma_l - \frac{4\gamma_s{}^d\gamma_l{}^d}{\gamma_s{}^d + \gamma_l{}^d} - \frac{4\gamma_s{}^p\gamma_l{}^p}{\gamma_s{}^p + \gamma_l{}^p} \quad \textbf{(2.28)}$$

The second is the geometric-harmonic-mean equation to utilize in high energy systems such as mercury, glass, metal oxides and graphite.

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\sqrt{\gamma_s{}^d\gamma_l{}^d} - 4\frac{\gamma_s{}^p\gamma_l{}^p}{\gamma_s{}^p + \gamma_l{}^p} \quad \textbf{(2.29)}$$

The third one is known as the geometric mean equation.

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\sqrt{\gamma_s{}^d\gamma_l{}^d} - 2\sqrt{\gamma_s{}^p\gamma_l{}^p} \quad \textbf{(2.30)}$$

Based on all this, he emphasized that instead of the geometric mean, the harmonic mean equation will be utilized to acquire the "optimum" wettability status for the solid-liquid interface. In this context, when Young's Equation and Wu's harmonic mean equation are combined, the following equation is obtained:

$$0.5\gamma_l(1+\cos\theta_y) = 4\frac{\sqrt{\gamma_s{}^d\gamma_l{}^d}}{\gamma_s{}^d + \gamma_l{}^d} + 4\frac{\sqrt{\gamma_s{}^p\gamma_l{}^p}}{\gamma_s{}^p + \gamma_l{}^p} \quad \textbf{(2.31)}$$

In the same way as the Owens-Wendt Methods, two contact angle measurements should be made using two different measuring fluids with known dispersive and polar components to solve the Wu Equation. With this method, water and diiodomethane measuring fluids are often used to determine the SFE of solids. Although the Owens Wendt and Wu methods seem similar, there are differences in terms of the assumptions made for the adhesion study. The Wu method is less preferred than the Owens-Wendt method, and it has been observed that higher variances are obtained in the results obtained using the harmonic mean approach compared to the SFE measurements using the

geometric mean. Therefore, the method underlying the approaches used to calculate the SFE should be considered [126],[128]-[129].

2.3.4. Van Oss-Chaudhury-Good method to determine solid SFE

This method is also called as the acid-base method, is rely on the Van Oss-Chaudhury-Good (1986) method. This method was presented by Van Oss, Good and Chaudhury considering the electron exchange interactions between molecules at the liquid and solid interface and dispersive of solid surface. They argued that SFE measurement includes two components, long-range and short-range interactions, and they focused to explain these hypotheses in detail in their studies. Namely, long-range interactions are defined the Lifshitz-van der Waals component, γ^{LW} , which includes dipole-dipole interactions described by Keesom, dipole-induced dipole interactions described by Debye, and wavy dipole-induced dipole interactions explained by London. Short-range interactions are defined as the acid-base component, γ^{AB} , which consists of interactions of γ^{+} and basic, γ^{-} related with Lewis acid-base description [126].

In this context, according to Van Oss, Chaudhury and Good, the surface tension of the solid is the sum of the Lifshitz-van der Waals forces γ^{LW} and Lewis acid-base interactions γ^{AB} between the two components and they suggested that it can be computed with the following equation:

$$y_{sl} = \{(\sqrt{y_s{}^{LW}}) - (\sqrt{y_l{}^{LW}})\}^2 + 2\{(\sqrt{y_s{}^{+}}) - (\sqrt{y_l{}^{+}})\}.\{(\sqrt{y_s{}^{-}}) - (\sqrt{y_l{}^{-}})\} \qquad \textbf{(2.32)}$$

When the 2.32 equation is combined with Young Equation which is, $y_{sl} = y_s - y_l \cos\theta$, then the new equation is obtained as follows:

$$0.5(1+\cos\theta) = (\sqrt{y_s{}^{LW} y_l{}^{LW}}) + (\sqrt{y_s{}^{+} y_l{}^{-}}) + (\sqrt{y_s{}^{-} y_l{}^{+}}) \qquad \textbf{(2.33)}$$

In equation 2.33, polar components can be separated into acid and base components by using the acid-base approach. Moreover, there are three different unknowns represented by $\gamma_s{}^{LW}, \gamma_s{}^{+}, \gamma_s{}^{-}$. [130]-[131]. Therefore, at least three SFE measuring fluids with known properties should be used to calculate SFE. At least one of the SFE measurement liquids to be selected should be apolar and the other two should be bipolar. Generally, liquids with known surface tension components such as diiodomethane, water and formamide

are used as standard test fluids. Diiodomethane is a non-dispersive liquid with a non-Lewis acid interaction. On the other hand, formamide is highly basic, while water shows a low acidic character, bipolar and equal acid-base character. The Van Oss-Chaudhury-Good method gives information about the properties of the solid surface. However, However, it has the advantage of being sensitive to small differences in contact angle measurements due to the use of three different fluids. [132]-[133].

2.3.5. Neumann method to determine solid SFE

It is known that many formulations derived from EQS and adaptation of the Berthelot hypothesis are included in the literature. One of the most frequently used of these is the formulation proposed by Neumann[115]-[122].

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s\gamma_l)^{0.5} e^{-\beta(\gamma_l-\gamma_s)^2} \quad \textbf{(2.34)}$$

In the equation, β is an experimentally determined coefficient equal to 0.0001247. When Equation 2.33 is merged with Young's Equation which is Equation 2.1, the equation is transformed into:

$$\cos\theta_y = 1 + 2\sqrt{\frac{\gamma_s}{\gamma_l}} e^{-\beta(\gamma_l-\gamma_s)^2} \quad \textbf{(2.35)}$$

There are 3 reasons related to the qualification that distinguish the Neumann Method from other SFE calculation methods. First, in the Neumann method, surface tension is not expressed by dividing it into components. Second, it is sufficient to use only one measuring fluid to determine the SFE of a solid with this method. In this regard, the SFE values determined using the Neumann Method are expected to yield similar results regardless of the measuring fluids used. The third one is that The Neumann Method is the only method that involved an experimentally determined coefficient, which has led to further questioning of this method. Hence, the Neumann Method has been examined by many researchers in their studies [120]-[121].

CHAPTER 3

3. EXPERIMENTAL PART

3.1. Material and Method

The main purpose of this study is to analyze SFE, which is one of the main characteristics of the material, of the surface, coated with polymer. In this regard, it is aimed to determine and compare the SFE of the different surfaces coated with the different PEG-PLA proportions. The reason for the use of PEG-PLA in the coating is to provide many advantages in various applications in the health field by eliminating each other's disadvantages when used together and giving the relevant surface biocompatibility property.

The experimental environment has normal temperature and pressure (NTP) characteristics of 20 ℃ (273.15 K) and 1 atm (101.325 kPa). The experiment consists of 4 different stages. Stage-1 is the preparation of the PEG-PLA coating materials in different proportions. Stage-2 is the application of the coating. Stage-3 is the measurement of static contact angle and finally, Stage-4 is the determination of SFE.

3.2. Preparation of the PEG-PLA Coating Mixtures

PEG with 50,000 Da molecular weight and PLA with 60,000 Da molecular weights were directly purchased from Merck. To prepare the PEG-PLA mixture, an environment suitable for melting temperatures was prepared. Different mixtures of PEG-PLA with different ratios of PEG and PLA were prepared. Proportions of coating materials are given in **Table 3.1.**

Table 3.1: The proportions of coating materials.

No	PEG (g)	PLA (g)	PEG (%)	PLA (%)
1	10	0	100%	0%
2	8	2	80%	20%
3	6	4	60%	40%
4	4	6	40%	60%
5	2	8	20%	80%
6	0	10	0%	100%

Since all experimental studies were carried out with highly pure chemicals, no further purification was required.

3.3. Application of Coating

The coating materials application material was glass slides. For this reason, glass slides were waited in chronic acid at room temperature to sterilize, then rinsed with distilled water and left to wait until dry at 100°C.

There are various methods for coating the application of the surface. Dip coating is one of the most widely performed methods for industrial and specifically laboratory studies due to its simple procedure, cost-effective, and high coating quality. Furthermore, other advantages of dip coating include the ability to make multi-layer coating, the ability to coat both sides of the sample with a single process, and the ability to obtain the same coating regardless of the geometry of the object to be coated. The dip-coating method is relying on the principle that the material to be coated is dipped into the prepared solution at a certain speed and withdrawn at the same speed. The dip-coating process consists of 5 stages: immersing, withdrawing, coating and evaporation. The material to be coated is dipped into the sol at a constant speed and in the uptake stage, it is pulled up without waiting at the dipped speed (10-107 mm/min). During the coating stage, the parts of the material to be coated that come into contact with the left are covered. A mechanical boundary layer forms between the material entering the solution and the fluid in the environment. A two-way flow is observed in this layer, which is formed while the substrate is being pulled. In this way, two layers, the lower layer and the outer layer, are formed. While the layer close to the material moves upward with the material, the layer on the outer parts tends to return to the solution [134]-[135]. The dip-coating process is demonstrated as in **Figure 3.1.**

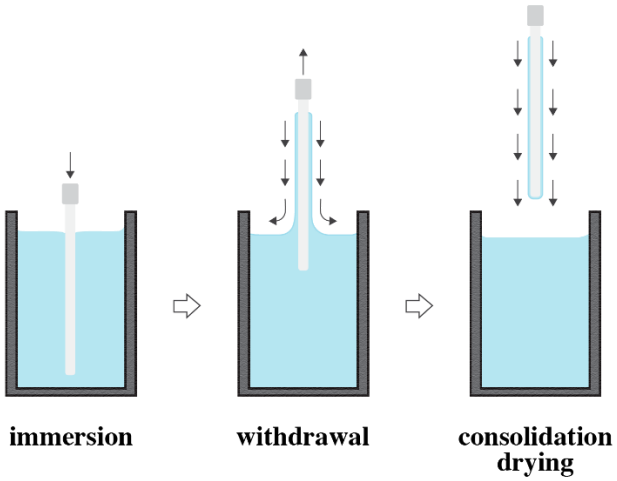

Figure 3.1: The dip-coating process

Mainly six forces act on the layer on the coating material. These forces are; [135]

- The upward pulling force of the mobile carrier due to the viscosity,
- The force of gravity,
- Surface tension force,
- The inertial force of the boundary layer of the liquid coming into the coating zone,
- Surface tension gradient,
- Breaking pressure

In this study, glass slides are coated with PEG-PLA coating liquids by dipping method. In this context, 6 different coated surfaces with 6 different PEG-PLA proportions were obtained. The immersion angle, duration and speed are adjusted to be the same in all dip coating processes. Coated surfaces were left to dry for 3 hours. After 3 hours of drying time, coating material was stored in an airtight container until analysis was performed.

3.4. Static Contact Angle Measurement

The sessile drop is the most carried out method consists of a solid/liquid dual-phase system. Drop sessile technique based on placing liquid drop onto the surface with a micro-syringe. Then, the contact angle of the liquid (water) drop formed is calculated by recording it in the computer-controlled camera. In this study, the sessile drop technique was utilized to determine contact angles of the PEG-PLA-coated glass slides. Static

contact angles were carried out in a contact angle meter system which consist of video camera, microscope, computer. Initially, PEG-PLA coated glass slides were placed on a smooth surface in accordance with the angle of the camera and microscope. Polar and apolar measurement fluids are needed to determine the contact angle. In this context, glycerol and water as polar measurement liquids and diiodemethane measurement liquid as apolar have been determined. In this context, drops of a volume of 10 μL of each were gently placed on PEG-PLA-coated glass layers with the help of a syringe. It was recorded for each measuring fluid and each coated surface, and then snapshots were obtained from the recorded videos. Angle measurement time is important because the measuring fluid evaporates over time and spreads on the surface. Therefore, 10 seconds after the droplet is placed on the surface was chosen as the standard time for taking snapshots. Water and glycerol were used as polar measuring liquids and diiodomethane as non-polar measuring fluids. Videos were recorded as each measuring liquid was placed on the coated surface. After taking snapshots for each coated surface and each droplet of measuring liquid placed on the surface of the coatings, the static contact angles of each droplet were measured by a program called ImageJ which open-source Java image processing. Since the shape of the droplets is asymmetrical, contact angles were measured from both left and right contact points. Therefore, the averages of the left and right contact angles for each droplet were calculated to determine the SFE's of the coated surfaces.

3.5. Surface Free Energy Determination

The process of determining the SFE of solid surfaces whose contact angles are measured was carried out in the computer environment in a cost-effective manner. A MATLAB program which is available in Appendix A1 for SFE determination was utilized. For common measuring fluids used to determine the SFE of solids, surface tension (with separate components with polar, non-polar, acid and base components), density and viscosity values are available in the program library. Since water, glycerol, formamide, ethylene glycol, dimethyl sulfoxide, diiodomethane, tetradecane and heptane are commonly used measurement fluids, their information has been included as relevant measuring fluids. The surface tension with separate components being polar, non-polar, acid and basic components density and viscosity values for these measurement liquids are given in **Table 3.2**. The functions in curve fitting and optimization toolboxes are utilized in the program.

Table 3.2: The properties of measuring liquids and units.

	γ_l (mJ /m^2)	γ_l^{LW} (mJ /m^2)	γ_l^{AB} (mJ /m^2)	γ_l^+ (mJ /m^2)	γ_l^- (mJ /m^2)	Density (kg /m^3)	Viscosity (kg /m.s)
Water	72	21.8	51	25.5	25.5	998.21	0.001002
Glycerol	64	34	30	3.92	57.4	1261.3	1.459
Formamide	58	39	19	2.28	39.6	1133.4	0.00323
Ethylene Glycol	48	29	19	1.92	47	1115	0.026
Dimethyl Sulfoxide	44	36	8	0.5	32	1100.3	0.002174
Diiodomethane	50.8	50.8	0	0	0	3321.2	0.00276
Tetradecane	26.4	26.4	0	0	0	762.8	0.00213
Heptane	19.9	19.9	0	0	0	683.8	0.000408

To make the desired calculations through the program, some relevant inputs that the user should enter are required. In the program, both SFE, friction factor, and dynamic interface tension calculations are available, but the inputs for these calculations are different.

The program develops two linear equations through Owens-Wendt. This equation includes polar and apolar parameters that are unknown in the SFE of the solid. It will be sufficient to enter information about which measurement liquids are used to determine SFE through the created equation since the surface tension components are already available in the program's library. The program uses Gauss-Jordan Elimination Method to solve these linear equation systems. Initially, a matrix with these linear equations is created by the program. Then, this matrix is converted into reduced order-echelon form to determine the polar and non-polar components of the solid SFE. Finally, the total SFE value of the solid is calculated through the determining components. The only difference between the commands that calculate SFE through Owens-Wendt and Acid-Base Method is that the system of linear equations consists of three linear equations in the Acid-based Method instead of two linear equations as in the Owens-Wendt Method since the unknowns in the base Method are three.

For SFE calculation through Wu's and Neumann's method, the program uses a nonlinear equation solver called "fsolve". Trust zone dogleg algorithm, which is a subspace trust zone method and based on the interior-reflective Newton method is used by this "fsolve" equation. Contrary to other methods, there is no numerical method to calculate SFE via

Fowkes Method. Calculation of SFE of the solid can be investigated into three steps in Fowkes Method. The first step is the calculation of the non-polar component of the SFE with the known surface tension of the non-polar measuring fluid and the static contact angle measured between the solid surface and the measuring fluid. The second step is the calculation of the polar component of SFE with the non-polar component of SFE of solid which is calculated in the first step, known surface tension components of the polar measuring liquid, and measured static contact angle between the solid surface and measuring liquid. The final step is the determination of the SFE of solid by using calculated values of polar and non-polar components of SFE of solid. The equation associated with each SFE determination method is summarized in **Table 3.3**.

Table 3.3: SFE determination method and related equations used in the program.

SFE Determination Method	Equations
Acid-Base	$2(\sqrt{\gamma_s^{LW}\gamma_l^{LW}}+\sqrt{\gamma_s^{+}\gamma_l^{-}}+\sqrt{\gamma_s^{-}\gamma_l^{+}})=\gamma_l(1+\cos\theta_y)$
Fowkes	$\gamma_s^{d}=0.25\gamma_l(1+\cos\theta_y)^2$, $\gamma_s^{p}=\frac{0.5\gamma_l(1+\cos\theta_y)-\sqrt{\gamma_s^{d}\gamma_l^{d}}^2}{\gamma_l^{p}}$
Owens-Wendt	$0.5\gamma_l(1+\cos\theta_y)=\sqrt{\gamma_s^{d}\gamma_l^{d}}+\sqrt{\gamma_s^{p}\gamma_l^{p}}$
Wu	$0.5\gamma_l(1+\cos\theta_y)=4\left[\left(\frac{\gamma_s^{d}\gamma_l^{d}}{\gamma_s^{d}+\gamma_l^{d}}+\frac{\gamma_s^{p}\gamma_l^{p}}{\gamma_s^{p}+\gamma_l^{p}}\right)\right]$
Neumann	$\cos\theta_y=1+2\sqrt{\frac{\gamma_s}{\gamma_l}}e^{-\beta(\gamma_l-\gamma_s)^2}$

Moreover, the Zisman Plot Method to compute the critical surface tension that can be explained as the surface tension of a liquid that completely wets a solid also included in the program. Extrapolation of this line when Cosθ = 1 point, ie θ = 0 °, gives the critical surface tension (γ_c) of the solid which is equal to the surface tension of the liquid at that point. In the program, Linear Regression Analysis is used to calculate the critical SFE for the Zisman Plot Method. As a result of all calculations, the program displays a graph. In the graph, cosine values of the CAs are located on the y-axis while the surface tension values of the measuring liquids are located on the x-axis. Next, the program performs Linear Regression to the points determined in the graph, and the program creates a linear model for these data points. Finally, the value of the line y = cos0 = 1 with the surface tension, which is the intersection of the linear model is calculated in the program [63].

The methods utilized in the program related to each SFE determination method are summarized in **Table 3.4**.

Table 3.4: SFE determination method and related equations.

SFE Determination Method	**Equations**
Acid-Base	Gauss Jordan Elimination Method
Fowkes	Mathematical Calculations
Owens-Wendt	Gauss Jordan Elimination Method
Wu	Newton-Raphson Method
Neumann	Newton-Raphson Method
Zisman Plot	Linear Regression Model

CHAPTER 4

4. RESULTS AND DISCUSSION

The SFE values of the coated surfaces are determined by the static contact angles in this study. Therefore, the result parts which is the part where the data regarding the results are obtained can be considered in two stages. The first stage is the measurement of contact angles to the coated surfaces utilizing measuring fluids. The second stage is the determination of SFEs by transferring the contact angles to the developed program in the computer environment.

4.1. Static Contact Angle Results

Sessile drop method based on the imaging technique was utilized to carry out the static contact angle measurement. In this context, water, glycerol and diiodomethane liquids were placed on 6 different surfaces coated with PEG-PLA in different proportions and video images were recorded using the experimental setup. Then, to have a standard measurement time, 10 seconds after the droplets were placed on the surface in all relevant videos were determined as suitable for taking snapshots. Angle measurements were carried out using the angle tool in the ImageJ program. Due to the right and left tendencies of the droplets, measurements were made from both right and left angles. In this context, the measurement from each angle was carried out through 3 reference points. Left and right contact points were designated as one and second points, and since the liquid-vapor interface is easily distinguishable from the surface and the background, it was measured by specifying a third point on the surface.

As mentioned in **Table 3.1**, 6 different coating applications consisting of different PEG-PLA ratios were carried out. However, static contact angle measurement could not be performed due to the interaction between the coated glass slide and the measurement liquid in the 6^{th} proportion. The first one, which is stated as no 1, consists of 100% PEG.

Water, glycerol and diiodomethane measurement liquids were dropped on the relevant surface respectively and screenshots were obtained from the recorded video. Images are demonstrated in **Figures 4.1-4.3.**

Figure 4.1: Snapshot of the water droplet on the no.1 surface

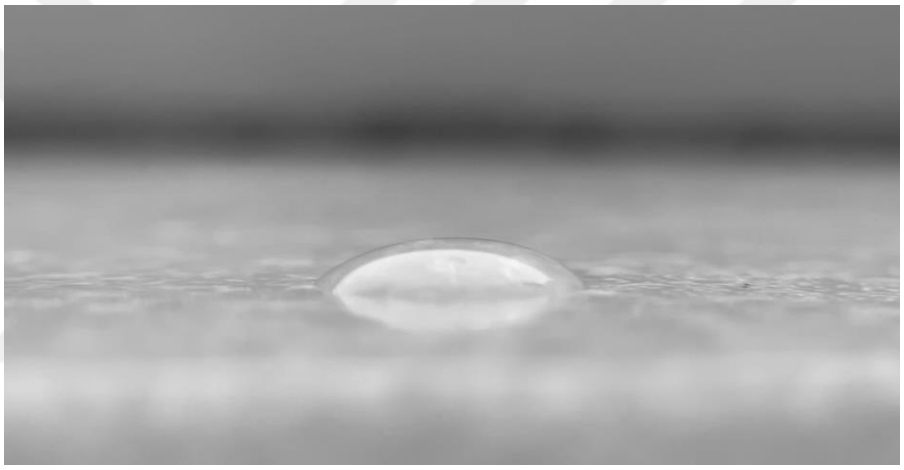

Figure 4.2: Snapshot of the glycerol droplet on the no.1 surface.

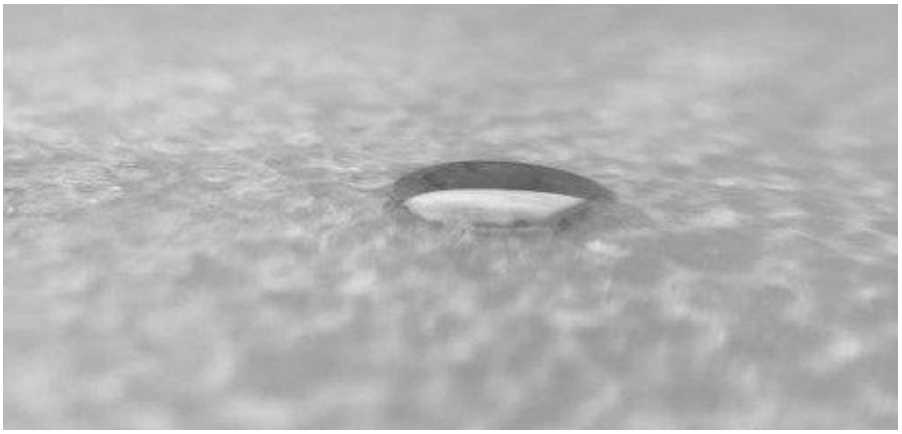

Figure 4.3: Snapshot of the diiodomethane droplet on the no.1 surface

The second one, which is stated as no.2, consists of 80% PEG and 20% PLA. Water, glycerol and diiodomethane measurement liquids were dropped on the relevant surface respectively and screenshots were obtained from the video. Images are demonstrated in **Figures 4.4-4.6**.

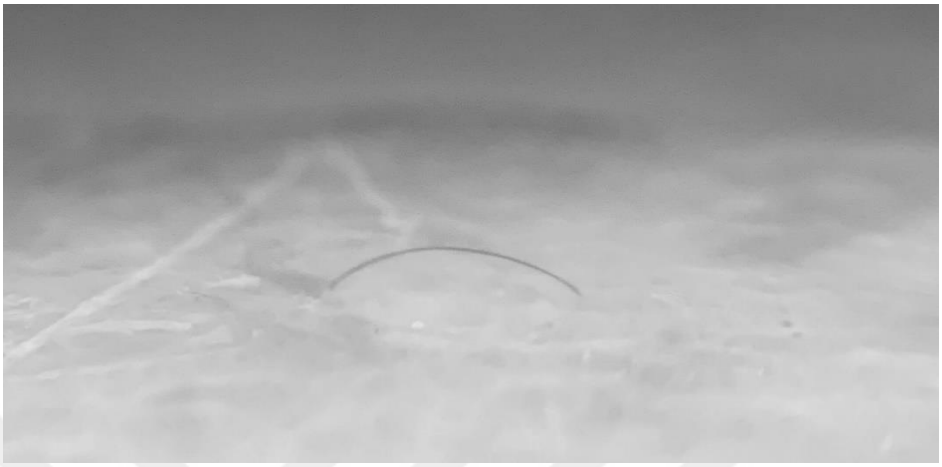

Figure 4.4: Snapshot of the water droplet on the no.2 surface.

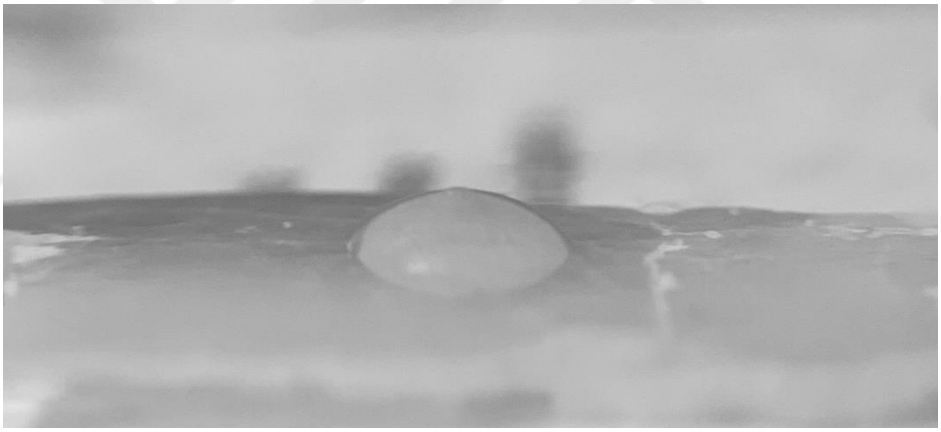

Figure 4.5: Snapshot of the glycerol droplet on the no.2 surface.

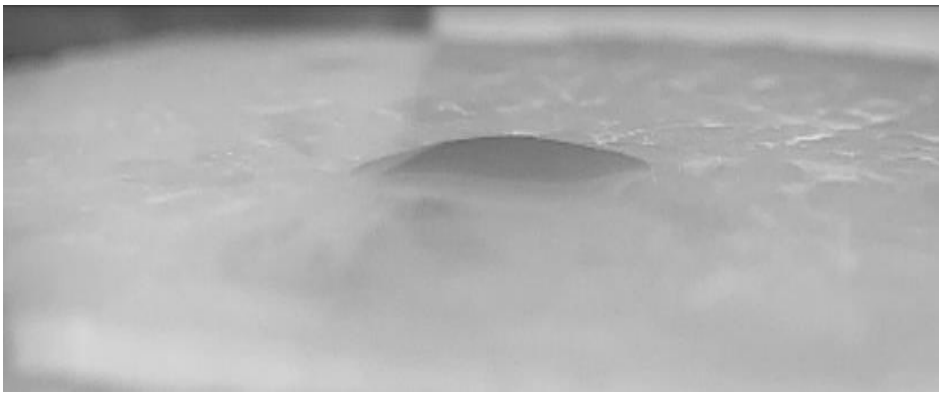

Figure 4.6: Snapshot of the diiodomethane droplet on the no.2 surface.

The third one, which is stated as no.3, consists of 60% PEG and 40% PLA. Water, glycerol and diiodomethane measurement liquids were dropped on the relevant surface respectively and screenshots were obtained from the video. Images are demonstrated in **Figures 4.7-4.9**.

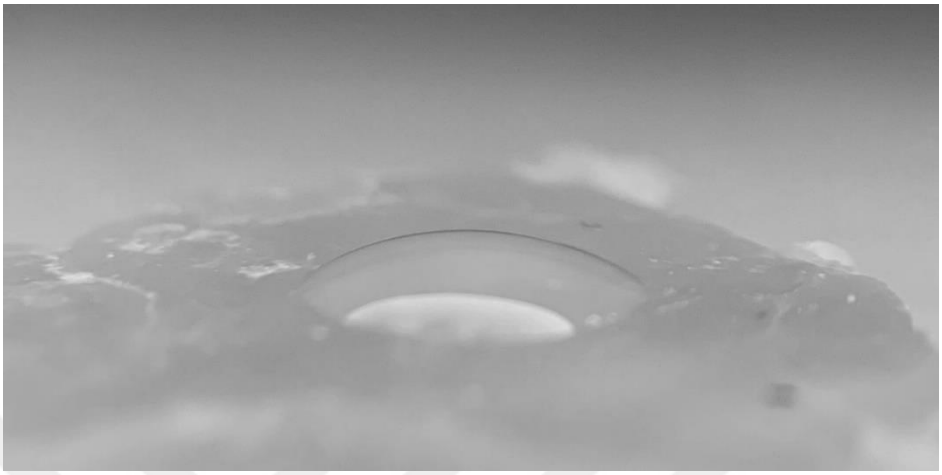

Figure 4.7: Snapshot of the water droplet on the no.3 surface.

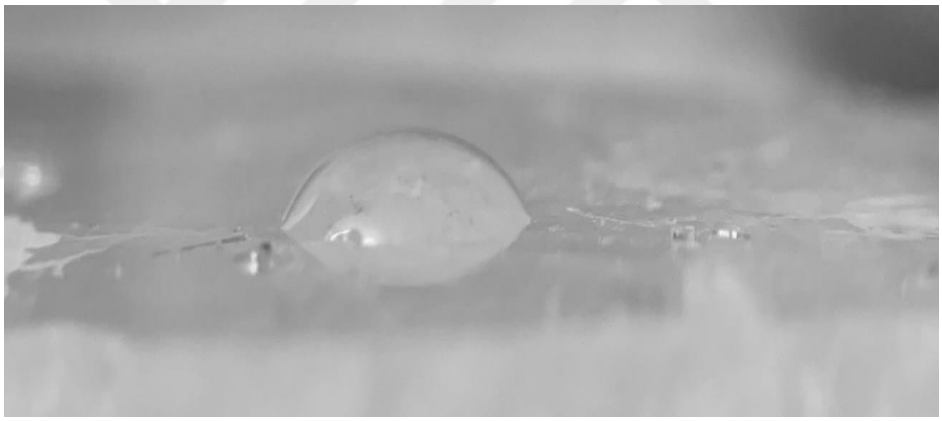

Figure 4.8: Snapshot of the glycerol droplet on the no.3 surface.

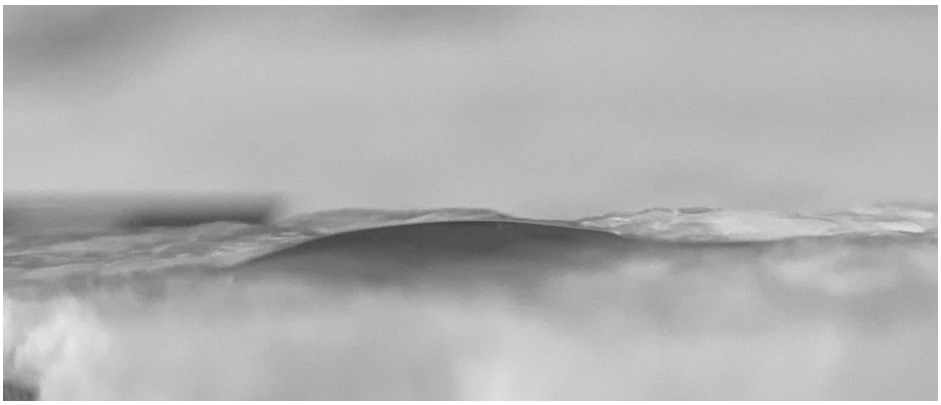

Figure 4.9: Snapshot of the diiodomethane droplet on the no.3 surface.

The fourth one, which is stated as no.4, consists of 40% PEG and 60% PLA. Water, glycerol and diiodomethane measurement liquids were dropped on the relevant surface respectively and screenshots were obtained from the video. Images are demonstrated in **Figures 4.10-4.12**.

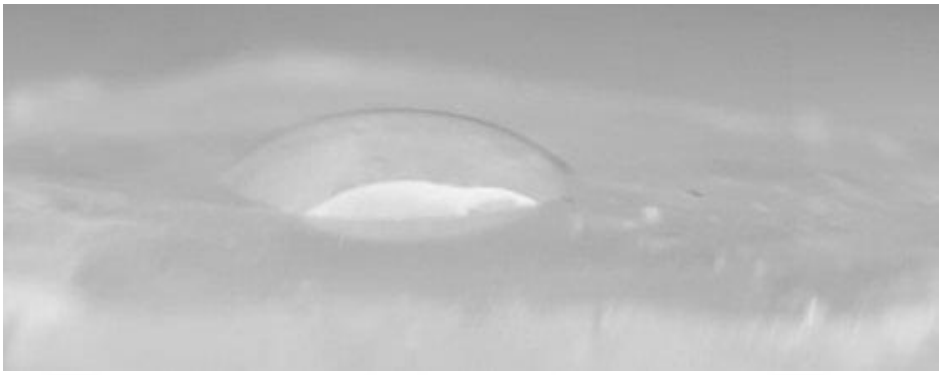

Figure 4.10: Snapshot of the water droplet on the no.4 surface.

Figure 4.11: Snapshot of the glycerol droplet on the no.4 surface.

Figure 4.12: Snapshot of the diidomethane droplet on the no.4 surface.

The fifth one, which is stated as no.5, consists of 20% PEG and 80% PLA. Water, glycerol and diiodomethane measurement liquids were dropped on the relevant surface

respectively and screenshots were obtained from the video. Images are demonstrated in **Figures 4.13-4.15**.

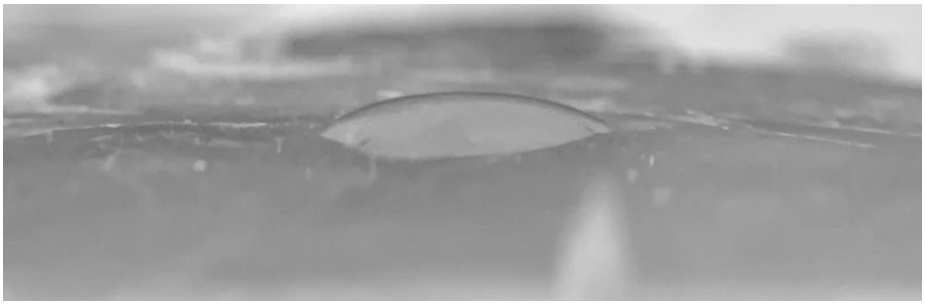

Figure 4.13: Snapshot of the water droplet on the no.5 surface.

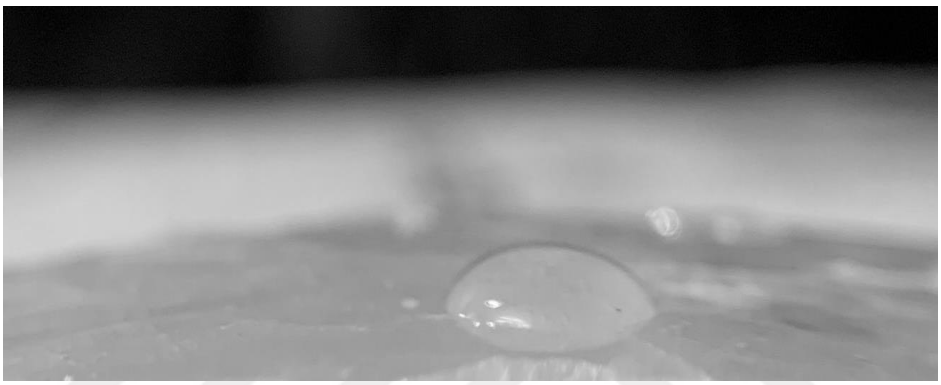

Figure 4.14: Snapshot of the glycerol droplet on the no.5 surface.

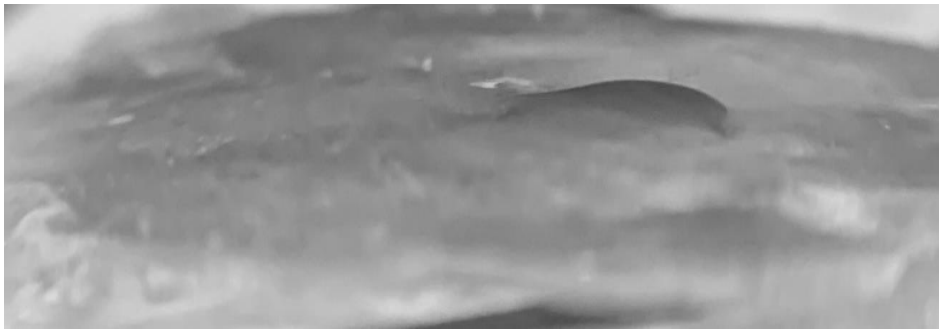

Figure 4.15: Snapshot of the diiodomethane droplet on the no.5 surface.

Since the surface coated with the coating material 6th which is containing 100% PLA is not in accordance with the measurement standards, SCA measurement of the 6th surface could not be performed.

Table 4.1: SCA of water droplets placed on the PEG-PLA coated surfaces.

No.	Left(°)	Right(°)	Average(°)
1	37.010	37.568	37.29
2	51.997	50.177	53.59
3	56.897	58.504	57.70
4	51.278	50.978	51.13
5	30.640	34.226	32.43

Table 4.2: SCA of glycerol droplets placed on the PEG-PLA coated surfaces.

No.	Left(°)	Right(°)	Average(°)
1	48.879	51.187	50.03
2	55.790	52.673	54.23
3	63.701	64.019	63.86
4	59.364	61.010	60.19
5	52.608	52.968	52.79

Table 4.3: SCA of diiodomethane droplets placed on the PEG-PLA coated surfaces.

No.	Left(°)	Right(°)	Average(°)
1	30.110	27.883	29.00
2	32.390	25.625	29.01
3	37.071	33.579	35.33
4	28.241	29.935	29.09
5	24.277	29.981	27.13

Number 1 surface contains 100% PEG. In the literature, it is emphasized that PEG is hydrophilic and its contact angle with the surface is between 36° and 39°. In this regard, it can be concluded that the angle of 37°formed by the water droplet on the surface numbered 1 with the surface supports the literature. The contact angle of the water drop of the 2nd surface is higher than the 1st surface. This situation is attributed to the hydrophobic nature of PLA. In the mixture containing 20% PLA and 80% PEG relative to 100% PEG content, the percentage of PEG decreased while the percentage of PLA increased. In this case, the 2nd surface is expected to show a more hydrophobic property than the 1st surface in the presence of PLA. Namely, the high SCA of the water is associated with an increase in the hydrophobic percentage of the surface. Moreover, with the increase in the percentage of PLA on surface number 3, the water contact angle increased. In conclusion from all these cases, the contact angle is expected to gradually increase as the percentage of PLA continues to increase. However, although the percentage of PLA by weight was higher on the 4th surface, it was observed that there was a decrease in the contact angle of water compared to the 3rd surface. Likewise, there was

a decrease in the contact angle on the 5th surface. While the contact angle increasing from the 1st mixture to the 3rd mixture was associated with the increasing PLA percentage, lower contact angles were observed in the 4th and 5th mixtures despite the increasing PLA percentage. This may be attributed to the fact that the continuous increase in fiber diameter, pore size and pore size distribution counter the increasing PLA concentration.

4.2. SFE Measurement Results

The determining contact angle values of the measuring liquid on the coated surface were transferred to the program as an input to calculate SFE. During the calculation of SFE, the program utilized the methods of Van Oss-Chaudhury-Good, Fowkes, Owens Wendt and Wu are used to make a comparison between SFE methodologies and determine the most suitable one. SFE results are demonstrated in **Table 4.4.**

Table 4.4: SFE measurement of PEG-PLA coated surfaces.

	Acid-Base (SFE)	**Fowkes (SFE)**	**Wu (SFE)**	**Owens-Wendt Method (SFE)**	**Neumann (SFE)**
1	45.13	55.52	-5,82	59.16	52.96
2	46.88	49.99	-17.72	53.98	49.14
3	45.12	45.67	53.91	49.48	45.64
4	48.9	49.54	-16.16	53.66	48.5
5	50.42	56.74	-4.43	60.27	53.53

SFE measurements which were calculated with different approaches gave similar results. However, the negative results obtained in Wu are due to the variety of variations compared to other methods due to the harmonic mean. For this reason, the statement in the literature that the Wu method deviates too much from other methods in the calculation of SFE and therefore should not be used was supported with these results. SFE measurements performed via the Neumann, Fowkes and Owens-Wendt methods gave results that best supported the SCA measurements. Moreover, since the best parabolic structure was obtained in the Neumann method, Neumann's results were taken into account in the study. In the Neumann method, the highest SFE value was measured in the 5th combination. Since SFE is related to interaction between molecules and strength of attraction, high SFE indicates strong molecular interaction. Therefore, it is deduced that 5th combination has a high molecular bond due to its high SFE value and this combination is the most suitable combination.

CHAPTER 5

5. CONCLUSIONS AND FUTURE WORK

Polymers and their composites have become a research frontier for several biomedical applications due to their various advantages. The polymer coating is to provide the desired properties by covering the surface of the material to be used in the body for the desired therapeutic purpose. When the development of polymer technology from past to present and promising results are examined, it is predicted that the importance of polymer coatings and thereby the number of studies conducted in this area will increase. When the polymer coating studies carried out in the last decade are examined, the increase in the number of studies with different application areas especially in recent years is another finding that emphasizes the importance of the studies in this field.

PEG and PLA are biocompatible polymers approved by the FDA for their use in various applications in the healthcare field. PLA has been approved by the FDA for applications in different medical systems and equipment, such as tissue engineering, medical supplies, drug carriers, as it provides biodegradability, reliability, low immunity and good mechanical resistance. However, when used alone, it may cause limitations in observing the desired developments in studies due to disadvantages such as weak hydrophilicity and excessively long disintegration time. Nevertheless, PEG has several advantages such as good water solubility, flexibility and biocompatibility. Coating material with a PEG-PLA mixture in a suitable combination provides different contributions such as wear rate, hydrophilicity, mechanical resistance and is considered as one of the promising approaches that minimize each other's deficiencies. However, achieving the desired level of properties is related to SFE, which is one of the critical factors. At the point where the coated surface can interact directly with the external environment, SFE plays a key role. In this regard, this study aimed to analyze the SFE of surfaces coated with PEG-PLA at different proportions.

By coating the surfaces with PEG-PLA mixtures with different ratios, PEG and PLA coatings could be compared and analyzed. In the experiment stage, PEG-PLA mixtures with 6 different ratios were prepared. The coating was carried out with the prepared PEG-PLA mixtures by the dip-coating method. SFE was carried out using the static contact angle method, which is a reliable and frequently used method in the literature. Firstly, for SCA, the image-based experimental environment was prepared, and SCA measurements were carried out with water, glycerol, diiodomethane measurement liquids. Images were analyzed in the computer environment, primarily in the ImageJ program, and static contact angles were determined. The static contact angle results once again revealed the hydrophobic nature of PLA while supporting the hydrophilicity of PEG. In the PEG-PLA mixtures, an increase in the static contact angle was observed with the PLA ratio increasing from 0% to 40%, however, when the PLA percentage continued to be increased, a decrease was observed in the contact angle. This situation can be associated with the continuous increase in fiber diameter, pore size and pore size distribution. In the Matlab program, the measured static contact angle information was entered by specifying the measuring fluids used, and the SFE's of the coatings were determined utilizing different SFE methods. Since the expected parabolic structure was properly obtained in Neumann among the SFE measurements performed by different methods, those results were taken into account. When the contact angles with SFE were compared, it was observed that the SFE of the polymer-coated surfaces increased as the contact angle decreased due to higher interaction between the liquid drop and solid polymer surface.

This study includes the determination of SFE, which plays an important role in designing a surface according to the desired level. SFE is a term used to describe excess energy at the surface of a particular substrate. The molecular force of attraction between different materials affects their adhesion. However, the attraction force depends on the SFE of the substrate. Since SFE means a strong molecular attraction, it is concluded the 5^{th} combination with the highest SFE value in the Neumann method is the most suitable proportion which consist of 80% PLA and 20% PEG in this study. Compared to other proportions, it provided a stronger interaction between different substances with higher SFE value.

Consequently, it was concluded that the most appropriate proportion was 80% PLA and 20% PEG through SFE values in this study, which was carried out with coatings on glass slides by considering the example of PEG-PLA coating, it is expected that this study will

contribute to the development of material surfaces with desired properties in the field of health, where new approaches are needed. It is recommended that future studies focus on applying SFE measurements to provide the desired benefit from the coating to be made for a material to be used in the body.

BIBLIOGRAPHY

[1] S. Bose, S. F. Robertson, and A. Bandyopadhyay, "Surface modification of biomaterials and biomedical devices using additive manufacturing," *Acta Biomater. J*, vol. 66, pp. 6–22, 2018, doi: 10.1016/j.actbio.2017.11.003.

[2] N. Özyakar and S. Arıoğul, "Yaşlanma ile meydana gelen fizyolojik değişiklikler," *İç Hast. Derg.*, vol. 14, no. 1, pp. 18-26., 2007, [Online]. Available: http://ichastaliklaridergisi.org/managete/fu_folder/2007-01/html/2007-14-1-018-026.htm.

[3] Ş. Y. Güven, "Biyouyumluluk ve Biyomalzemelerin Seçimi," *Journal of Engineering Sciences and Design* vol. 2, no. 3, pp. 303-311–311, 2014, doi: 10.21923/mbtd.11616.

[4] E. Z. Boyacioğlu, "The Importance of Health Expenditures on Sustainable Development," *International Journal of Social Sciences and Humanity Studies*, vol. 4, no. 2, pp. 147–158, 2012.

[5] A. Nouri and C. Wen, "Introduction to surface coating and modification for metallic biomaterials," Elsevier, 2015, pp.3-60.

[6] B. D. Castner and D. G. Ratner, "Biomedical surface science: Foundations to frontiers," in Surface Science, vol. 500, no. 1, Elsevier, 2002, pp. 28-60.

[7] J. C. Vickerman, "Surface analysis: the principal techniques," 2nd Ed. J. C. Vickermann and I. S. Gilmore, Elsevier, 2011, pp. 13-20.

[8] J. Yang, F. Cui, and I. S. Lee, "Surface modifications of magnesium alloys for biomedical applications," *Ann. Biomed. Eng. J.*, vol. 39, no. 7, pp. 1857–1871, 2011, doi: 10.1007/s10439-011-0300-y.

[9] B. D. Ratner and D. G. Castner, "Surface Properties and Surface Characterization of Biomaterials," in Biomaterial Science, 4th Ed. Elsevier, 2020, pp.53-75.

[10] C. Cantürk, "Surface Free Energy Evaluation, Plasma Surface Modification and Biocompatibility Studies of PMMA Films," Master Thesis, Dept. of Chemistry, Istanbul Technical University, Istanbul, Turkey,2006.

[11] Y. Ikada, "Surface Modification of Polymers for Medical Applications," *Biomater. J.*, vol. 15, no. 10, pp. 725–736, 1994, doi: 10.1016/0142-9612(94)90025-6.

[12] J. Yang, F. Cui, and I. S. Lee, "Surface Modifications of Magnesium Alloys for Biomedical Applications," *J. Ann. Biomed. Eng.*, vol. 39, no. 7, pp. 1857–1871, 2011, doi: 10.1007/s10439-011-0300-y.

[13] P. Kingshott, G. Andersson, S. L. McArthur, and H. J. Griesser, "Surface modification and chemical surface analysis of biomaterials," *J. Curr. Opin. Chem. Biol.*, vol. 15, no. 5, pp. 667–676, 2011, doi: 10.1016/j.cbpa.2011.07.012.

[14] H. Li, D. Huang, K. Ren, and J. Ji, "Inorganic-polymer composite coatings for biomedical devices," *Smart Mater. Med. J.*, vol. 2, no. October 2020, pp. 1–14, 2021, doi: 10.1016/j.smaim.2020.10.002.

[15] J. R. Smith and D. A. Lamprou, “Polymer coatings for biomedical applications: A review,” *Trans. Inst. Met. Finish. J.*, vol. 92, no. 1, pp. 9–19, 2014, doi: 10.1179/0020296713Z.000000000157.

[16] W. He and R. Benson, “Polymeric biomaterials,” in Applied plastics engineering handbook, William Andrew, 2017, pp.145-164.

[17] K. Pulidindi and A. Prakash, “Medical Polymers Market Size and Share: Industry Analysis - 2024,” Global Market Insights, Available: https://www.gminsights.com/industry-analysis/medical-polymers-market (accessed Jan. 6, 2021).

[18] İstatistiklerle Yaşlılar, Türkiye İstatistik Kurumu (TÜİK), Mar 2021. [Online]. Available: https://data.tuik.gov.tr/Bulten/Index?p=Istatistiklerle-Yaslilar-2020-37227

[19] A. H. Doulabi, K. Mequanint, and H. Mohammadi, “Blends and nanocomposite biomaterials for articular cartilage tissue engineering,” Materials (Basel)., vol. 7, no. 7, pp. 5327–5355, 2014, doi: 10.3390/ma7075327.

[20] D. K. Owens and R. C. Wendt, “Estimation of the surface free energy of polymers,” *Appl. Polym. Sci. J*, vol. 13, no. 8, pp. 1741–1747, 1969, doi: 10.1002/app.1969.070130815.

[21] D. Li and A. W. Neumann, “Contact angles on hydrophobic solid surfaces and their interpretation,” *Colloid Interface Sci. J.*, vol. 148, no. 1, pp. 190–200, 1992, doi: 10.1016/0021-9797(92)90127-8.

[22] K. L. Menzies and L. Jones, “The impact of contact angle on the biocompatibility of biomaterials,” *Optom. Vis. Sci. J.*, vol. 87, no. 6, pp. 387–399, 2010, doi: 10.1097/OPX.0b013e3181da863e.

[23] M. S. Hamid Akash, K. Rehman, and S. Chen, “Natural and synthetic polymers as drug carriers for delivery of therapeutic proteins,” *Polym. Rev. J.*, vol. 55, no. 3, pp. 371–406, 2015, doi: 10.1080/15583724.2014.995806.

[24] O. Olatunji, “Natural polymers: Industry techniques and applications,” Springer, 2015 pp.93-114.

[25] X. Tang et al., “Polymeric Biomaterials in Tissue Engineering and Regenerative Medicine,” Elsevier, 2014, pp. 351-371.

[26] N. Angelova and D. Hunkeler, “Rationalizing the design of polymeric biomaterials,” *Trends Biotechnol. J.*, vol. 17, no. 10, pp. 409–421, 1999, doi: 10.1016/S0167-7799(99)01356-6.

[27] A. W. Bridges and A. J. García, “Anti-inflammatory polymeric coatings for implantable biomaterials and devices,” *Diabetes Sci. Technol. J.*, vol. 2, no. 6, pp. 984–994, 2008, doi: 10.1177/193229680800200628.

[28] B.İmece, “İbuprofen ve Parasetamolün Çeşitli Polimerik Malzemelerden Kontrollü Salınımı” Master Thesis, Dept. of Polimer Science and Technology, Marmara University, Istanbul, Turkey, 2020.

[29] F, N, Çetin, "Polietilenglikol Esasli Blok Kopolimerin Sentezi ve Karakterizasyonu," Master Thesis, Dept. of Chemistry, Zonguldak Bülent Ecevit University, Zonguldak, Turkey, 2020.

[30] Ç. Çakıcı, "Synthesis and Characterization of Peg-B-Pla Copolymer for The Targeted Nano Drug Delivery System", Master Thesis, Dept. of Polymer Science and Technology, Istanbul Technical University, Istanbul, Turkey,2019.

[31] D. E. Henton, P. Gruber, J. Lunt, and J. Randall, "Natural Fibers, Biopolymers, and Biocomposites. 16. Polylactic acid technology," *Nat. Fibers, Biopolym. Biocomposites* J., pp. 527–578, 2005.

[32] İ. Üner and E. D. KOÇAK, "Poli(laktik asit)'in kullanim alanlari ve nano lif üretimdeki uygulamalari," İstanbul Commerce University Fen Bilim., vol.11,no. 22, pp. 79–88, 2013.

[33] K. Deshmukh, M. B. Ahamed, R. R. Deshmukh, S. K. K. Pasha, and P. R. Bhagat, "Biopolymer composites in electronics 3 – biopolymer composites with high dielectric performance : interface," Elsevier Inc., 2018.

[34] S. M. Cannizzaro et al., "A novel biotinylated degradable polymer for cell-interactive applications," *Biotechnol. Bioeng. J.*, vol. 58, no. 5, pp. 529–535, 1998, doi: 10.1002/(SICI)1097-0290(19980605)58:5<529::AID-BIT9>3.0.CO;2-F.

[35] W. Song, "The Role of Zinc Ionomer in the Impact Performance of Polylactide (PLA) Ternary Blends: Effect of Acid Content and Degree of Neutralization," Master Thesis, Dept. of Mechanical and Materials Engineering, Washington State University School, Washington, United States of America,2011.

[36] Sigma Aldrich, Product Comparison Guide, Polylactic acid. Accessed on: January 10, 2021. [Online]. Available: https://www.sigmaaldrich.com/catalog/substance/polylacticacid123452610051611?lang=en&region=TR

[37] Y. C. Ching, T. U. Gunathilake, K. Y. Ching, C. H. Chuah, C. H., Sandu, V., Singh, R., N. S. Liou, "Effects of high temperature and ultraviolet radiation on polymer composites. In Durability and Life Prediction in Biocomposites, Fibre-Reinforced Composites and Hybrid Composites", 2019, pp. 407-426.

[38] Driver, M., Coatings for Biomedical Applications. Elsevier, 2012.

[39] S. J. Owonubi, L. Z. Linganiso, T. E. Motaung, S. P. Songca, N. Revaprasadu, "Polymer and Carbon-Based Coatings for Biomedical Applications," In Photoenergy and Thin Film Materials," Elsevier, 2019, pp. 499–535.

[40] V. O. Fasiku *et. al.* "Polymeric Materials in Coatings for Biomedical Applications. Advanced Coating Materials," Scrivener Publishing LLC, 2018, pp. 492–536.

[41] A. Strohbach and R. Busch, "Polymers for Cardiovascular Stent Coatings," *Int. J. Polym. Sci*., vol. 2015, 2015, doi: 10.1155/2015/782653.

[42] L. Cvrček and M. Horáková, "Plasma Modified Polymeric Materials for Implant Applications," in Non-Thermal Plasma Technology for Polymeric Material, Elsevier, 2019, pp. 367-407.

[43] S. Bucak and E. Can, “Polimerik Kalp Stentleri,” *J. Sci. Tech.*, pp. 46–51, 2010.

[44] D. Kersani et al., “Stent coating by electrospinning with chitosan/poly-cyclodextrin based nanofibers loaded with simvastatin for restenosis prevention,” *Eur. J. Pharm. Biopharm.*, vol. 150, pp. 156–167, 2020, doi: 10.1016/j.ejpb.2019.12.017.

[45] L. Y. Li et al., “Advances in functionalized polymer coatings on biodegradable magnesium alloys – A review,” J. *Acta Biomater.*, vol. 79, pp. 23–36, 2018, doi: 10.1016/j.actbio.2018.08.030.

[46] R. Bakhshi, A. Darbyshire, J. E. Evans, Z. You, J. Lu, and A. M. Seifalian, “Polymeric coating of surface modified nitinol stent with POSS-nanocomposite polymer,” *Colloids Surfaces B Biointerfaces J.*, vol. 86, no. 1, pp. 93–105, 2011, doi: 10.1016/j.colsurfb.2011.03.024.

[47] X. Liu et al., “Evaluation of two polymeric blends (EVA/PLA and EVA/PEG) as coating film materials for paclitaxel-eluting stent application,” *J. Mater. Sci. Mater. Med.*, vol. 22, no. 2, pp. 327–337, 2011, doi: 10.1007/s10856-010-4213-3.

[48] N. Bege et al., “Drug eluting stents based on Poly(ethylene carbonate): Optimization of the stent coating process,” *Eur. J. Pharm. Biopharm.*, vol. 80, no. 3, pp. 562–570, 2012, doi: 10.1016/j.ejpb.2011.12.006.

[49] G. Acharya, C. H. Lee, and Y. Lee, “Optimization of cardiovascular stent against restenosis: Factorial design-based statistical analysis of polymer coating conditions,” PLoS One, vol. 7, no. 8, pp. 1–12, 2012, doi: 10.1371/journal.pone.0043100.

[50] L. D. Kimble, D. Bhattacharyya, and S. Fakirov, “Biodegradable microfibrillar polymer-polymer composites from poly(L-lactic acid)/poly(glycolic acid),” Express Polym. Lett., vol. 9, no. 3, pp. 300–307, 2015, doi: 10.3144/expresspolymlett.2015.27.

[51] S. A. Park et al., “In vivo evaluation and characterization of a bio-absorbable drug-coated stent fabricated using a 3D-printing system,” Mater. Lett., vol. 141, pp. 355–358, 2015, doi: 10.1016/j.matlet.2014.11.119.

[52] Y. Farhatnia, J. H. Pang, A. Darbyshire, R. Dee, A. Tan, and A. M. Seifalian, “Next generation covered stents made from nanocomposite materials: A complete assessment of uniformity, integrity and biomechanical properties,” *Nanomedicine Nanotechnology, Biol. Med. J.*, vol. 12, no. 1, pp. 1–12, 2016, doi: 10.1016/j.nano.2015.07.002.

[53] K. Nishimiya et al., “Beneficial Effects of a Novel Bioabsorbable Polymer Coating on Enhanced Coronary Vasoconstricting Responses After Drug-Eluting Stent Implantation in Pigs in Vivo,” JACC Cardiovasc. Interv., vol. 9, no. 3, pp. 281–291, 2016, doi: 10.1016/j.jcin.2015.09.041.

[54] R. Belibel, N. Marinval, H. Hlawaty, and C. Barbaud, “Poly((R,S)-3,3-dimethylmalic acid) derivatives as a promising cardiovascular metallic stent coating: Biodegradation and biocompatibility of the hydrolysis products in human endothelial cells,” *Polym. Degrad. Stab. J.*, vol. 130, pp. 288–299, 2016, doi: 10.1016/j.polymdegradstab.2016.06.008.

[55] X. Tang et al., “Polymeric Biomaterials in Tissue Engineering and Regenerative Medicine,” in Natural and Synthetic Biomedical Polymers, Elsevier Inc., 2014, pp.351-371, doi: 10.1016/B978-0-12-396983-5.00022-3

[56] A. Abhyankar, U. Kaul, and S. K. Sinha, “Seven-year clinical outcomes in patients undergoing percutaneous coronary intervention with biodegradable polymer coated sirolimus-eluting stent: Results from a single-center real-world experience,” *Indian Heart J.*, vol. 70, pp. S280–S284, 2018, doi: 10.1016/j.ihj.2018.05.014.

[57] A. S. Baikin et al., “Polylactide-based stent coatings: Biodegradable polymeric coatings capable of maintaining sustained release of the thrombolytic enzyme prourokinase,” in Materials , vol. 12, no. 24, 2019, doi: 10.3390/ma1224107.

[58] Y. X. Yang et al., “Biodegradation, hemocompatibility and covalent bonding mechanism of electrografting polyethylacrylate coating on Mg alloy for cardiovascular stent,” *J. Mater. Sci. Technol.*, vol. 46, pp. 114–126, 2020, doi: 10.1016/j.jmst.2019.12.011.

[59] M. A. Sevostyanov et al., “Biodegradable stent coatings on the basis of PLGA polymers of different molecular mass, sustaining a steady release of the thrombolityc enzyme streptokinase,” *J. React. Funct. Polym.*, vol. 150, no. March, p. 104550, 2020, doi: 10.1016/j.reactfunctpolym.2020.104550.

[60] C. M. McKittrick, M. J. Cardona, R. A. Black, and C. McCormick, “Development of a Bioactive Polymeric Drug Eluting Coronary Stent Coating Using Electrospraying,” *Ann. Biomed. Eng. J.*, vol. 48, no. 1, pp. 271–281, 2020, doi: 10.1007/s10439-019-02346-6.

[61] R. Duncan and J. Kopecek, “Advances in Polymer Science”, SpringerLink, vol, 57, no.51, 1984.

[62] G. Özgül, “Linear and Multi-arm Functionalizable Polymeric Constructs for Targeted Drug Delivery and Imaging Linear and Multi-Arm Functionalizable Polymeric Constructs for Targeted Drug Delivery And Imaging,” PhD dissertation, Dept. of Chemistry, Boğaziçi University, Istanbul, Turkey,2014.

[63] M. O. Arıcan, “İlaç Salim Sistemleri İçin Yeni Poli(Diizopropil Glikolid)-Peg Blok Kopolimerlerinin Sentezleri ve Özellikleri,” Master’s Thesis, Dept. of Chemistry, Kocaeli University, Kocaeli, Turkey, 2014.

[64] A. Dizdar, “Kopolimer-İlaç Taşiyici Sisteminin Çeşitli Özelliklerinin Farkli Ortamlarda İncelenmesi,” Dept. of Chemistry, Master Thesis, Yıldız Technical University, İstanbul, Türkiye, 2016.

[65] S. J. Lee et al., “Heparin coating on 3D printed poly (l-lactic acid) biodegradable cardiovascular stent via mild surface modification approach for coronary artery implantation,” *Chem. Eng. J.*, vol. 378, no. June, p. 122116, 2019, doi: 10.1016/j.cej.2019.122116.

[66] W. B. Liechty, “NIH Public Access Polymer for Drug Delivery,” *Annu Rev Chem Biomol Eng. J.*, vol. 1, no. 1, pp. 149–173, 2010, doi: 10.1146/annurev-chembioeng-073009-100847.Polymers.

[67] S. K. Prajapati, A. Jain, A. Jain, and S. Jain, “Biodegradable polymers and constructs: A novel approach in drug delivery,” *Eur. Polym. J.*, vol. 120, no. August, p. 109191, 2019, doi: 10.1016/j.eurpolymj.2019.08.018.

[68] E. Calzoni, A. Cesaretti, A. Polchi, A. Di Michele, B. Tancini, and C. Emiliani, “Biocompatible polymer nanoparticles for drug delivery applications in cancer and neurodegenerative disorder therapies,” *J. Funct. Biomater.*, vol. 10, no. 1, pp. 1–15, 2019, doi: 10.3390/jfb10010004.

[69] M. Alsehli, “Polymeric nanocarriers as stimuli-responsive systems for targeted tumor (cancer) therapy: Recent advances in drug delivery,” *Saudi Pharm. J.*, vol. 28, no. 3, pp. 255–265, 2020, doi: 10.1016/j.jsps.2020.01.004.

[70] D. F. Williams, “On the mechanisms of biocompatibility,” Biomaterials, vol. 29, no. 20, pp. 2941–2953, 2008, doi: 10.1016/j.biomaterials.2008.04.023.

[71] S. Anju, N. Prajitha, V. S. Sukanya, and P. V. Mohanan, “Complicity of degradable polymers in health-care applications,” *Mater. Today Chem. J.*, vol. 16, p. 100236, 2020, doi: 10.1016/j.mtchem.2019.100236.

[72] N. Scharnagl and C. Blawert, “Polymer-based degradable coatings for metallic biomaterials,” in Surface Coating and Modification of Metallic Biomaterials, Elsevier Ltd, 2015, pp. 393-422, https://doi.org/10.1016/B978-1-78242-303-4.00014-4

[73] J. A. Burdick and G. Vunjak-Novakovic, “Engineered microenvironments for controlled stem cell differentiation,” Tissue Eng. - Part A, vol. 15, no. 2, pp. 205–219, 2009, doi: 10.1089/ten.tea.2008.0131.

[74] W. B. Tsai, W. T. Chen, H. W. Chien, W. H. Kuo, and M. J. Wang, “Poly(dopamine) coating of scaffolds for articular cartilage tissue engineering,” *J. Acta Biomater.*, vol. 7, no. 12, pp. 4187–4194, 2011, doi: 10.1016/j.actbio.2011.07.024.

[75] C. Radhakumary, A. M. Nandkumar, and P. D. Nair, “Hyaluronic acid-g-poly(HEMA) copolymer with potential implications for lung tissue engineering,” *J. Carbohydr. Polym.*, vol. 85, no. 2, pp. 439–445, 2011, doi: 10.1016/j.carbpol.2011.03.007.

[76] R. Ravichandran, J. R. Venugopal, S. Sundarrajan, S. Mukherjee, R. Sridhar, and S. Ramakrishna, “Composite poly-l-lactic acid/poly-(α,β)-dl-aspartic acid/collagen nanofibrous scaffolds for dermal tissue regeneration,” *J. Mater. Sci. Eng. C.*, vol. 32, no. 6, pp. 1443–1451, 2012, doi: 10.1016/j.msec.2012.04.024.

[77] A. M. Haaparanta et al., “Preparation and characterization of collagen/PLA, chitosan/PLA, and collagen/chitosan/PLA hybrid scaffolds for cartilage tissue engineering,” *J. Mater. Sci. Mater. Med.*, vol. 25, no. 4, pp. 1129–1136, 2014, doi: 10.1007/s10856-013-5129-5.

[78] C. T. Kao, C. C. Lin, Y. W. Chen, C. H. Yeh, H. Y. Fang, and M. Y. Shie, “Poly(dopamine) coating of 3D printed poly(lactic acid) scaffolds for bone tissue engineering,” Mater. Sci. Eng. C, vol. 56, pp. 165–173, 2015, doi: 10.1016/j.msec.2015.06.028.

[79] İ. A. Kanneci Altinişik, F. N. Kök, D. Yücel, and G. Torun Köse, "In vitro evaluation of PLLA/PBS sponges as a promising biodegradable scaffold for neural tissue engineering," *Turkish J. Biol.*, vol. 41, no. 5, pp. 734–745, 2017, doi: 10.3906/biy-1701-6.

[80] B. S. Kim, S. S. Yang, and C. S. Kim, "Incorporation of BMP-2 nanoparticles on the surface of a 3D-printed hydroxyapatite scaffold using an ε-polycaprolactone polymer emulsion coating method for bone tissue engineering," *J. Colloids Surfaces B Biointerfaces*, vol. 170, no. May, pp. 421–429, 2018, doi: 10.1016/j.colsurfb.2018.06.043.

[81] M. C. Araque-Monrós, D. M. García-Cruz, J. L. Escobar-Ivirico, L. Gil-Santos, M. Monleón-Pradas, and J. Más-Estellés, "Regenerative and Resorbable PLA/HA Hybrid Construct for Tendon/Ligament Tissue Engineering," *Ann. Biomed. Eng J.*, vol. 48, no. 2, pp. 757–767, 2020, doi: 10.1007/s10439-019-02403-0.

[82] L. Guo, Z. Du, Y. Wang, Q. Cai, and X. Yang, " Degradation behaviors of three-dimensional hydroxyapatite fibrous scaffolds stabilized by different biodegradable polymers," *Ceram. Int. J.*, vol. 46, no. 9. Techna Group S.r.l., 2020.

[83] S. Sadeghzade, R. Emadi, F. Tavangarian, and A. Doostmohammadi, "In vitro evaluation of diopside/baghdadite bioceramic scaffolds modified by polycaprolactone fumarate polymer coating," *Mater. Sci. Eng. J*, vol. 106, no. September 2018, p. 110176, 2020, doi: 10.1016/j.msec.2019.110176.

[84] G. Balasundaram and T. J. Webster, "An overview of nano-polymers for orthopedic applications," *J. Macromol. Biosci.*, vol. 7, no. 5, pp. 635–642, 2007, doi: 10.1002/mabi.200600270.

[85] H. M. Wong et al., "A biodegradable polymer-based coating to control the performance of magnesium alloy orthopaedic implants," in Biomaterials, vol. 31, no. 8, Elsevier, 2010, pp. 2084-2096.

[86] S. B. Kim, J. H. Jo, S. M. Lee, H. E. Kim, K. H. Shin, and Y. H. Koh, "Use of a poly(ether imide) coating to improve corrosion resistance and biocompatibility of magnesium (Mg) implant for orthopedic applications," *J. Biomed. Mater. Res. - Part A*, vol. 101 A, no. 6, pp. 1708–1715, 2013, doi: 10.1002/jbm.a.34474.

[87] N. Kahraman "Metalik implant malzeme yüzeylerinin biyo uyumlu polimerlerle kaplanarak biyo aktif hale getirilmesi," PhD Thesis, Dept. of Metallurgical and Materials Engineering, Dokuz Eylül University, Izmir, Turkey, 2013.

[88] S. K. Mishra and S. Kannan, "Development, mechanical evaluation and surface characteristics of chitosan/polyvinyl alcohol based polymer composite coatings on titanium metal," *J. Mech. Behav. Biomed. Mater.*, vol. 40, pp. 314–324, 2014, doi: 10.1016/j.jmbbm.2014.08.014.

[89] P. Chen et al., "Corrosion resistance of biodegradable Mg with a composite polymer coating," *J. Biomater. Sci. Polym. Ed.*, vol. 27, no. 17, pp. 1763–1774, 2016, doi: 10.1080/09205063.2016.1239852.

[90] P. Neacsu et al., “Characterization and in vitro and in vivo assessment of a novel cellulose acetate-coated Mg-based alloy for orthopedic applications,” Materials (Basel)., vol. 10, no. 7, 2017, doi: 10.3390/ma10070686.

[91] A. Abdal-hay et al., “Magnesium-particle/polyurethane composite layer coating on titanium surfaces for orthopedic applications,” *Eur. Polym. J.*, vol. 112, pp. 555–568, 2019, doi: 10.1016/j.eurpolymj.2018.10.012.

[92] D. Bhagya Mathi, D. Gopi, and L. Kavitha, “Implication of lanthanum substituted hydroxyapatite/poly(n-methyl pyrrole) bilayer coating on titanium for orthopedic applications,” *J. Mater. Today Proc.*, vol. 24, no. 4, 2019, pp. 3526-3530, doi: 10.1016/j.matpr.2019.06.152.

[93] A. M. Kumar, A. Y. Adesina, M. A. Hussein, S. A. Umoren, S. Ramakrishna, and S. Saravanan, “Preparation and characterization of Pectin/Polypyrrole based multifunctional coatings on TiNbZr alloy for orthopaedic applications,” *J. Carbohydr. Polym.*, vol. 242, no. March, p. 116285, 2020, doi: 10.1016/j.carbpol.2020.116285.

[94] W. C. Lee, Y. C. Li, and I. M. Chu, “Amphiphilic poly(D,L-lactic acid)/poly(ethylene glycol)/poly(D,L-lactic acid) nanogels for controlled release of hydrophobic drugs,” *J. Macromol. Biosci.*, vol. 6, no. 10, pp. 846–854, 2006, doi: 10.1002/mabi.200600101.

[95] X. Xiao, G. Wu, H. Zhou, K. Qian, and J. Hu, “Preparation and property evaluation of conductive hydrogel using poly (vinyl alcohol)/polyethylene glycol/graphene oxide for human electrocardiogram acquisition,” Polymers (Basel)., vol. 9, no. 7, pp. 1–15, 2017, doi: 10.3390/polym9070259.

[96] P. A. Vila, A. Sánchez, C. Évora, I. Soriano, J.L. Vila Jato, and M.J. Alonso, “PEG-PLA Nanoparticles as Carriers for,” *J. Aerosol Med.*, vol. 17, no. 2, pp. 174–185, 2004, https://doi.org/10.1089/0894268041457183

[97] H. Chen and S. He, “PLA-PEG coated multifunctional imaging probe for targeted drug delivery,” *Mol. Pharm. J.*, vol. 12, no. 6, pp. 1885–1892, 2015, doi: 10.1021/mp500512z.

[98] Z. Li et al., “PEGylated stereocomplex polylactide coating of stent for upregulated biocompatibility and drug storage,” *Mater. Sci. Eng. C. J.*, vol. 81, no. July, pp. 443–451, 2017, doi: 10.1016/j.msec.2017.08.019.

[99] A. Amani, T. Kabiri, S. Shafiee, and A. Hamidi, “Preparation and characterization of PLA-PEG-PLA/PEI/DNA nanoparticles for improvement of transfection efficiency and controlled release of DNA in gene delivery systems,” *Iran. J. Pharm. Res.*, vol. 18, no. 1, pp. 125–141, 2019, doi: 10.22037/ijpr.2019.2365.

[100] M. Kłonica and J. Kuczmaszewski, “Determining the Value of Surface Free Energy on the Basis of the Contact Angle,” *Adv. Sci. Technol. Res. J.*, vol. 11, no. 1, pp. 66–74, 2017, doi: 10.12913/22998624/68800.

[101] G. Agrawal, Y. S. Negi, S. Pradhan, M. Dash, and S. K. Samal, Wettability and contact angle of polymeric biomaterials. Elsevier Ltd., 2017.

[102] N. K Adam. “Physics and chemistry of surfaces,” Oxford University Press, 1941.

[103] F. Pelik, “Contact Angle Change and Wetting of Droplets on Planar Surface,” PhD dissertation, Dept. of Physics, Koç University, Istanbul, Turkey, 2010.

[104] O. Özkan, “Contact Angle Evaluation and Modeling by Using Immiscible Fluids,” PhD Dissertation, Dept. of Chemical, Istanbul Technical University, Istanbul, Turkey, 2010.

[105] H. Gu, C. Wang, S. Gong, Y. Mei, H. Li, and W. Ma, “Investigation on contact angle measurement methods and wettability transition of porous surfaces,” J. *Surf. Coatings Technol.*, vol. 292, pp. 72–77, 2016, doi: 10.1016/j.surfcoat.2016.03.014.

[106] A. Krishnan, Y. H. Liu, P. Cha, R. Woodward, D. Allara, and E. A. Vogler, “An evaluation of methods for contact angle measurement,” *J. Colloids Surfaces B Biointerfaces*, vol. 43, no. 2, pp. 95–98, 2005, doi: 10.1016/j.colsurfb.2005.04.003.

[107] R. S. Hebbar, A. M. Isloor, and A. F. Ismail, “Contact Angle Measurements,” in Membrane Characterization, Elsevier B.V., pp. 219-255, 2017.

[108] F. M. Etzler, “Determination of the surface free energy of solids,” in Reviews of Adhesion and Adhesives, vol. 1 no.1, pp. 3-45, 2013, https://doi.org/10.7569/RAA.2013.097301

[109] E. Lugscheider and K. Bobzin, “The influence on surface free energy of PVD-coatings,” *J. Surf. Coatings Technol*., vol. 142–144, pp. 755–760, 2001, doi: 10.1016/S0257-8972(01)01315-9.

[110] D. Y. Kwok and A. W. Neumann, “Contact angle measurement and contact angle interpretation,” in Advances in Colloid and Interface Science, vol. 81, no. 3, pp. 167-249,1999, https://doi.org/10.1016/S0001-8686(98)00087-6

[111] D. H. Bangham, “The gibbs adsorption equation and adsorption on solids,” Trans. Faraday Soc., vol. 33, pp. 805–811, 1937, doi: 10.1039/tf9373300805.

[112] D. H. Bangham and R. I. Razouk, “Adsorption and the wettability of solid surfaces,” *J. Trans. Faraday Soc*., vol.33, pp.1459-1463,1937, https://doi.org/10.1039/TF9373301459.

[113] O.N. Dredgier, A.W. Neumann, P.J. Sell, “Über die grenzflächenenergetische Zustandsfunktion II, Kolloid – Zeitschrift und Zeitschrift für Polymere,” vol:204 pp.102-112, 1965

[114] D. Li and A. W. Neumann, “Contact angles on hydrophobic solid surfaces and their interpretation,” *J. Colloid Interface Sci*., vol. 148, no. 1, pp. 190–200, 1992, doi: 10.1016/0021-9797(92)90127-8.

[115] D. Li, & A. W. Neumann, “A reformulation of the equation of state for interfacial tensions,” *Journal of Colloid and Interface Science*, vol:137 no:1, pp.304-307, 1990, https://doi.org/10.1016/0021-9797(90)90067-X

[116] D. Li, &, A. W. Neumann, “Equation of state for interfacial tensions of solid-liquid systems,” in Advances in Colloid and Interface Science, vol:39, pp.299-345, 1992, https://doi.org/10.1016/0001-8686(92)80064-5

[117] A. W. Neumann, R. David, & Y. Zuo (Eds.). “Applied surface thermodynamics,” vol:151, CRC press, 2010.

[118] D. Y. Kwok, A. Li, and A. W. Neumann, “Low-rate dynamic contact angles on poly(methyl methacrylate/ethyl methacrylate, 30/70) and the determination of solid surface tensions,” *J. Polym. Sci. Part B Polym. Phys.*, vol. 37, no. 16, pp. 2039–2051, 1999, doi: 10.1002/(SICI)1099-0488(19990815)37:16<2039::AID-POLB8>3.0.CO;2-O.

[119] D. Y. Kwok and A. W. Neumann, “Contact angle measurement and contact angle interpretation,” in Advances in Colloid and Interface Science, vol. 81, no: 3. pp.167-249,1999.

[120] C. Della Volpe, D. Maniglio, M. Brugnara, S. Siboni, and M. Morra, “The solid surface free energy calculation: I. In defense of the multicomponent approach,” *J. Colloid Interface Sci.*, vol. 271, no. 2, pp. 434–453, 2004, doi: 10.1016/j.jcis.2003.09.049.

[121] S. Siboni, C. Della Volpe, D. Maniglio, and M. Brugnara, “The solid surface free energy calculation: II. The limits of the Zisman and of the ‘equation-of-state’ approaches,” *J. Colloid Interface Sci.*, vol. 271, no. 2, pp. 454–472, 2004, doi: 10.1016/j.jcis.2003.09.050.

[122] M. Żenkiewicz, “Methods for the calculation of surface free energy of solids,” *Journal of Achievements in Materials and Manufacturing Engineering*, Proc. Int. Conf. Port Ocean Eng. under Arct. Cond. POAC, vol. 2, no. 1, pp. 1013–1023, 2009.

[123] F. M. Fowkes, “Attractive forces at interfaces,” *Ind. Eng. Chem*, vol. 56, no. 12, pp. 40–52, 1964, doi: 10.1109/CHICC.2008.4605198.

[124] F. M. Fowkes, “Donor-acceptor interactions at interfaces,” *J. Adhes.*, vol. 4, no. 2, pp. 155–159, 1972, doi: 10.1080/00218467208072219.

[125] F. M. Fowkes, “Calculation of work of adhesion by pair potential summation,” *Journal of colloid and interface science*, vol:28 no.3-4, pp.493-505, 1968

[126] O. Uygun, “Investigation of surface characteristics and flow dynamics of microchannels coated with various resin systems,” Master Thesis, Dept. of Chemical Engineering, Marmara University, Istanbul, Turkey, 2020.

[127] D. K. Owens and R. C. Wendt, “Estimation of the surface free energy of polymers,” *J. Appl. Polym. Sci.*, vol. 13, no. 8, pp. 1741–1747, 1969, doi: 10.1002/app.1969.070130815.

[128] S. Wu, “Calculation of interfacial tension in polymer systems,” *J. Polym. Sci. Part C Polym. Symp.*, vol. 34, no. 1, pp. 19–30, 1971, doi: 10.1002/polc.5070340105.

[129] S. Wu, “Polar and nonpolar interactions in adhesion,” *J. Adhes.*, vol. 5, no. 1, pp. 39–55, 1973, doi: 10.1080/00218467308078437.

[130] C. J. Van Oss, R. J. Good, and M. K. Chaudhury, “The role of van der Waals forces and hydrogen bonds in ‘hydrophobic interactions’ between biopolymers and low energy surfaces,” *J. Colloid Interface Sci.*, vol. 111, no. 2, pp. 378–390, 1986, doi: 10.1016/0021-9797(86)90041-X.

[131] C. J. Van Oss, M. K. Chaudhury, and R. J. Good, “Interfacial Lifshitz—van der Waals and Polar Interactions in Macroscopic Systems,” *Chem. Rev. J.*, vol. 88, no. 6, pp. 927–941, 1988, doi: 10.1021/cr00088a006.

[132] T. Gün, “Nanopartikül temelli süperhidrofobik yüzeyin sentezi ve karakterizasyonu,” Master’s Thesis, Dept. of Chemical, Uludağ University, Bursa, 2017.

[133] F. K. Hansen, “The measurement of surface energy of polymers by means of contact angles of liquids on solid surfaces,” A short overview of frequently used methods. University of Oslo, Oslo, 2004.

[134] J. Puetz and M. A. Aegerter, “Dip coating technique,” in Sol-gel technologies for glass producers and users” pp. 37-48, Springer, Boston, MA.

[135] K. C. Atar, “Nanoyapılı SnO2 filmlerinin sol jel daldırarak kaplama metodu ile elde edilmesi ve optik özellikleri,” Master's thesis, Anadolu University, Eskişehir, Turkey, 2013.

APPENDIX A

Appendix A1. The Matlab Code for SFE Calculations

```
% This program can be used to calculate:

% 1) Surface free energy for solid surfaces with static contact angle measurement

% 2) Friction factor with measuring liquid flow velocity measurement for laminar flow

% 3) Interfacial surface tension between a solid and a liquid with dynamic contact angle measurement (for microchannel flow)

% "Curve Fitting" and "Optimization" toolboxes are used in this program and required to run.

% a1-20: cycle repeater

a2 = 1;

while a2==1

clc;

clear;

close all;

options = optimoptions('fsolve','Display','off');

format bank;

neumann_beta = 0.0001247; % Neumann constant

fprintf('This program can be used to calculate:\n\t1) Surface free energy for solid 15 surfaces with static contact angle measurement\n\t2) Friction factor with measuring liquid flow velocity measurement for laminar flow\n\t3) Interfacial surface tension between a solid and a liquid with dynamic contact angle measurement (for microchannel flow)\n');

probes = {'water' 'glycerol' 'formamide' 'ethyleneglycol' 'dimethyl sulfoxide' 'diiodomethane' 'tetradecane' 'heptane'};

%% Data values for probes

%% Polar probes

% 1)gamma.L 2)gamma.L_LW 3)gamma.L_AB 4)gamma.L_acidic 5)gamma.L_basic 6)density 7)viscosity
```

```
water = [ 72.80 21.80 51.00 25.50 25.50 998.21 0.001002 ];

glycerol = [ 64.00 34.00 30.00 3.92 57.40 1261.30 1.459 ];

formamide = [ 58.00 39.00 19.00 2.28 39.60 1133.40 0.00323 ];

ethyleneglycol = [ 48.00 29.00 19.00 1.92 47.00 1115.00 0.026 ];

dmso = [ 44.00 36.00 8.00 0.50 32.00 1100.3 0.002174 ]; % dimethyl sulfoxide

% Number of polar probes: 25

pprobesize = 5; % Change this value if you add new polar probe(s)!

%% Apolar probes

% 1)gamma.L 2)gamma.L_LW 3)gamma.L_AB 4)gamma.L_acidic 5) gamma.L_basic 6)density 7)viscosity

diiodomethane = [ 50.80 50.80 0.00 0.00 0.00 3321.2 0.00276 ];

tetradecane = [ 26.40 26.40 0.00 0.00 0.00 762.8 0.00213 ];

heptane = [ 19.90 19.90 0.00 0.00 0.00 683.8 0.000408 ];

% If you add new probe information, please add variable name in below too!

data = [water;glycerol;formamide;ethyleneglycol;dmso; % polar probes

diiodomethane;tetradecane;heptane]; % apolar probes

n_data = size(data);

approbestart = pprobesize + 1;

%% Calculation Selection

a1 = 1;

while a1==1

calcfunc = input('\nWhich calculation do you want to use?\nSFE calculation with static 40 contact angle (use S)\nNote: You need to input contact angles measured with at least 2 measuring liquid!\n\nFriction factor calculation (use F)\nNote: You need to input flowing velocity and channel diameter! Also, flow have to be laminar (low velocity flow)!\n\nInterfacial surface tension between a solid and liquid with dynamic contact angle (Use D)\nNote: You need to input static and dynamic contact angles with one measuring liquid, SFE of solid surface, flow velocity,\ndiameter and length of the
```

```
channel, SFE of solid surface, and pressure difference between inlet and outlet of the channel!\n\n','s');

if isempty(calcfunc)==1

fprintf('You didn''t enter anything!\n');

elseif strcmpi(calcfunc,'S')==1

calculation = 1;

a1 = 0;

elseif strcmpi(calcfunc,'F')==1

calculation = 2;

a1 = 0;

elseif strcmpi(calcfunc,'D')==1

calculation = 3;

a1 = 0;

else

fprintf('Wrong entry!\n');

end

end

%% Static Calculations

while calculation==1

vars
={'n','probe','proben','polar','apolar','w_polar','w_apolar','n_polar','n_apolar','probeninput'
,'teta','R','result','gamma_s_LWx','gamma_s_acidicx','gamma_s_basicx','gamma_s_ABx'
,'gamma_sx','results_ABx','gamma_s_LW','gamma_s_acidic','gamma_s_basic','gamma_
s_AB','gamma_s','results_AB','gamma_s_fowkes2','selected','gamma_s_d_fowkes','gam
ma_s_p_fowkes','gamma_s_fowkes','gamma_s_fowkes_av','gamma_s_owrk2','R_OWR
K','OWRK','gamma_s_d_owrk','gamma_s_p_owrk','gamma_s_owrk','gamma_s_owrk2',
'gamma_s_owrk_av','gamma_s_wu2','gamma_s_wu_av','gamma_s_neumanns','gamma_
s_neumann','zis1','zis2','gamma_c','zis2_1','zis2_2'};
```

```
clear(vars{:})
% Entering the probes that are used
a4 = 1;
while a4==1
fprintf('\nProbes that you can choose are:\n');
for i=1:n_data(1)
fprintf('%d)%s\n',i,probes{i});
end
fprintf('How many probes will you use?\n')
n = input('');
if isempty(n)==1
fprintf('You didn''t enter the number of the probes!\n');
else
if n>=2 && n<=n_data(1)
a4 = 0;
else
fprintf('\nPlease enter a value that more than or equal to 2 and less than or equal to 75 %.0f!\n',n_data(1));
end
end
end
if n==n_data(1)
probe = probes;
proben = 1:1:n_data(1);
polar = 1:1:pprobesize;
apolar = approbestart:1:9;
```

```
w_polar = polar;

w_apolar = apolar;

n_polar = numel(polar);

n_apolar = numel(apolar);

else

a13 = 1;

while a13==1

fprintf('\nWhich probes did you use?(Please enter the numerical value!)\n\t\t\t');

a_p = 1;

a_ap = 1;

c_p = 0;

c_ap = 0;

for i=1:n

a5 = 1;

while a5==1

a9 = i;

probeninput = input('');

if isempty(probeninput)==1

fprintf('You didn"t enter the probe!\nPlease enter the numerical value of the probe you want to use!\n\t\t\t');

else

proben(i) = probeninput;

if proben(i)>=1 && proben(i)<=n_data(1)

a1 = 1;

if i==2 && n==2

if proben(1)<=pprobesize && proben(2)<=pprobesize
```

```
a12 = 0;

a1 = 0;

fprintf('Wrong entry! YOU ENTERED TWO POLAR PROBE!!\nIf the number of the probes is 2, You must enter one polar and one apolar probe!!\nPlease enter the numerical value of the probe you want to use!\n\t\t\t');

else

if proben(1)>pprobesize && proben(2)>pprobesize

a12 = 0;

a1 = 0;

fprintf('Wrong entry! YOU ENTERED TWO NON-POLAR PROBE!!\nIf the number of the probes is 2, You must enter one polar and one apolar probe!!\nPlease enter the numerical value of the probe you want to use!\n\t\t\t');

else

a12 = 1;

end

end

else

a12 = 1;

end

if i>1

for j=i-1:-1:1

if proben(j)==proben(i)

fprintf('Wrong entry! YOU ENTERED THE SAME PROBE!!\nPlease enter the numerical value of the probe you want to use!\n\t\t\t');

else

a9 = a9 - 1;

end
```

```
end
end
if a9==1 && a12==1
probe{i} = probes{proben(i)};
if proben(i)>= 1 && proben(i)<=pprobesize
polar(a_p) = proben(i);
w_polar(a_p) = i;
a_p = a_p + 1;
c_p = c_p + 1;
else
apolar(a_ap) = proben(i);
w_apolar(a_ap) = i;
a_ap = a_ap + 1;
c_ap = c_ap + 1;
end
a5 = 0;
if i~=n
fprintf('next one:\t');
end
end
if a1==0
a5 = 0;
i = n;
end
else
```

```
fprintf('Wrong entry! YOU ENTERED A NUMBER DIFFERENT THAN 1-%.0f!!\nPlease enter the numerical value of the probe you want to use!\n\t\t\t',n_data(1));
end
end
end
end
if n>2 && c_p<2
a13 = 1;
fprintf('Wrong entry! YOU ENTERED LESS THAN 2 POLAR PROBES!\nYOU MUST ENTER AT LEAST 2 POLAR PROBES WHEN NUMBER OF PROBES BIGGER THAN 2!!\n');
elseif n>2 && c_ap<1
a13 = 1;
fprintf('Wrong entry!\nYOU MUST ENTER AT LEAST 1 NON-POLAR PROBES WHEN NUMBER OF PROBES BIGGER THAN 2!!\n');
elseif n==2 && a1==0
a13 = 1;
else
a13 = 0;
end
end
n_polar = numel(polar);
n_apolar = numel(apolar);
end
a10 = 1;
while a10==1
% Reading contact angles
```

```
for i=1:n
fprintf('Please enter the contact angle of %s in degrees\n',probe{i});
a15 = 1;
while a15==1
a16 = input('');
if isempty(a16)==1
fprintf('Wrong entry!\n');
else
teta(i) = a16;
a15 = 0;
end
end
teta(i) = (teta(i).*pi)./180;
end
% Calculations
% Calculation (1) - Van Oss-Chaudhury-Good Method / Acid - Base Approach 3 probes
fprintf('\n Van Oss-Chaudhury-Good Method / Acid - Base Approach\n');
c = 1;
if n>2
for a=1:n_polar-1
for b=a+1:n_polar
for d=1:n_apolar
R(1,1) = sqrt(data(apolar(d),2));
R(1,2) = sqrt(data(apolar(d),5));
R(1,3) = sqrt(data(apolar(d),4));
R(1,4) = ((data(apolar(d),1).*(1+cos(teta(w_apolar(d))))./2);
```

```
R(2,1) = sqrt(data(polar(a),2));

R(2,2) = sqrt(data(polar(a),5));

R(2,3) = sqrt(data(polar(a),4));

R(2,4) = ((data(polar(a),1).*(1+cos(teta(w_polar(a))))./2);

R(3,1) = sqrt(data(polar(b),2));

R(3,2) = sqrt(data(polar(b),5));

R(3,3) = sqrt(data(polar(b),4));

R(3,4) = ((data(polar(b),1).*(1+cos(teta(w_polar(b))))./2);

result = rref(R);

gamma_s_LWx(c) = result(1,4).^2;

gamma_s_acidicx(c) = result(2,4).^2;

gamma_s_basicx(c) = result(3,4).^2;

gamma_s_ABx(c) = 2*sqrt(gamma_s_acidicx(c).*gamma_s_basicx(c));

gamma_sx(c) = gamma_s_LWx(c) + gamma_s_ABx(c);

results_ABx = {'polar probe 1' 'polar probe 2' 'apolar probe' " ";

probe{w_polar(a)} probe{w_polar(b)} probe{w_apolar(d)} " ";

'gamma_s' 'gamma_s_LW' 'gamma_s_AB' 'gamma_s_acidic' 'gamma_s_basic';

gamma_sx(c) gamma_s_LWx(c) gamma_s_ABx(c) gamma_s_acidicx(c)
gamma_s_basicx(c)};

disp(results_ABx);

c = c + 1;

end

end

end

gamma_s_LW = mean(gamma_s_LWx);

gamma_s_acidic = mean(gamma_s_acidicx);
```

```
gamma_s_basic = mean(gamma_s_basicx);

gamma_s_AB = 2*sqrt(gamma_s_acidic.*gamma_s_basic);

gamma_s = gamma_s_LW + gamma_s_AB;

results_AB = {'gamma_s' 'gamma_s_LW' 'gamma_s_AB' 'gamma_s_acidic' 'gamma_s_basic';

gamma_s gamma_s_LW gamma_s_AB gamma_s_acidic gamma_s_basic};

disp(results_AB)

end

% Calculation (2) - Fowkes Method (Geometrical Mean)

fprintf('\nFowkes Method (Geometrical Mean)\n');

c = 1;

a17 = n_polar*n_apolar;

gamma_s_fowkes2 = zeros(1,a17);

for a=1:n_polar

for b=1:n_apolar

selected = [polar(a) apolar(b)];

gamma_s_d_fowkes = ((0.5).*data(selected(2),1).*(1+cos(teta(w_apolar(b)))))./sqrt(data(selected(2),2))).^2;

gamma_s_p_fowkes = (((0.5).*data(selected(1),1).*(1+cos(teta(w_polar(a))))-(sqrt(data(selected(1),3)).*sqrt(gamma_s_d_fowkes)))./sqrt(data(selected(1),2))).^2;

gamma_s_fowkes = gamma_s_d_fowkes + gamma_s_p_fowkes;

results_AB = {'probe(1)' 'probe(2)' 'gamma_s' 'gamma_s_d' 'gamma_s_p';

probe{w_polar(a)} probe{w_apolar(b)} gamma_s_fowkes gamma_s_d_fowkes gamma_s_p_fowkes};

disp(results_AB);

gamma_s_fowkes2(c) = gamma_s_fowkes;

c = c + 1;
```

```
end

end

gamma_s_fowkes_av = mean(gamma_s_fowkes2);

fprintf('Overall average surface energy of solid = %.2f mj/m^2\n\n',gamma_s_fowkes_av);

% Calculation (3) - Owens-Wendt Method (Geometrical Mean)

fprintf('\nOWRK/Owens-Wendt Method (Geometrical Mean)\n');

c = 1;

gamma_s_owrk2 = zeros(1,a17);

for a=1:n_polar

for b=1:n_apolar

selected = [polar(a) apolar(b)];

R_OWRK(1,1) = sqrt(data(selected(1),2));

R_OWRK(1,2) = sqrt(data(selected(1),3));

R_OWRK(1,3) = (0.5).*data(selected(1),1).*(1+cos(teta(w_polar(a))));

R_OWRK(2,1) = sqrt(data(selected(2),2));

R_OWRK(2,2) = sqrt(data(selected(2),3));

R_OWRK(2,3) = (0.5).*data(selected(2),1).*(1+cos(teta(w_apolar(b))));

OWRK = rref(R_OWRK);

gamma_s_d_owrk = OWRK(1,3).^2;

gamma_s_p_owrk = OWRK(2,3).^2;

gamma_s_owrk = gamma_s_d_owrk + gamma_s_p_owrk;

results_AB = {'probe(1)' 'probe(2)' 'gamma_s' 'gamma_s_d' 'gamma_s_p';

probe{w_polar(a)} probe{w_apolar(b)} gamma_s_owrk gamma_s_d_owrk gamma_s_p_owrk};

disp(results_AB);

gamma_s_owrk2(c) = gamma_s_owrk;
```

```
c = c + 1;
end
end
gamma_s_owrk_av = mean(gamma_s_owrk2);
fprintf('Overall average surface energy of solid = %.2f 282mj/m^2\n\n',gamma_s_owrk_av);
% Calculation (4) - Wu Equation (Harmonic Mean)
fprintf('\nWu Equation (Harmonic Mean)\n');
c = 1;
gamma_s_wu2 = zeros(1,a17);
for a=1:n_polar
for b=1:n_apolar
selected = [polar(a) apolar(b)];
p1 = data(selected(1),2);
r1 = data(selected(1),3);
s1 = 0.25.*data(selected(1),1).*(1+cos(teta(w_polar(a))));
p2 = data(selected(2),2);
r2 = data(selected(2),3);
s2 = 0.25.*data(selected(2),1).*(1+cos(teta(w_apolar(b))));
z11 = (p1.*r1)-(r1.*s1);
z12 = (p1.*r1)-(p1.*s1);
z13 = p1+r1-s1;
z14 = p1.*r1.*s1;
z21 = (p2.*r2)-(r2.*s2);
z22 = (p2.*r2)-(p2.*s2);
z23 = p2+r2-s2;
```

```
z24 = p2.*r2.*s2;

f = @(x) [z11.*x(1) + z12.*x(2) + x(1).*x(2).*z13 - z14; z21.*x(1) + z22.*x(2) + x(1).*x(2).*z23 - z24];

x0 = [ 1 ; 1 ];

options = optimoptions(@fsolve,'Display','off');

res = fsolve(f,x0,options);

gamma_s_d_wu = res(1);

gamma_s_p_wu = res(2);

gamma_s_wu = gamma_s_d_wu + gamma_s_p_wu;

results_AB = {'probe(1)' 'probe(2)' 'gamma_s' 'gamma_s_d' 'gamma_s_p';

probe{w_polar(a)} probe{w_apolar(b)} gamma_s_wu gamma_s_d_wu gamma_s_p_wu};

disp(results_AB);

gamma_s_wu2(c) = gamma_s_wu;

c = c + 1;

end

end

gamma_s_wu_av = mean(gamma_s_wu2);

fprintf('Overall average surface energy of solid = %.2f mj/m^2\n\n',gamma_s_wu_av);

% Calculation (5) - Neumann's Method (Equation of State - EQS)

fprintf('\nNeumann''s Method (Equation of State - EQS)\n');

for i=1:n

f_neumann = @(gamma_s_neumannx) cos(pi-teta(i))-1+2.*sqrt(gamma_s_neumannx./data(i,1)).*exp(-1.*neumann_beta.*((data(i,1)-gamma_s_neumannx).^2));

gamma_s_neumanns(i) = fsolve(f_neumann,gamma_s_wu,options);

results_AB = {'probe' 'gamma_s' ; probe{i} gamma_s_neumanns(i)};
```

```
disp(results_AB);
end
gamma_s_neumann = mean(gamma_s_neumanns);
fprintf('Overall average surface energy of solid = %.2f mj/m^2\n\n',gamma_s_neumann);
% Critical Surface Tension - Zisman Plot
figure(1);
for i=1:n
zis1(i) = (data(proben(i),1));
zis2(i) = (cos(teta(i)));
end
[linearfit,goodnessoffit] = fit(zis1',zis2','poly1');
plot(linearfit,zis1,zis2);
title('Zisman Plot Analysis'),
xlabel('Liquid Surface Tension [mN/m]'),
ylabel('Cosine of Contact Angle'),
axis on,
gamma_c = (1 - linearfit.p2)./linearfit.p1;
fprintf('\nZisman Plot Analysis\n\nThe critical surface energy = %.2f mj/m^2\n',
gamma_c');
fprintf('R^2 = %.2f\n',goodnessoffit.rsquare);
n_fig = 2;
for a=1:n_polar
for b=1:n_apolar
figure(n_fig);
selected = [polar(a) apolar(b)];
zis2_1(1) = (data(proben(w_polar(a)),1));
```

```
zis2_1(2) = (data(proben(w_apolar(b)),1));

zis2_2(1) = (cos(teta(w_polar(a))));

zis2_2(2) = (cos(teta(w_apolar(b))));

[linearfit2,goodnessoffit2] = fit(zis2_1',zis2_2','poly1');

plot(linearfit2,zis2_1,zis2_2);

title(['Zisman Plot Analysis (',probe{w_polar(a)},'+',probe{w_apolar(b)},')']);

xlabel('Liquid Surface Tension [mN/m]'),

ylabel('Cosine of Contact Angle');

gamma_c2 = (1 - linearfit2.p2)./linearfit2.p1;

fprintf('\nSelected probes: %s and %s.\n',probe{w_polar(a)},probe{w_apolar(b)});

fprintf('The critical surface energy = %.2f mj/m^2\n',gamma_c2');

fprintf('R^2 = %.2f\n',goodnessoffit2.rsquare);

n_fig = n_fig + 1;

end

end

% Calculation with same probes

fprintf('\n Do you want to make another calculation with same probes?(yes or no)\n Default:Yes\n');

a11 = 1;

while a11==1

q = input('','s');

if isempty(q)==1

a10 = 1;

a11 = 0;

elseif strcmpi(q,'no')==1

a10 = 0;
```

```
a11 = 0;
elseif strcmpi(q,'yes')==1
a10 = 1;
a11 = 0;
else
fprintf('Wrong entry!\n');
end
end
end
% Calculation with different probes
fprintf('\n Do you want to make another calculation with different probes?(yes or no)\n Default:Yes\n');
a11 = 1;
while a11==1
q = input('','s');
if isempty(q)==1
calculation = 1;
a11 = 0;
elseif strcmpi(q,'no')==1
calculation = 0;
a11 = 0;
elseif strcmpi(q,'yes')==1
calculation = 1;
a11 = 0;
else
fprintf('Wrong entry!\n');
```

```
end
end
end
%% Friction Factor Calculations
while calculation==2
varsff = {'channel_diameter','flow_velocity','Re','ff'};
clear(varsff{:})
fprintf('\nProbes that you can choose are:\n');
for i=1:n_data(1)
fprintf('%d)%s\n',i,probes{i});
end
a20 = 1;
while a20==1
selectedPRB = input('Which probe do you want to calculate with?\n');
if isempty(selectedPRB)==1
fprintf('Wrong entry!\n');
elseif selectedPRB>n_data(1)
fprintf('Wrong entry!\n');
elseif selectedPRB<1
fprintf('Wrong entry!\n');
else
a20 = 0;
fprintf('Selected measuring liquid is: %s\n',probes{selectedPRB});
end
end
a10 = 1;
```

```
while a10==1
a20 = 1;
while a20==1
channel_diameter = input('Please enter the channel diameter in meters.\n');
if isempty(channel_diameter)==1
fprintf('Wrong entry!\n');
elseif channel_diameter<0
fprintf('Wrong entry!\n');
else
a20 = 0;
end
end
a20 = 1;
while a20==1
flow_velocity = input('Please enter the flow velocity of measuring fluid in meters per second.\n');
if isempty(flow_velocity)==1
fprintf('Wrong entry!\n');
elseif flow_velocity<0
fprintf('Wrong entry!\n');
else
a20 = 0;
end
end
Re = data(selectedPRB,6)*channel_diameter*flow_velocity/data(selectedPRB,7);
if Re<=2000
```

```
fprintf('Flow is laminar!\nRe = %.0f\n',Re);
ff = 64/Re;
fprintf('\nFriction factor = %.2f\n',ff);
else
fprintf('Flow is not laminar! Repeat the experiment with lower flow velocity!');
end
% Calculation with same probe 458
fprintf('\n Do you want to make another calculation with same probe?(yes or no)\n Default:Yes\n');
a11 = 1;
while a11==1
q = input('','s');
if isempty(q)==1
a10 = 1;
a11 = 0;
elseif strcmpi(q,'no')==1
a10 = 0;
a11 = 0;
elseif strcmpi(q,'yes')==1
a10 = 1;
a11 = 0;
else
fprintf('Wrong entry!\n');
end
end
end
```

```
% Calculation with different probe fprintf('\n Do you want to make another calculation with same probe liquid?(yes or no)\n Default:Yes\n');
a11 = 1;
while a11==1
q = input('','s');
if isempty(q)==1
calculation = 2;
a11 = 0;
elseif strcmpi(q,'no')==1
calculation = 0;
a11 = 0;
elseif strcmpi(q,'yes')==1
calculation = 2;
a11 = 0;
else
fprintf('Wrong entry!\n');
end
end
end
%% Interfacial Surface Tension Calculations
while calculation==3
varsff ={'channel_diameter','flow_velocity','Re','length','pressure_diff','dca','sca','SFEofsolid','interfacialST'};
clear(varsff{:})
fprintf('\nProbes that you can choose are:\n');
for i=1:n_data(1)
```

```
fprintf('%d)%s\n',i,probes{i});
end
a20 = 1;
while a20==1
selectedPRB = input('Which probe do you want to calculate with?\n');
if isempty(selectedPRB)==1
fprintf('Wrong entry!\n');
elseif selectedPRB>n_data(1)
fprintf('Wrong entry!\n');
elseif selectedPRB<1
fprintf('Wrong entry!\n');
else
a20 = 0;
fprintf('Selected measuring liquid is: %s\n',probes{selectedPRB});
end
end
a10 = 1;
while a10==1
a20 = 1;
while a20==1
channel_diameter = input('Please enter the channel diameter in meters (m).\n');
if isempty(channel_diameter)==1
fprintf('Wrong entry!\n');
elseif channel_diameter<0
fprintf('Wrong entry!\n');
else
```

```
a20 = 0;
end
end
a20 = 1;
while a20==1
flow_velocity = input('Please enter the flow velocity of measuring fluid in meters per second (m/s).\n');
if isempty(flow_velocity)==1
fprintf('Wrong entry!\n');
elseif flow_velocity<0
fprintf('Wrong entry!\n');
else
a20 = 0;
end
end
Re = data(selectedPRB,6)*channel_diameter*flow_velocity/data(selectedPRB,7);
if Re<=2000
fprintf('Flow is laminar!\nRe = %.2f\n\n',Re);
ff = 64/Re;
fprintf('Friction factor = %.2f\n\n',ff);
a20 = 1;
while a20==1
length = input('Please enter the length of the channel in meters (m).\n');
if isempty(length)==1
fprintf('Wrong entry!\n');
elseif length<0
```

```
fprintf('Wrong entry!\n');
else
a20 = 0;
end
end
a20 = 1;
while a20==1
pressure_diff = input('Please enter the pressure difference between inlet and outlet of the channel in Newton per second squared (N/m2).\n');
if isempty(pressure_diff)==1
fprintf('Wrong entry!\n');
elseif pressure_diff<0
fprintf('Wrong entry!\n');
else
a20 = 0;
end
end
a20 = 1;
while a20==1
dca = input('Please enter the dynamic contact angle in degrees.\n');
if isempty(dca)==1
fprintf('Wrong entry!\n');
elseif dca<0
fprintf('Wrong entry!\n');
else
a20 = 0;
```

```
end
end
dcacos = cos(dca*pi/180);
a20 = 1;
while a20==1
sca = input('Please enter the static contact angle in degrees.\n');
if isempty(sca)==1
fprintf('Wrong entry!\n');
elseif sca<0
fprintf('Wrong entry!\n');
else
a20 = 0;
end
end
scacos = cos(sca*pi/180);
a20 = 1;
while a20==1
SFEofsolid = input('Please enter the SFE of solid surface in miliJoules per meter 595 squared (mJ/m2).\n');
if isempty(SFEofsolid)==1
fprintf('Wrong entry!\n');
elseif SFEofsolid<0
fprintf('Wrong entry!\n');
else
a20 = 0;
end
```

```
end
interfacialST = SFEofsolid-((0.25*((scacos/dcacos)*(((32*flow_velocity*length*data(selectedPRB,7))/(channel_diameter.^2))+(channel_diameter*(pressure_diff*(-1))))))*1000);
fprintf('\nDynamic interfacial tension between solid and liquid is %.2f 605 mJ/m2\n',interfacialST);
else
fprintf('Flow is not laminar! Repeat the experiment with lower flow velocity!');
end
% Calculation with same probes
fprintf('\n Do you want to make another calculation with same probe?(yes or no)\n Default:Yes\n');
a11 = 1;
while a11==1
q = input('','s');
if isempty(q)==1
a10 = 1;
a11 = 0;
elseif strcmpi(q,'no')==1
a10 = 0;
a11 = 0;
elseif strcmpi(q,'yes')==1
a10 = 1;
a11 = 0;
else
fprintf('Wrong entry!\n');
end
```

```
end
end
% Calculation with different probe
fprintf('\n Do you want to make another calculation with different probe liquid?(yes or no)\n Default:Yes\n');
a11 = 1;
while a11==1
q = input('','s');
if isempty(q)==1
calculation = 3;
a11 = 0;
elseif strcmpi(q,'no')==1
calculation = 0;
a11 = 0;
elseif strcmpi(q,'yes')==1
calculation= 3;
a11 = 0;
else
fprintf('Wrong entry!\n');
end
end
end
%% Restarting program
a3 = 1;
while a3==1
fprintf('\n Do you want to make another calculation?(yes or no)\n Default:Yes\n');
```

```
p = input('','s');
if isempty(p)==1
a2 = 1;
a3 = 0;
elseif strcmpi(p,'no')==1
a2 = 0;
a3 = 0;
elseif strcmpi(p,'yes')==1
a2 = 1;
a3 = 0;
else
fprintf('Wrong entry!\n');
end
end
end
```

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OTHER PUBLICATIONS, PRESENTATIONS AND PATENTS:

- M. A. Karadayı, B. Ö. Yilmaz, B. E. Erol, and H. Tozan "Sağlık Teknolojisi Değerlendirmede Çok Kriterli Karar Verme Yaklaşımları Üzerine Bir Derleme Çalışması," *Düzce Üniversitesi Bilim ve Teknol. Derg.,* vol. 8, pp. 264–289, 2020.
- B. Ö. Yilmaz, M. A. Karadayı and H. Tozan "Multi-Criteria Decision Making (MCDM) Applications in Military Healthcare Field," *Journal of Heal. Syst. Policies,* vol. 2, no. 2, pp. 149–181, 2020.
- E. Erol, B. Ö. Yilmaz, M. A. Karadayi, and H. Tozan, "An MCDM-based health technology assessment (HTA) study for evaluating kidney stone treatment alternatives," Multiple Criteria Decision Making: Beyond the Information Age, vol.99, Springer, 2021, pp.99-129.

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