



Kaunas University of Technology

Faculty of Mechanical Engineering and Design

Research on the Influence of Polyamide PA6 Surface Properties Modification to Wetting Angle

Master's Final Degree Project

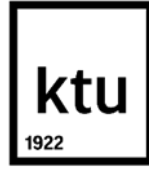
Ram Pramod Monikantan

Project author

Lect. Vaidas Bivainis

Supervisor

Kaunas, 2020



Kaunas University of Technology

Faculty of Mechanical Engineering and Design

Research on the Influence of Polyamide PA6 Surface Properties Modification to Wetting Angle

Master's Final Degree Project

Industrial Engineering and Management (6211EX018)

Ram Pramod Monikantan

Project author

Lect. Vaidas Bivainis

Supervisor

Lect. Laura Gegeckienė

Reviewer

Kaunas, 2020



Kaunas University of Technology

Faculty of Mechanical Engineering and Design

Ram Pramod Monikantan

Research on the Influence of Polyamide PA6 Surface Properties Modification to Wetting Angle

Declaration of Academic Integrity

I confirm that the final project of mine, Ram Pramod Monikantan, on the topic “Research on the Influence of Polyamide PA6 Surface Properties Modification to Wetting Angle” is written completely by myself; all the provided data and research results are correct and have been obtained honestly. None of the parts of this thesis have been plagiarised from any printed, Internet-based or otherwise recorded sources. All direct and indirect quotations from external resources are indicated in the list of references. No monetary funds (unless required by Law) have been paid to anyone for any contribution to this project.

I fully and completely understand that any discovery of any manifestations/case/facts of dishonesty inevitably results in me incurring a penalty according to the procedure(s) effective at Kaunas University of Technology.

(name and surname filled in by hand)

(signature)



Kaunas University of Technology

Faculty of Mechanical Engineering and Design

Task of the Master's final degree project

Given to the student – Ram Pramod Monikantan

1. Title of the project –

Research on the Influence of Polyamide PA6 Surface Properties Modification to Wetting Angle

(In English)

Poliamido PA6 paviršiaus savybių modifikavimo poveikio drėkinimo kampui tyrimai

(In Lithuanian)

2. Aim and tasks of the project –

Aim:

To carry out the experimental investigation research on the influence of Polyamide PA6 surface properties modification to wetting angle.

Tasks:

1. To do experiments of surface abrasion wearing to increase the surface roughness of PA6.
2. To evaluate the influence of mechanical abrasion to material wetting angle.
3. To evaluate the influence of thermal effect and plasma treatment to material wetting angle.
4. To carry out the experiments to set the influence of chemical treatment to PA6 surface wetting angle.

3. Initial data of the project –

NA

4. Main requirements and conditions –

Mitutoyo SJ-210, Taber Abraser 5131, JSC Kvarztz Plasma-600T, Pocket Goniometer 3 (PG3)

Project author

Ram Pramod MONIKANTAN

(Name, Surname)

(Signature)

(Date)

Supervisor

Vaidas BIVAINIS

(Name, Surname)

(Signature)

(Date)

Head of study
field programs

Regita BENDIKIENĖ

(Name, Surname)

(Signature)

(Date)

Monikantan Ram Pramod. Research on the Influence of Polyamide PA6 Surface Properties Modification to Wetting Angle. Master's Final Degree Project, supervisor Lect. Vaidas Bivainis; Faculty of Mechanical Engineering and Design, Kaunas University of Technology.

Study field and area (study field group): Production and Manufacturing Engineering (E10), Engineering Sciences (E).

Keywords: Polyamide PA6, Taber abrasive wear, surface roughness, plasma surface treatment, chemical surface treatment, surface wetting angle.

Kaunas, 2020. 52p.

Summary

The use of polyamides in consumer applications has increased in developed countries. Preferably, Polyamide PA6 is considered in a wide range of global surroundings and also utilized in different industries and relevant scientific fields that make it an important reason for greater production. Numerous applications of Polyamide PA6 lead to greater benefits because of the improved properties of strength, stiffness, and elasticity that has played a major role in decreasing the manufacturing cost. The improved properties are important to determine the effect of PA6 modified surface and the adhesion layer. The research was concentrated on the 1 mm thickness of boiled and non-boiled Polyamide PA6 modified by abrasion, plasma, and chemical treatment methods. The improved surface by different abraded disc rotations on the boiled and non-boiled R_a roughness is observed as 75% and 68% coefficient of determination (R^2) and for R_z roughness, it is observed as 31% and 56% coefficient of determination (R^2). The wetting angle of the surfaces for all samples was determined using water and ethylene glycol. For abrasion wetting, the coefficient of determination (R^2) observed with water on the boiled surface is 63% and on the non-boiled surface is 35%. Likewise, with ethylene glycol on the boiled surface is 84% and on the non-boiled surface is 40%. The contact angle for plasma wetting with water on the boiled surface is 21.21° and on the non-boiled surface is 30.94° . Also, with ethylene glycol on the boiled surface is 11.95° and on the non-boiled surface is 11.38° . The water wetting contact angle for 3M KOH treated on the boiled and non-boiled surface is observed as 55.0° and 56.7° but with the ethylene glycol wetting contact angle for 3M KOH treated on the boiled surface is observed as 44.3° and 3M HCl treated on the non-boiled surface is observed as 32.9° .

Monikantan Ram Pramod. Poliamido PA6 paviršiaus savybių modifikavimo poveikio drėkinimo kampui tyrimai. Magistro baigiamasis projektas, Lekt. Vaidas Bivainis; Kauno technologijos universitetas, Mechanikos inžinerijos ir dizaino fakultetas.

Studijų kryptis ir sritis (studijų krypčių grupė): Gamybos inžinerija (E10), Inžinerijos mokslai (E).

Reikšminiai žodžiai: Poliamidas PA6, Taber abrazyvinis dilimas, paviršiaus šiurkštumas, plazminis paviršiaus apdorojimas, cheminis paviršiaus apdorojimas, paviršiaus vilgymo kampas.

Kaunas, 2020. 52p.

Santrauka

Pastaruoju metu įvairiose pramonės ir aktualiose mokslo srityse yra pastebimas vis didesnis Poliamido PA6 panaudojimas. Šios polimerinės medžiagos panaudojimo spektro platumą lemia palyginti nedidelė medžiagos savikaina, galimybė šį plastiką rūšiuoti ir perdirbti, gana geros mechaninės-fizikinės ir kt. šios medžiagos savybės. Tikslu pagerinti abiejų medžiagų adhezinės savybės, yra svarbu nustatyti PA6 paviršiaus modifikavimo poveikį jo paviršiaus adhezinėms savybėms. Atliktų eksperimentinių tyrimų metu skaidraus PA6 1 mm storio bandiniai buvo paveikti termiškai – išvirti distiliuotame vandenyje, taip pat šių bandinių paviršius, siekiant padidinti paviršiaus šiurkštumą, buvo veikiamas naudojant Taber abrazyvinio dilinimo diskus. PA6 bandiniai buvo ėsdinamai naudojant dujinę plazmą bei KOH šarmą ir HCl rūgštį. Visų šių bandinių paviršiams buvo nustatytas vilgymo kampas, naudojant distiliuotą vandenį ir etilenglikolį. Tyrimų metu gauta, kad keičiant abrazyvinių diskų apsisukimų skaičių, galima pasiekti norimą PA6 paviršiaus R_a ir R_z šiurkštumą. Gautos gana artimos regresinei tiesei priklausomybės: virinto PA6 paviršiaus šiurkštumo R_a tiesinės priklausomybės determinacijos koef. (R^2) parodė tarpinių rezultatų 75%, o nevirinto PA6 – 68% atitikimo tikimybę. Taip pat atitinkamai buvo gauta R_z priklausomybių tarpinių rezultatų tarpinių taškų atitikimas virintam – 31%, o nevirintam – 56%. Vertinant šių paviršių vandens vilgymo kampo vertes, tiesinių priklausomybių virintam $R^2=0,63$, o nevirintam – $R^2=0,35$. Etilenglikolio vilgymo kampo tiesinių priklausomybių R^2 atitinkamai buvo gauta 0,84 ir 0,40. Atlikus bandinių ėsdinimą plazma, buvo gauta, kad vandens drėkinimo kampas virintam buvo $21,21^\circ$, o nevirintam – $30,94^\circ$. Etilenglikolio vilgymo kampas virintam – $11,95^\circ$, o nevirintam paviršiui – $11,38^\circ$. Atlikus PA6 bandinių paviršių cheminį ėsdinimą gauta, kad vandens vilgymo kampas naudojant 3M KOH virintiems bandiniams buvo $55,0^\circ$, o nevirintiems – atitinkamai $56,7^\circ$. Etilenglikolio vilgymo kampas virintiems 3M KOH paveiktiems bandiniams buvo $44,3^\circ$. O paveikus bandinius 3M HCl nevirintų bandinių etilenglikolio vilgymo kampas – $32,9^\circ$.

Table of contents

| | |
|--|-----------|
| List of figures | 8 |
| List of tables | 10 |
| List of abbreviations and terms..... | 11 |
| Introduction | 12 |
| 1. Relevance of the research | 13 |
| 1.1. Surface properties modification | 14 |
| 1.2. Adhesion behavior on solid surface | 19 |
| 1.3. Contact angle | 21 |
| 2. Material and methodology | 24 |
| 2.1. Surface abrasion wearing | 24 |
| 2.2. Surface roughness measurement | 26 |
| 2.3. Surface plasma treatment | 27 |
| 2.4. Surface chemical treatment | 28 |
| 2.5. Contact angle determination..... | 29 |
| 3. Results and discussion | 31 |
| 3.1. Surface roughness measurement | 31 |
| 3.2. Abraded surface contact angle..... | 35 |
| 3.3. Plasma treatment contact angle | 39 |
| 3.4. Chemical treatment contact angle | 41 |
| 4. Managerial aspects | 43 |
| 4.1. Environmental limitations of Polyamide PA6..... | 43 |
| 4.2. Economical views of Polyamide PA6 | 44 |
| Conclusions | 47 |
| List of references..... | 48 |
| Appendices | 50 |
| Appendix 1. Article for publishing in upcoming International Young Researchers Conference 2020..... | 50 |

List of figures

| | |
|---|----|
| Fig. 1. Formation of Polyamide PA6 from caprolactam polymerization [4] | 13 |
| Fig. 2. Thermograph indicating PA6 weight dropping as a function of temperature [6]..... | 14 |
| Fig. 3. Surface roughness by wearing treatment: (a) before abrasion; (b) after abrasion [12]..... | 16 |
| Fig. 4. Shear strength effect of different transportor gases by plasma surface treatment [15]..... | 16 |
| Fig. 5. Cracked surface due to limited nano-filler additives [22]..... | 18 |
| Fig. 6. Droplet interface of surface tension: (a) Very high; (b) High; (c) Low; (d) Very low [26] .. | 19 |
| Fig. 7. Schematic diagram of wetting angle measurements on a solid surface [32] | 22 |
| Fig. 8. Pocket goniometer (PG3) device for contact angle measurements | 22 |
| Fig. 9. Experimental setup of surface abrasion treatment: 1- mechanical arm; 2- abrader wheels; 3- PA6 specimen; 4- rotating disc; 5- digital meter | 25 |
| Fig. 10. Improved abraded surface: (a) non-boiled PA6 under 100 rotations; (b) boiled PA6 under 100 rotations | 25 |
| Fig. 11. Mitutoyo SJ-210 surface roughness tester [36] | 26 |
| Fig. 12. Atmospheric pressure plasma treatment: (a) schematic view; (b) actual view [37] | 27 |
| Fig. 13. Simplified view of surface chemical treatment | 28 |
| Fig. 14. Formation of cracked layer on non-boiled PA6 treated with 3M HCl | 29 |
| Fig. 15. Experimental setup of contact angle measurement technique: 1- USB cable; 2- pocket goniometer 3 (PG3); 3- syringe (1 ml); 4- tailored specimen (15 mm × 100 mm); 5- micro connecting tube; 6- ‘‘PG’’ application..... | 30 |
| Fig. 16. Dependency of the abrasion disc rotations to surface roughness (R_a , μm) on non-boiled PA6: 1- linear regression with the coefficient of determination; 2- confidence interval | 31 |
| Fig. 17. Dependency of the abrasion disc rotations to surface roughness (R_z , μm) on non-boiled PA6: 1- linear regression with the coefficient of determination; 2- confidence interval | 32 |
| Fig. 18. Dependency of the abrasion disc rotations to surface roughness (R_a , μm) on boiled PA6: 1- linear regression with the coefficient of determination; 2- confidence interval..... | 33 |
| Fig. 19. Dependency of the abrasion disc rotations to surface roughness (R_z , μm) on boiled PA6: 1- linear regression with the coefficient of determination; 2- confidence interval..... | 34 |
| Fig. 20. Abraded non-boiled surface wetting with water: (a) low wetting for 0 rotation; (b) high wetting wetting for 100 rotations | 35 |
| Fig. 21. Dependency of the abrasion disc rotations to water wetting angle on non-boiled PA6. 1- linear regression with the coefficient of determination; 2- confidence interval..... | 35 |
| Fig. 22. Abraded non-boiled surface wetting with ethylene glycol: (a) high wetting for 0 rotation; (b) low wetting for 10 rotations | 36 |
| Fig. 23. Dependency of the abrasion disc rotations to ethylene glycol wetting angle on non-boiled PA6. 1- linear regression with the coefficient of determination; 2- confidence interval | 36 |
| Fig. 24. Abraded boiled surface wetting with water: (a) low wetting for 20 rotations; (b) high wetting for 50 rotations | 37 |
| Fig. 25. Dependency of the abrasion disc rotations to water wetting angle on boiled PA6. 1- linear regression with the coefficient of determination; 2- confidence interval | 37 |
| Fig. 26. Abraded boiled surface wetting with ethylene glycol: (a) low wetting for 20 rotations; (b) high wetting for 50 rotations | 38 |
| Fig. 27. Dependency of the abrasion disc rotations to ethylene glycol wetting angle on boiled PA6. 1- linear regression with the coefficient of determination; 2- confidence interval | 38 |

| | |
|--|----|
| Fig. 28. Plasma surface wetting with water: (a) high wetting on boiled surface; (b) low wetting on non-boiled surface | 39 |
| Fig. 29. Influence of PA6 surface plasma treatment to water wetting angle: <i>l</i> - confidence interval | 39 |
| Fig. 30. Plasma surface wetting with ethylene glycol: (a) low wetting on boiled surface; (b) high wetting on non-boiled surface | 40 |
| Fig. 31. Influence of PA6 surface plasma treatment to ethylene glycol wetting angle: <i>l</i> - confidence interval | 40 |
| Fig. 32. Chemical surface wetting with water; (a) low wetting on 0.5M HCl of non-boiled PA6; (b) high wetting on 3M KOH of boiled PA6. | 41 |
| Fig. 33. Influence of PA6 surface chemical treatment to water wetting angle: <i>l</i> - confidence interval | 41 |
| Fig. 34. Chemical surface wetting with ethylene glycol; (a) low wetting on 0.5M HCl of boiled PA6; (b) high wetting on 3M HCl of non-boiled PA6. | 42 |
| Fig. 35. Influence of PA6 surface chemical treatment to ethylene glycol wetting angle: <i>l</i> - confidence interval | 42 |
| Fig. 36. Global consumption and production of polyamides | 44 |
| Fig. 37. Market shares of Polyamide PA6 utilized globally | 45 |
| Fig. 38. Market trade comparison of polyamides..... | 46 |

List of tables

| | |
|---|----|
| Table 1. Synthesis of modified Polyamide PA6 [7] | 15 |
| Table 2. Methods of surface plasma treatments [17] [18][19]..... | 17 |
| Table 3. Surface tension of different wetting liquids [29] | 20 |
| Table 4. Properties and values of Polyamide PA6 [34] | 24 |

List of abbreviations and terms

Abbreviations:

PA – Polyamide

PA 6 – Polyamide 6

PG 3 – Pocket goniometer 3

3M KOH – 3 Molarity concentration of Potassium lye pellets

0.5M HCl – 0.5 Molarity concentration of Hydrochloric acid

3M HCl – 3 Molarity concentration of Hydrochloric acid

R^2 – Coefficient of determination

Introduction

Engineering polyamides discover wide applications in many manufacturing zones due to their numerous great properties which progressively used to produce high performance and lightweight designs in the industry. By the production of different polyamides across the globe, Polyamide PA6 has been utilized in major applications because of the surface properties and inexpensive pricing. The scope of their properties is applicable for wettability, adhesive joining, sealing, and coating influence on the surface layer. The relation of the previous improvement states that, due to the consumption of low energy and easy processing, several surface modification techniques are greatly involved in the present field of surface science. From an adhesion perspective, the solid surface determination of different wetting liquids was observed to be compelling by the upgrade of different properties. To improve such properties and determine the wettability, two types of Polyamide PA6 are set up for the procedures. However, the existing research on similar concepts has not been much involved, therefore the attention towards surface treatments was focused to find a way to reduce the wetting angle of liquids applicable in the future research of material coating experiments. The experiments can assess the ideal change technique, yet additionally, investigates the interface connection between surface modification and wetting angle. Specifically, the research shows the wettability, contact angle, and surface adhesion identified by the changes in surface properties. The hypothesis of the research is - mechanical, thermal, and chemical modification of Polyamide PA6 material influences the surface wetting angle.

The project aims to carry out the experimental investigation research on the influence of Polyamide PA6 surface properties modification to wetting angle.

To accomplish the aim, the following tasks were performed;

1. To do experiments of surface abrasion wearing to increase the surface roughness of PA6.
2. To evaluate the influence of mechanical abrasion to material wetting angle.
3. To evaluate the influence of thermal effect and plasma treatment to material wetting angle.
4. To carry out the experiments to set the influence of chemical treatment to PA6 surface wetting angle.

1. Relevance of the research

The global use of plastics from existing production has been possible in recent years. Beyond most artificial materials other than steel and cement in the construction sector, the emerging quick spread of plastic production is becoming exceptional [1]. Without knowing the characteristic of plastics, it cannot be defined on how their importance has been surrounded in the environment and modern applications. Most of their applications include in the industries such as clothing, packaging, and consumer electronics. Although plastics offer drawbacks such as the cost of recycling, they adapt to attract designers and engineers by the mixture of properties that cannot be gained in any other material. However, plastics and polymers have a similar definition, but in the growing evolution, plastics belong to the family of synthetic polymers. Most of the synthetic polymers can be classified by their structure, properties, process, and qualities. There are some cases in which the classification of thermoplastic polymers is mainly dependent on the polymer standard and material selection. The relevance of a crystalline (formed) or amorphous (unformed) shape is considered as a notable section among the thermoplastic division of polymers. In such cases, polyethylene and polyamide that maintains the crystalline shape is defined as limited occupied crystalline. Different polymer materials such as polyamide (PA), polyoxymethylene (POM), polycarbonate (PC), and polyphenylene oxide (PPO) have been a remarkable type for producing engineering thermoplastics [2]. Therefore, thermoplastic crystalline polymers that can be melted into fibres, films, or shapes is the general definition of polyamide [3].

Depending on the aliphatic or semi-aromatic polyamides, they belong to the family of synthetic polymers. The aliphatic polyamide groups such as Polyamide PA66, Polyamide PA6, Polyamide PA610, Polyamide PA11, Polyamide PA612, Polyamide PA12, Polyamide PA69, and Polyamide PA46 are defined from the character of a carbon atom and are used in different fields of applications. Fig. 1 shows the change integrity of lactams leads to ring-opening polymerization which forms Polyamide PA6. Also, different varieties are achieved mixing with additives. Polyamide PA6, a caprolactam thermoplastic monomer with great physical, electrical, mechanical, chemical, and thermal properties is generally utilized in different applications. It is the most attractive substance because of cost, execution, and adaptability.

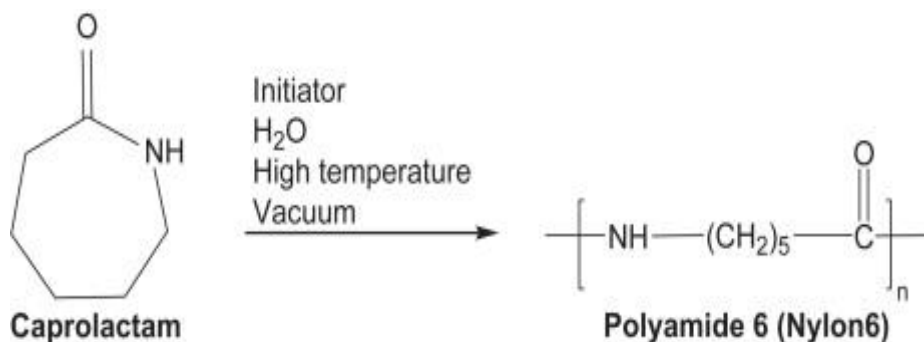


Fig. 1. Formation of Polyamide PA6 from caprolactam polymerization [4]

Based on engineering thermoplastic, Polyamide PA6 is applied in the resistance polymer groups. By the applications, the concentration of the micro composites guided by microparticles encounters outstanding influence in physical properties. High protection from the abraded surface and greasing up the trademark with moderately low cost and proper process make this material for broader and wider applications [3]. The surface of the Polyamide PA6 structure is the stage limit between the

mass polyamide and external condition. The surface is inclined to change because of the connection with nature. This is critical because modification in the surface properties can change the substance creations, conductivity, and cross-connecting thickness. Possible solutions upon the surface changes that occurred can be utilized for various applications with high strength and abrasion resistance applicable in the textile and automotive industry [5].

Conduct towards Polyamide PA6 with non-explicit growth continues with an imperative solid change that is realistic and the water particle element is examined with the narrow height by the methods for wetting tendency. Different types of development and goal techniques were utilized for control. The procedure of improvement towards the substance and water particles were delivered by a natural compound. The improvement exhibits that various mixtures were distinguished on the substance that impacts the duration of natural mixes. As shown in Fig. 2, groupings with solid and improved activity, the progressions lead to minor weight dropping [5]. The impact of the alteration exhibits the reduction in the surface. It is outstanding that the wear execution of the material is enormously overwhelmed by atomic weight, level of crystalline, and water retention.

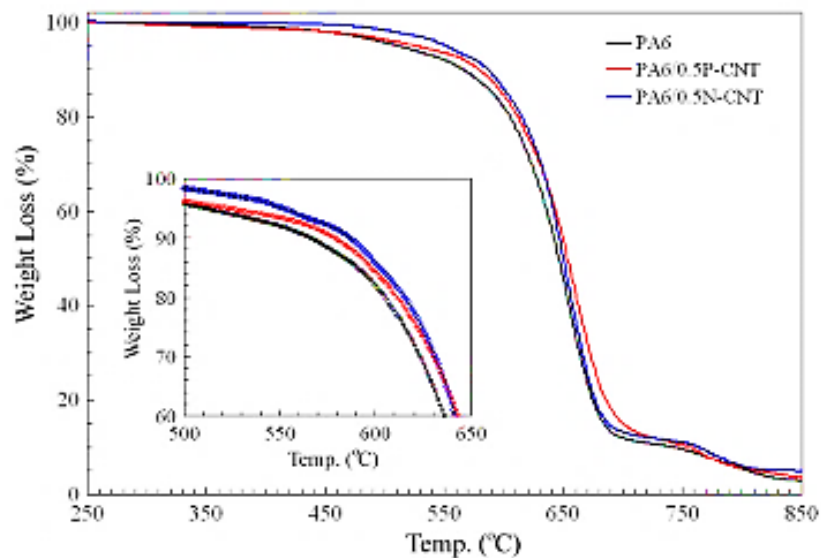


Fig. 2. Thermograph indicating PA6 weight dropping as a function of temperature [6]

Therefore, the improvement by combining different traditional lubricants and filaments were observed to be compelling at high loadings and seeing that 20% of graphite included in Polyamide PA6 results in the best tribological execution accomplished by the upgrade of mechanical properties and warmth dissemination [7].

1.1. Surface properties modification

The outcome by remarkable surface properties of Polyamide PA6 such as dimension stability, conductivity, and fire resistance exhibits a tremendous change in different areas of industrial applications. Previously, to enhance the properties they are loaded with a blended mixture of minerals for cost reduction. In general, higher dampness sense is less dimensionally steady and the effective surface quality has high strength even at low temperatures. When mating the material with an external force it results in the better-improved surface layer. Due to the consumption of low energy and easy processing, surface modification changes greatly effects to the present field of surface science. Improvement on the surface takes place across the Polyamide PA6 structure, but sometimes if the

size exceeds different process may be selected [8]. The usual method of grouping surface properties is divided into non-modification and modification techniques. In non-modification, the non-thermal plasma force method is used on the concentrated structure and in modification techniques methods of mechanical, thermal, and chemical functionalization are used on the structure.

One direct system to change the surface properties by the non-modification technique is by utilizing non-thermal plasma treatment. The modification by different techniques can be raised to a better state because of the poor surface energy and adhesive properties. The modified properties give unique thoughtfulness regarding grip, printability, and water obstruction of the regarded material that involves descriptive methods and practical utilization from logical research to wider applications. Table 1 shows the perspective of the modified Polyamide PA6. Besides, plasma treatment is an extremely adaptable procedure as different transporter gases might be utilized giving special importance to the material that has been dealing with [9][10]. Each Polyamide PA6, either organic or modified carry on diversely within the view of the water or some other fluid that can be systematic among most applicable parameters of the treated surface and material customization.

Table 1. Synthesis of modified Polyamide PA6 [7]

| Adjustment | Utilization | Approach |
|------------------|--|---|
| Light dyeable | Monacid or diacid stabilizers for Polyamide PA6 blocking – NH ₂ gatherings. | By diminishing – NH ₂ groups fixation to 10 – 15 eq/ton. |
| Profound dyeable | To acquire the required amount of diamines. | By expanding – NH ₂ groups fixation to 25 – 30 eq/ton. |
| Fire resistant | Alkyl phosphonic corrosive and antimony. | By gathering phosphorus/ halogen-based additives or monomer or nano clay. |
| Cationic dyeable | Disodium 3, 5'-disulphobenzoic corrosive as stabilizer. | By fuse of sulphonic corrosive gatherings. |

One of the most important characteristics of surface blending is by improving their wear properties utilized in a wide variety of possible applications. The treatment with a low or high surface energy of abrasion alters the visible macro surface roughness of the material. This has been an essential concept to guard the toughness of mechanical properties on the surface. The theory was proposed by Jin et al. [11] to explore the abrasion strength with sandpaper on fluorinated silica aerogels which maintains the mechanical property after abrasion. The mechanical abrasion process is suitable for the economic and environmental ways of changing the Polyamide PA6 surface. The basic approach used here is surface roughness. In practice, cleaning the surface with a solution is the significant limitation to this process. The resistance of the material towards abrasion can be examined by various test procedures. To locate better clarity for the material the number of turns or cycles of rotations is made [12]. The techniques are utilized by a described controlled abrasive substance. In this method, the abrasions rate is measured on the surface for different rotations. In general, the advance rate is the quantity of mass detained per 1000 cycles of rotation.

The principle property of abrasion is defined to plan the wearing activity involved. In the science of interacting surface, wear is caused by solid molecules that are operated on a hard surface that reacts to the transfer of material from another surface. It is important to know that a minimum of 60% of overall wear cost is reduced by abrasion wearing test. The wear process influences the different mechanical properties of the material [13]. During friction and frequent sliding, the surface comes in

contact with another by wear which controls the process. Fig. 3 represents the difference in the modified surface of Polyamide PA6 generated after abrasion treatment. Hard tension and excellent chemical resistance combined with energy force make the material perfect for mechanical applications. By conducting abrasive wear treatment, the surface counterface is influenced by the size of the material. The effectiveness in abrasion and resistance falls on the size and shape of the structure [14]

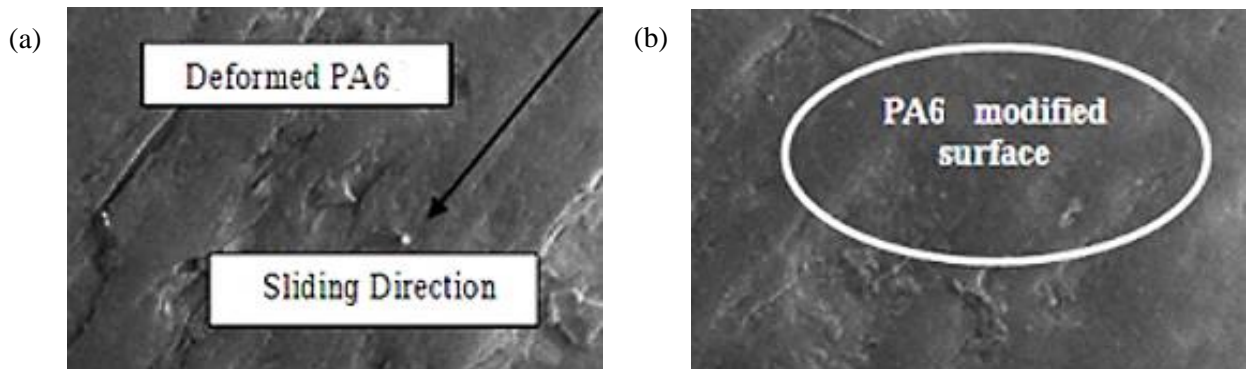


Fig. 3. Surface roughness by wearing treatment: (a) before abrasion; (b) after abrasion [12]

To gain the maximum excellence in surface changes, various wetting and adhesion effects are therefore appearing to require extra surface processing to upgrade wettability. Non-polar materials like polyamides require surface treatment to generate wetting as they have very low surface energy. This shows an improvement in the surface adhesion on how to bombard a Polyamide PA6 by plasma treatment. The development of bond strength extends the cohesive energy of the adhesive only in the case of a different plasma treatment at low intensity. In specific, the treatment confirms to be an outstanding and energy-saving substitute to the standard process.

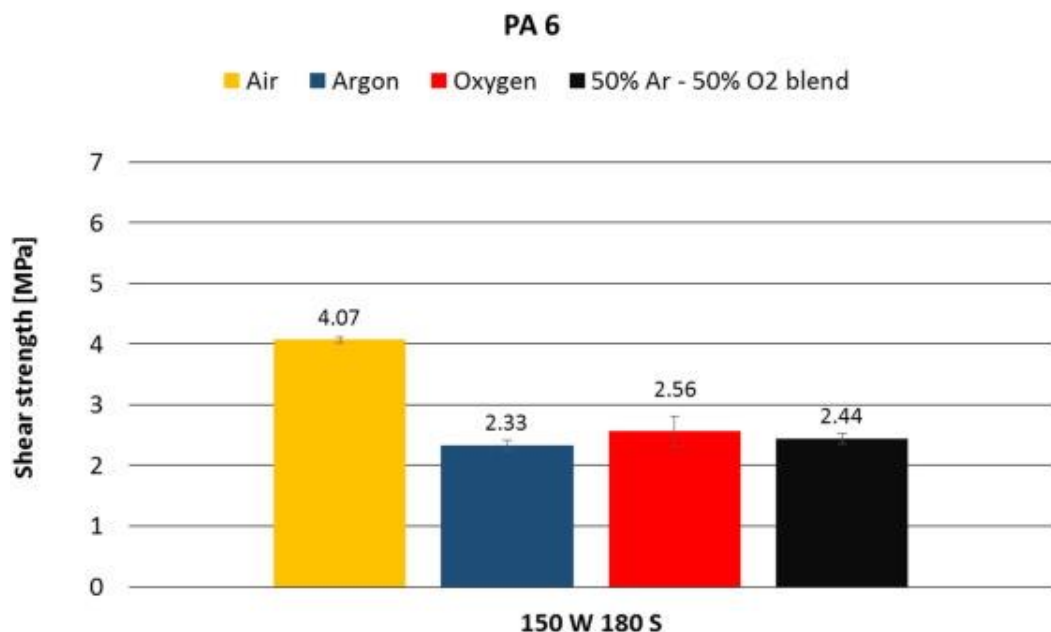


Fig. 4. Shear strength effect of different transporter gases by plasma surface treatment [15]

As mentioned earlier, the influence of plasma technology on the surface structure allocates to modify the surface by anyone of the gases used during the plasma treatments. The comparison in Fig. 4 shows the shear strength values on each surface directed by individual transporter gases and different

variation of values. Therefore, the concluding results display that no such gases show much influence except air. For materials that achieve more different surfaces, it enables the adhesion linking between material and adhesive which is an indication of stunning forces among atoms. To practically achieve wettability and better adhesion, the surface plasma treatment plays an important role in it. There are no ample techniques of plasma treatment but the main method concentrates on the surface modification of a thin-film. By understanding, plasma treatment can modify the surface and the treatment relationship actively depends on the plasma technology which is considered for adhesive bonding developing better viscous effects of composites [15][16].

From Table 2, different treatment of plasma proves to be a fundamental procedure on the surface wettability as the shear strength of the surface is greater than the traditionally treated surface. The approach towards different methods at adaptable situations can be differentiated between moderate and standard pressure.

Table 2. Methods of surface plasma treatments [17] [18][19]

| Method | Description | Treatment |
|-----------------------|---|---|
| Microwave plasma | The absorption of ions and radicals is high. Allows maximum etching rates. | Increases surface energy and contamination by flexible operating conditions. |
| Induction plasma | Restored by flowing gas. The Temperature obtained is high. | Enhances wettability by an etching process with the effects of surface oxidation and increased roughness. |
| Radiofrequency plasma | The Flow of gas applied by the Rf field. Power accepted by plasma to the incident power. | Advancing and receding contact angle is relatively easy and economical by wettability improvement. |
| Active gas plasma | Produced by plasma torches with $T_e \sim T_{gas}$. Extensive time and high-pressure discharge. | Dissociate gas vacuum by energy electric field to modify surface physically and chemically. |
| Oxygen plasma | Introducing oxygen to the plasma chamber. Increases wettability. | Correlate with discharge power and treatment time which increases surface oxygen content. |

In recent studies, dielectric barrier discharge (DBD) technology has been considered as the main treatment to modify the surface properties This technology was successful because of its inexpensive cost and allowing frequent procedures of surface treatments. It generates remarkable physical and chemical investigation on the surface of the modified material. For Polyamide PA6 it was the acrylic (Loctite 330), that exhibited improved adhesion. This eventually had a moderate result on the adhesion properties and with enough polar group which increased the surface energy as well as improved wettability. Also, the plasma discharge treatment studied by Hnilica et al. evaluated the surface modification of Polyamide PA12 utilizing atmospheric plasma jet resulted from the increased change in wetting was due to the chemical and morphological changes of the surface [15]. The sheer energy of the various plasma-treatment results in the surface plane expansion due to plasma etching and efficient functionalization with oxygen-containing groups [19]. The process is concluded by insertion or exchange of polar substance onto the surface which is called plasma activation. This method does not bend or damage the Polyamide PA6 surface in any case.

With great properties of chemical stability and transition temperature, their applications towards engineering and technologies lead to the major use of polyamides [20]. With the presence of a catalyst to improve the rate of chemical reaction on the surface, the method can be utilized with an excess amount of acids and base acting as an outsourcing agent. This regeneration method can also reduce the amount of waste without any use of elevated surface pressure. The enriched solvents reveal effects on a greater degree of interchain attraction to the greater molecular pattern [21]. This affects their potential energy to encounter hydrogen bonding. Therefore, by making changes in the molecular system it is feasible to modify different properties.

In the field of nanotechnology, the composites such as nanoparticles, silicate compounds, and synthetic clays have been discovered to a greater extent of properties improvement. But the complexity which restricted the processing of polyamides was due to the primary problem linked with surface adhesion. The methods have a better contact angle because of their impression on the hydrophobic layer. When treated with chemicals such as acids, base, and alcohols the surface might result in multiple breaks depending on the molarity content of the chemicals used. The crack modes on the surface were previously examined by Silva et al [22]. The resulted cracks showed in Fig. 5 were due to the nano-filler dilution of occupied energy. To raise the occupied energy, 3% wt of nano-fillers was added to avoid breakage.

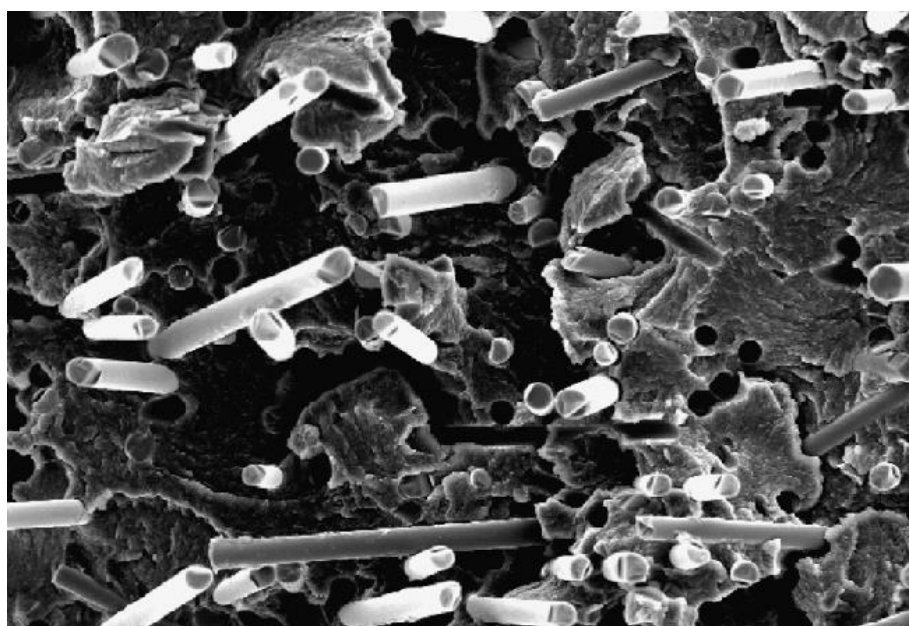


Fig. 5. Cracked surface due to limited nano-filler additives [22]

In recent studies, Lv et al. developed a superhydrophobic angle ($<120^\circ$) by depositing dissolved granulated polypropylene on the Polyamide PA6 surface [23]. Depending on the polar amide groups present in the Polyamide PA6 chain, the treatment can react with the chemical agents. With the presence of a catalyst to improve the rate of chemical reaction on the surface, the method can be utilized with an excess amount of chemicals:

(a) Organic chemicals: The substance reacts extraordinary resistance to organic solutions as diluted solvents show better results, but phenols show a minimum result. Glycols, esters, and halogenated hydrocarbons have no results on the surface. Other organic solvents such as benzyl alcohol [20] and nitro alcohol can make the surface dissolve at high temperatures. Organic solvents are well resistant to oils and fuels proving to be that there are no visible modifications and constant chemical change.

(b) Inorganic chemicals: They are generally strong in most inorganic substances like sulfurous acid and ammonia, but maybe eroded with oxidants such as hydrogen peroxide and chlorine-based decolorants. Acids and alkali substance is strong up to 25% at room temperature as the surface is resistant to alkaline solvents and halogens. Fluid halogens oxidize the surface which results in the modification of the physical effects on the surface.

1.2. Adhesion behavior on solid surface

The atoms of fluid are held together by fascinating powers. A total of every single attracting power on any particle present in the greater part of a fluids midpoint is zero. The net power otherwise called as standard power on a surface is a non-zero amount towards the path of the mass. This is the surface tension that must be neutralized to expand the surface region and the vitality consumed by this procedure is called surface vitality. Liquid droplets are circular because a circle has the least surface region for a given volume among every single geometric shape. Although strain and vitality of fluid are equivalent, it is not valid for a strong surface. The surface energy of solid is characterized as a material that is unbending and opposes pressure. An efficient surface might be portrayed by free vitality energy [24]. Surface vitality (pressure) of liquids cannot be estimated along these lines to that of fluid because of the errors brought by the reversible development. The adhesion fabrication of bond is characterized as the reversible thermodynamic work that is expected to isolate the interface from the harmony condition of different stages to a division separation of limitlessness. The trial and logical techniques illustrate to gauge the vitality of fluids and solids. Surface arrangement procedures are somewhat gone for changing surface vitality of materials and that has been applied to growing industrial sectors in which the shaping of polyamide surface is applied before involving the material [25].

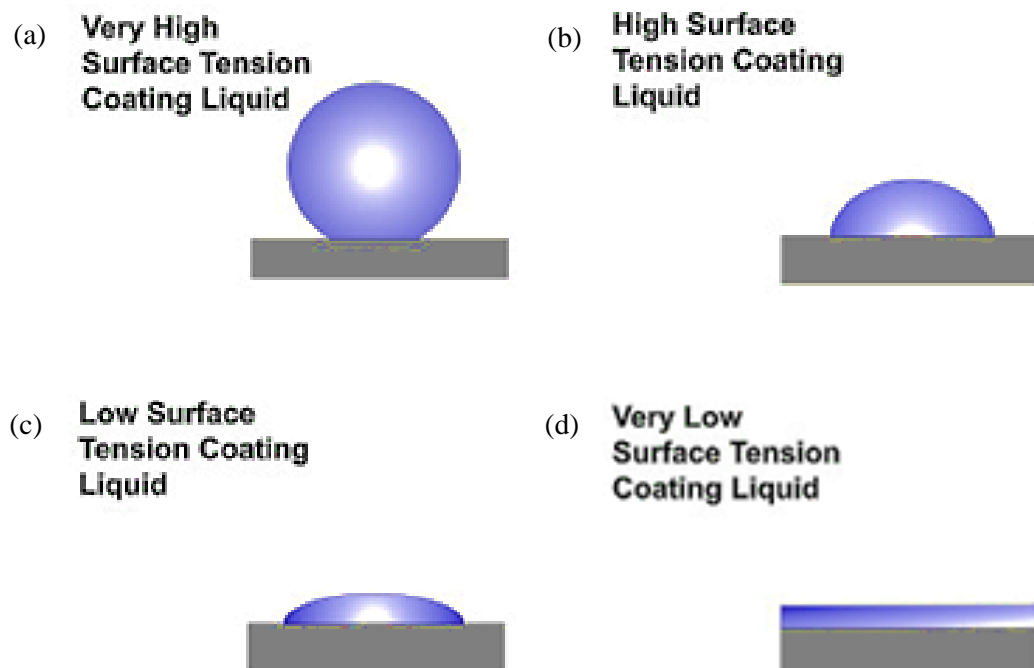


Fig. 6. Droplet interface of surface tension: (a) Very high; (b) High; (c) Low; (d) Very low [26]

Low, high, and anisotropic [26] are the types of adhesion behaviors of different liquids on a hydrophilic surface. Generally, a low-adhesion can be described as the low surface tension of entry liquids whereas high-adhesion is of high surface tension and anisotropic adhesion is of moderate surface tension as shown in Fig. 6. This gives clarity to the adhesion of liquids on a solid surface and

the roughness analyzed by solid-liquid influence results to have the highest wettability. A high wetting surface has surface vitality energy that makes a solid appealing force to pull the fluid down and making it spread out. This is known as wettability. This surface energy is more grounded than the surface pressure of the fluid's atoms that would regularly keep it in drop structure. The surface strain of the fluid does not change but instead, the surface vitality of the droplet is more grounded than the fluid's surface pressure and overwhelms it making the fluid spread out over the strong surface. The minimum contact angle is equal to the maximum surface vitality [27] and high interfacial tension. For a low wetting surface, the surface vitality is unstable than the surface strain of the fluid involving that the fluid can more likely keep the drop shape. The interconnection between the solid and liquid is not strong due to the interfacial tension. The maximum contact angle is equal to the minimum surface vitality and low interfacial tension. Numerous innovative procedures require the control of fluid spreading over strong surfaces. At the point when a drop is set on a surface, it can wet, halfway wet, or not wet. By diminishing the surface pressure with a wetting agent, a non-wetting material can be made to turn out to be somewhat wet [9].

The influence of wetting angle on a hard surface with different wetting liquids has been a foremost application in various studies. Young's law is used as the main regulation in different wetting procedures [28]. Liquids based on different chemical compounds reveal a changing behavior as they result in superior transit without any exterior pressure. The surface tension range of liquids as shown in Table 3 can develop adhesion on a Polyamide PA6 surface with high energy. By planning of different surface modification methods, the wetting properties, adhesion, and contact angle can be measured.

Table 3. Surface tension of different wetting liquids [29]

| Liquid | Surface Tension (mJ/m ²) | Supplier/Quality |
|--------------------|--------------------------------------|----------------------|
| Water | 72.8 | Elgastst (> 18MΩ cm) |
| Formamide | 58.2 | Aldrich 98% |
| Ethylene glycol | 47.7 | Sigma 99+% |
| Dimethyl sulfoxide | 42.7 | BDH Chemicals 99% |
| Methylnaphthalene | 38.3 | Aldrich 95% |
| Dimethylformamide | 35.2 | Sigma 100% |
| Hexadecane | 27.6 | Aldrich 99% |
| Octane | 21.8 | Aldrich 99% |
| Heptane | 20.1 | BDH Chemicals 99.5% |
| Hexane | 18.4 | EM Science 98.5% |

The testing of wetting liquids such as water and ethylene glycol have been considered for different fabrics of chemical coupling and graft polymerization [30]. Thus, the above properties of wetting liquids are therefore considered and tested for the different modified surface of Polyamide PA6. The movement and distribution of wetting droplets impact the surface adhesion because the sticking of liquids relies on the grouping of each drop, boundary layer, and roughness properties of the surface. The arrival of droplets can be studied when the number of droplets is filled on the surface tip, therefore the excess amount of water reserved and start to disappear [25]. Different contact angles are measured by the adhesion on the surface.

Water has been used as a key solution as one of the wettability liquids, therefore their general properties are;

- Water exhibits high polarity of solid molecules which can dissolve easily because it contains two hydrogen atoms of positive charge and one oxygen atoms of negative charge. This positive and negative is responsible for high polarity substance in water.
- The property of water is of cohesion in nature in which all molecules stick together and attracted because of the positive and negative charge present in it creates an imbalance to the liquid.
- The dissolving intensity of water assumes the fundamental task for the life on earth so that wherever water goes, it breaks up into minerals and synthetic compounds that are utilized for living things. As a result of extremity, water particles are pulled into each other which gives a high surface tension.
- The water has a high boiling point of 100°C and its atoms are connected by strong hydrogen molecules. To break the hydrogen bonding in the water molecules, it needs to have the highest temperature that allows the liquid to escape as steam.
- Water is good at moderate temperatures where it can absorb the highest amount of heat by creating a stable environment. This causes a relatively small change in temperature. That is why large water bodies with lands nearby exhibits cooler environment after water bodies absorb heat.

Ethylene glycol used as the secondary solution of the wetting liquids has already been a part of the surface wettability for different polyester fibers. Their tendency towards polyester surface has been a successful growth that has great parameters of hydrophilic and hydrophobic wetting angles [30]. Their properties focused on the research has been the main choice for selecting the wetting liquid;

- Ethylene glycol acts as a humidifying and plasticizing agent because it has a self-adjusting humidifier that stabilizes the humidity at an optimum level and it is also used as a plasticizing agent that helps to produce plastics.
- The natural gas industry utilizes ethylene glycol as a dehydrating agent to remove water vapor from the gas stream while processing.
- Ethylene glycol resins can be soft and flexible so it can be used as softeners in the textile industry.
- Ethylene glycol acts as a median in a wide range of reactions especially in resin formation and in the condensation process of polymer production.
- The colorless, odorless, and viscous liquid treated with water becomes soluble whereas with ether it is less soluble.

1.3. Contact angle

The contact angle analysis has been involved and developing in various industries like aviation and medical. The main investigation used is by the sessile drop method because of less cost, adaptable and handy system that directs to propose the wettability of a surface. When a liquid-vapor interface meets on a solid surface the contact point is evaluated through the liquid. It measures the wettability on a solid surface with liquid by methods according to Young's condition. On a high contact point as shown in Fig. 7, the surface has low wetting. A low contact point demonstrates that the surface is high wetting. The plan of solid, liquid, and vapor at a given temperature and weight has a unique

understanding of the contact angle. The equalization contact is inside those characteristics and can be resolved from them. The equality contact edges reflect the general nature of the liquid, solid, and vapor correspondence [31].

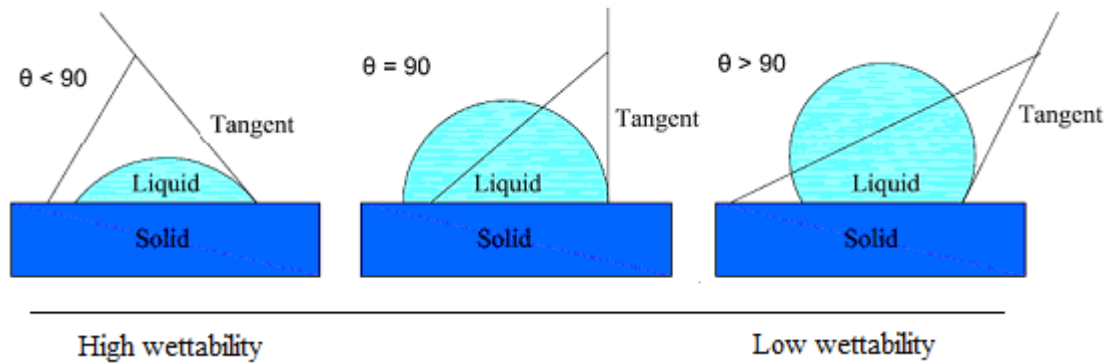


Fig. 7. Schematic diagram of wetting angle measurements on a solid surface [32]

To accomplish the sessile drop technique, one direct method is by utilizing the pocket goniometer 3 (PG3) device shown in Fig. 8. This device can measure in different conditions such as static, dynamic, and advancing modes of contact angles applicable in the field of surface engineering science. The frameworks of the traditional method were minimal as they utilized a magnifying lens with backdrop brilliance. Later, the rise of the developed goniometer with software applications is used to analyze the angles under different conditions. Current-age frameworks utilize high definition cameras and software programming to analyze the contact angle.



Fig. 8. Pocket goniometer 3 (PG3) device for contact angle measurements

The primary method of examining the liquid droplet angles by sessile drop flow is when an entry of liquid is pumped on the surface. The range differs from surface factors like modified topography and roughness defined by the angle hysteresis. The sessile drop contact angle is estimated by a pocket goniometer 3 utilizing an optical subsystem to catch the profile of an absolute fluid on a strong substrate. Different wettability contact shapes using testing liquids states that the advancing contact angle is less sensitive to the high energy of the surface while the receding contact angle is less sensitive to low energy. The wettability of the contact angle has been an excellent technique to identify the advancing and receding angles by the liquid-solid interface. Apart from it, the volume, base, and height of the pumped droplet coordinating upto 95% interval can be calculated. The point

framed between the liquid-vapor interfaces is the contact angle. Points estimated in such a way are frequently very near propelling contact angle and can be acquired through the utilization of all-around characterized vibrations [33]. Thus, the least complex method for estimating the sessile drop is with a pocket goniometer 3 (PG3) that enables the user to gauge the contact edge outwardly.

The concept involving Polyamide PA6 surface modification by different methods were studied. The methods focus on the improved surface roughness depending on the properties of the specimen. Besides, a general point of view towards adhesion with chosen liquids has been researched to measure the wettability of the surface. The primary properties are defined from the chosen wetting liquids and have been considered as a testing solution for the contact angle measurements.

2. Material and methodology

At a molecular size of dispersed allowance and polarity on wetting, Polyamide PA6 is heterogeneously exploring the influence of a compulsive substance. Before conducting the experiments, the specimens were kept for 48 hours at an environmental condition of $23 \pm 1^\circ\text{C}$ standard temperature and $50 \pm 2\%$ relative humidity. The main specification includes a white Polyamide PA6 specimen of size $100 \text{ mm} \times 100 \text{ mm}$ and a thickness of 1 mm. Initially, the required number of specimens is heated at 100°C in water for 10 minutes using the laboratory heating device for improving the characterization of turning it into a boiled surface. The actual specimens without any characterization are used as the non-boiled surface. Thus, the types of Polyamide PA6 specimens of the boiled and non-boiled surface under transparent and heat stabilized conditions were used in this investigation. The tribological execution of analysis was accomplished by involving the modification of boiled and non-boiled surfaces by abrasion, plasma, and chemical treatment methods. Later, the modified boiled and non-boiled surfaces are used as a substrate for discovering wetting angle measurements. The analysis was measured within the surface by a captive drop pocket goniometer.

Table 4. Properties and values of Polyamide PA6 [34]

| Property | Value |
|--|---------------|
| Shrinkage | 1 – 1.3% |
| Dielectric Strength | 16 – 26 kV/mm |
| Dielectric Factor @ 1MHz | 2.7 |
| Dissipation Point @ 1MHz | 0.025 |
| Sealing Temperature ($^\circ\text{C}$) | 193 - 232 |
| Elongation to break (%) | 150 – 300 |
| Flexibility and Stiffness | 1 – 2 GPa |
| Young's Modulus | 1 – 2 GPa |
| Tensile Strength at Break and Yield | 50 – 65 MPa |

2.1. Surface abrasion wearing

The Polyamide PA6 behavior of the boiled and non-boiled surface to abrasion was performed using a mechanical Taber Abrader model 5131 with the abrasive resistance standard ISO 5470-1:2016. As shown in Fig. 9, the device is provided with a set of abrader wheels fixed to a mechanical arm, a rotating disc, a digital program meter, and a lubricating injection tube. The concept of the treatment is to discover improved roughness on each boiled and non-boiled surface abraded under different rotations. The material specification with the size $100 \text{ mm} \times 100 \text{ mm}$ and thickness 1 mm is utilized. At first, a radius of 5 mm is tailored in the center of each boiled and non-boiled squared surface for the position on the rotating disc. A set of CS-10 rubber abrading wheels with a minimum thickness of 12 mm and a radius of 23 mm are located to the left and right side of the mechanical arm. The number of rotations is manually entered into the digital program meter after placing each surface in contact with the abrading wheels. Six evaluations of abrasion wearing treatment under 0, 5, 10, 20, 50, and 100 rotations are performed on 6 sets of the boiled and non-boiled surfaces. For 0 rotations, it means that the actual surface is without abrasion wearing test. The selection of the rotations was based on the visual difference of each boiled and non-boiled abraded surface. The mechanism is

involved by the set of rubber abrading wheels pressed with 250 grams vertically with the surface, spins in the opposite direction by improving abrasion during the increased rotating speed of 60 revolutions/minute. Besides, to avoid noisy situations during the treatment, a fluid injection tube is utilized to provide efficient lubrication to the mechanical arm for the smooth running of the operation. After each required surface rotations, it is necessary to carefully release the mechanical arm to replace the abraded surface. To avoid fingerprints on the finished abraded surface, it is recommended to handle the edges of the surface.



Fig. 9. Experimental setup of surface abrasion treatment: 1- mechanical arm; 2- abrader wheels; 3- PA6 specimen; 4- rotating disc; 5- digital meter

The running period of each rotation was determined to discover the wear value and the initial time of abrasion conducted for different rotations. By the positive composition of increased surface abrasion for different rotations shown in Fig. 10, it is utilized for surface roughness measurements and wetting angle experiments.

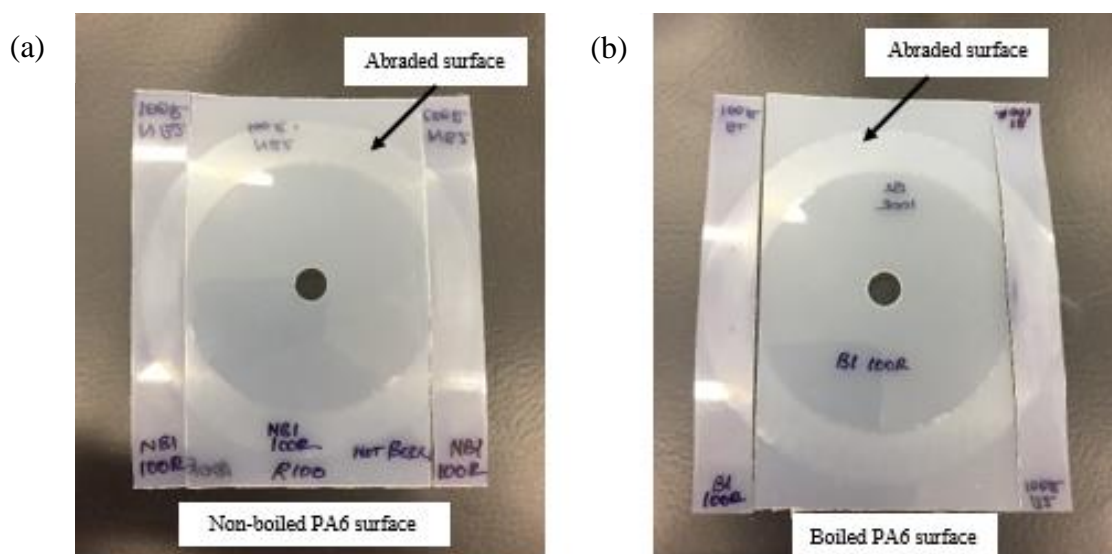


Fig. 10. Improved abraded surface: (a) non-boiled PA6 under 100 rotations; (b) boiled PA6 under 100 rotations

2.2. Surface roughness measurement

Owing to the development of digital handheld devices the roughness measurement for different abraded boiled and non-boiled Polyamide PA6 surface is measured by the standard ISO 1997 roughness tester Mitutoyo SJ-210 as shown in Fig. 11. The measurement tool is used to detect the accurate roughness of each boiled and non-boiled surface abraded with 0, 5, 10, 20, 50, and 100 rotations. The specification of each material is tailored to 15 mm × 100 mm on the edges of the abraded surface and is utilized for roughness measurements. Initially, two marking are made randomly on each side of the abraded surface. The device is equipped with a 2.4-inch display screen that shows the menu options of two indicators R_a and R_z . The indicators are fixed as the output roughness parameters. The default conditions depending on the tolerance λ_c are 0.25 and based on the selected λ_c , the λ_s are set as 2.50. The detachable drive unit connected with a three feet flexible cable can be removed easily from the case and it is kept at 90° perpendicular to the abraded surface for the measurements of R_a and R_z parameters. The portable measuring instrument equipped by the metal stylus is used in practical on-site applications to move over the abraded area. During measurements, the screen will self correct the distribution curves (roughness profile R_z). A series of ×4 times roughness measurements R_a and R_z are taken on each boiled and non-boiled abraded surfaces. The measurements are measured by the markings on each side of the surface and the value is displayed on the LCD screen at the speed of 0.28 mm/sec. The R_z calculates the variation between the lower and the highest distribution curve and R_a calculates the average roughness of the surface [35]. The external storage can accumulate up to 1000 measurement results under 10 measurement conditions for 1 measurement profile with highspeed USB interface and SPC ports. Maximum results of upto 10 measurement conditions can be stored in the internal memory saving the last inputted nominal value. A set of 4 roughness measurements are noted for R_a and R_z with each boiled and non-boiled surface under different rotations.



Fig. 11. Mitutoyo SJ-210 surface roughness tester [36]

Thus, the readings of R_a and R_z parameters for each side of the surface were recorded. The dependency of abrasion disc rotations to the roughness parameters on the boiled and non-boiled surface is presented as a graph for analysis.

2.3. Surface plasma treatment

The low surface energy of Polyamide PA6 can be improved by the plasma treatment method. The treatment improves how wetting liquids can increase the overall adhesion by changing the thermal appearance of the surface. Under the fourth state of matter, plasma treatment was experimental set up by the JSC Kvartz Plasma-600T device at 23°C room condition and 50% humidity. The main properties of the device include a radio frequency range of 13.56 MHz kept at a plasma power density 0.3 W/cm² and atmospheric gas pressure 133 Pa. The specification of each material with size 100 mm × 100 mm is utilized for the thermal effect of plasma treatment. During the treatment, the boiled and non-boiled surface is kept in a fixed position facing towards the nozzle of the plasma 600-T device. The space between the nozzle and the surface can be adjusted suitably and the interval between the gaps is 12 mm [37]. As shown in Fig. 12, once the set up is in a fixed position the plasma system discharges flame inside pushing the pressurized air by single electrodes. The electrode creates positively charged ions inside the device by electrical discharge. The atmospheric pressure accelerates the air particles and discharges from the tip of the nozzle at high velocity to the boiled and non-boiled surface. The Plasma conduct towards the surface is treated to one side of each boiled and non-boiled surface under safety conditions. The method involves a fast treatment of surface functionalization treated for 60 seconds. After the treatment, the specimens are carefully replaced without touching the treated surface avoiding fingerprints and dust particles. The surface process repeats and is treated for other specimens of boiled and non-boiled Polyamide PA6.

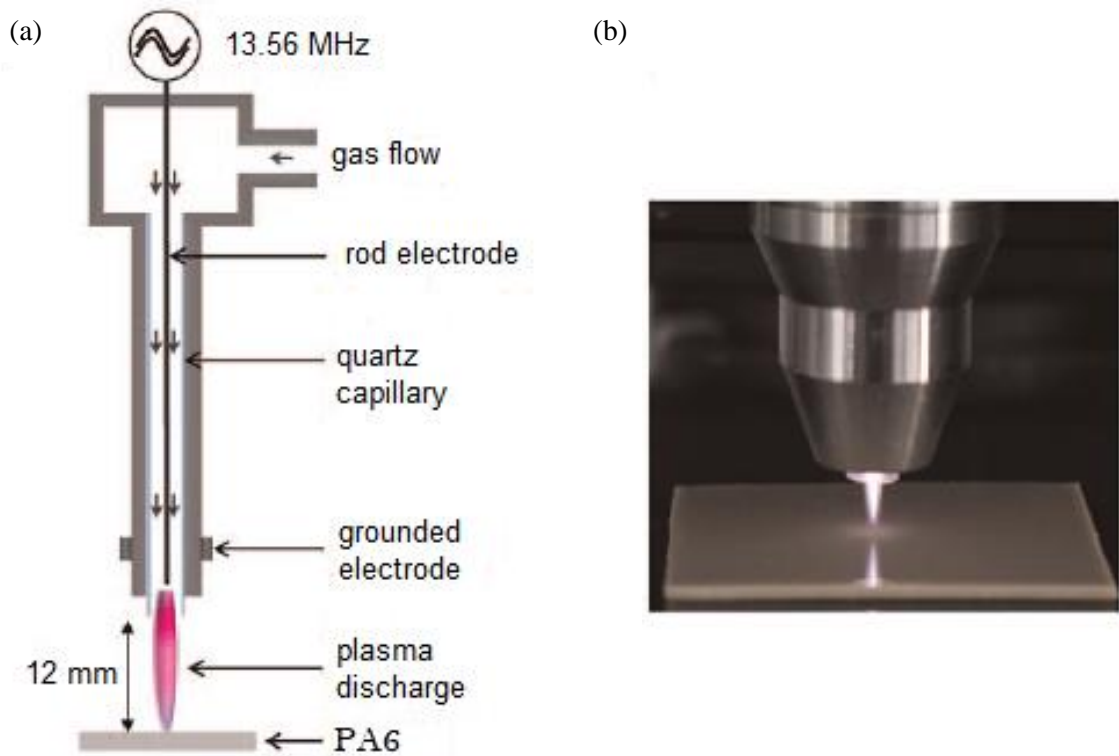


Fig. 12. Atmospheric pressure plasma treatment: (a) schematic view; (b) actual view [37]

Through direct contact, the particles discharged increases the surface energy and generate concentrated discharge that bombards on the surface. Within 2 hours, the wetting angle measurements of the plasma treated on the boiled and non-boiled surface are conducted and the results were analyzed.

2.4. Surface chemical treatment

The surface chemical composition on the structure of Polyamide PA6 has been to a great extent in manufacturing applications. The finishing method of the surface properties modification will be ended with the treatment of boiled and non-boiled Polyamide PA6 with acids and base chemical compounds. The compounds of acids and base solvents will experience moisture content to increase dissolvable nature on the surface of Polyamide PA6 suitable for this research. To consume less amount of chemical solutions, the specimen structure is tailored to the size of 15 mm × 100 mm which can directly be utilized for wetting angle experiments. The main focus leads to the chemical changes on the surface with inorganic acids and base used with three types of molarity conditions such as (1) standard CAS 1310-58-3, 3M Potassium lye pellets base (KOH), (2) standard CAS 7674-01-0, 0.5M Hydrochloric acid (HCl), and (3) standard CAS 7674-01-0, 3M Hydrochloric acid (HCl) showed as a schematic view in Fig. 13. The chemicals (1), (2), (3) were included for changing the surface properties of the specimens. The changes show the effect on the surface layer, hardness, and rigidity. The foremost application of this research to the microstructure surface layer helps in bringing the suitable formation of different phases. To enhance the strength of the chemical solutions, the structure of size 15 mm × 100 mm was initially treated with two different chemical compounds with the molar concentrations. The treatments to prepare: (i) 3 molarity Potassium lye pellets base with property effects of calculated density 1.456 g/ml, molar mass 56.11 g/mol for 50 ml final volume is to add 12.846 ml of the solution to 12.5 ml purified water. (ii) 0.5 molarity Hydrochloric acid with property effects of calculated density 1.2 g/ml, molar mass 36.46 g/mol for 50 ml final volume is to add 2.053 ml of the solution to 12.5 ml purified water. (iii) 3 molarity Hydrochloric acid with property effects of calculated density 1.2 g/ml, molar mass 36.46 g/mol for 50 ml final volume is to add 12.318 ml of the solution to 12.5 ml purified water.

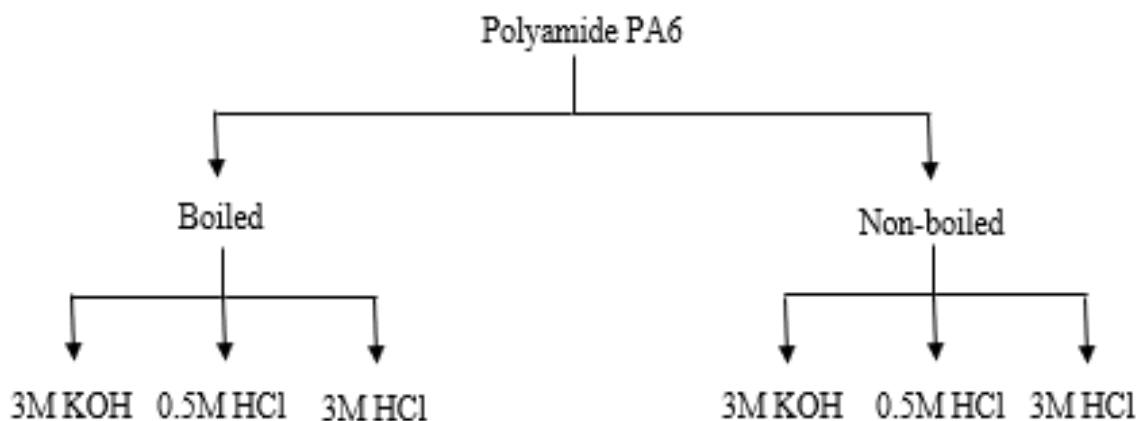


Fig. 13. Simplified view of surface chemical treatment

Once the solutions are prepared they are individually treated with each boiled and non-boiled surface and heated at 60°C for 60 minutes. After the treatments, each specimen is carefully handled due to the chemical presence and washed with distilled water at 60°C for 30 minutes to remove the moisture content of added chemicals. The systematic procedure repeats for (i),(ii),(iii) conditions. After treatment, it is found that the surface of non-boiled Polyamide PA6 treated with 3M Hydrochloric acid, loses the rigidity on the surface layer and results in a cracked surface as shown in Fig. 14. The

defects may be caused due to the molarity content of Hydrochloric acid. Later, the treated surfaces under different conditions are utilized for the wetting angle experiments.

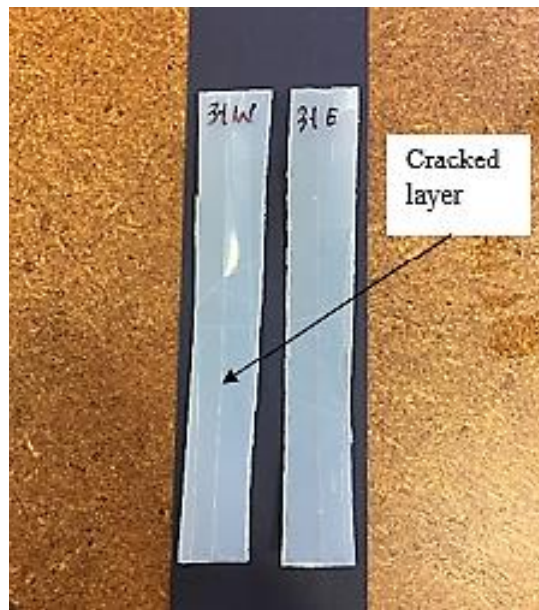


Fig. 14. Formation of cracked layer on non-boiled PA6 treated with 3M HCl

2.5. Contact angle determination

The wettability measurement of contact angle on different modified Polyamide PA6 surfaces by certain liquids is performed in connection with an inclined tangent. The liquid-solid-vapor (LSV) interface line is calculated by the numerical expression angle depending on the structure of the droplet. The experimental procedure is performed at room temperature through a positive perspective to measure the droplet of different liquids position on each modified specimens. The determination is applied to boiled and non-boiled specimens under different abrasion rotations, the thermal effect of plasma treatment, and types of treated acids and base chemicals. Water and ethylene glycol with the surface tension of 72.8 mJ/m^2 and 47.7 mJ/m^2 is used as the wetting liquids for the contact angle investigation on the different modified surface. The experiment is supported by a commercial sessile drop pocket goniometer 3 (PG3) device connected by the USB interface with computer control. By needle drop, the wetting liquids are pumped as droplets on the surface of the modified specimens thus forming a contact angle and droplet image visible from the "PG" application already installed to the computer control. Initially, the syringe of 1 ml capacity and the micro connecting tube of length 180 mm is rinsed with an ethanol solution to remove previous liquid moisture content in it. The syringe is filled with water and pumped to check that no air bubbles exist at the tip of the syringe and connecting tube. As shown in Fig. 15 the experiment is set up by a connecting tube from the syringe is inserted to the pocket goniometer and the location of the liquid entry point is adjusted by the visible view from computer control. The alignment of the camera angle is very important as the experimental analysis is completely dedicated to it. The initial step of the arrangement is prepared and set. Each tailored boiled and non-boiled modified surface of size $15 \text{ mm} \times 100 \text{ mm}$ is inserted to the pocket goniometer 3 (PG3) by careful handling without finger contact to the surface. The measurements are set under static conditions with water as primary wetting liquid. By manual finger pressure, the loaded water is pumped on the surface of the modified specimen to measure the contact angle and capture the video image. The specimen is kept flexible and are pushed by 10 mm length after pumping each droplet. A maximum of 10 droplet measurements are taken for each surface and their captured image

is saved to the computer and later examined for wetting analysis. The measured specimens are replaced from the pocket goniometer and the experiment procedure repeats for other modified boiled and non-boiled specimens.

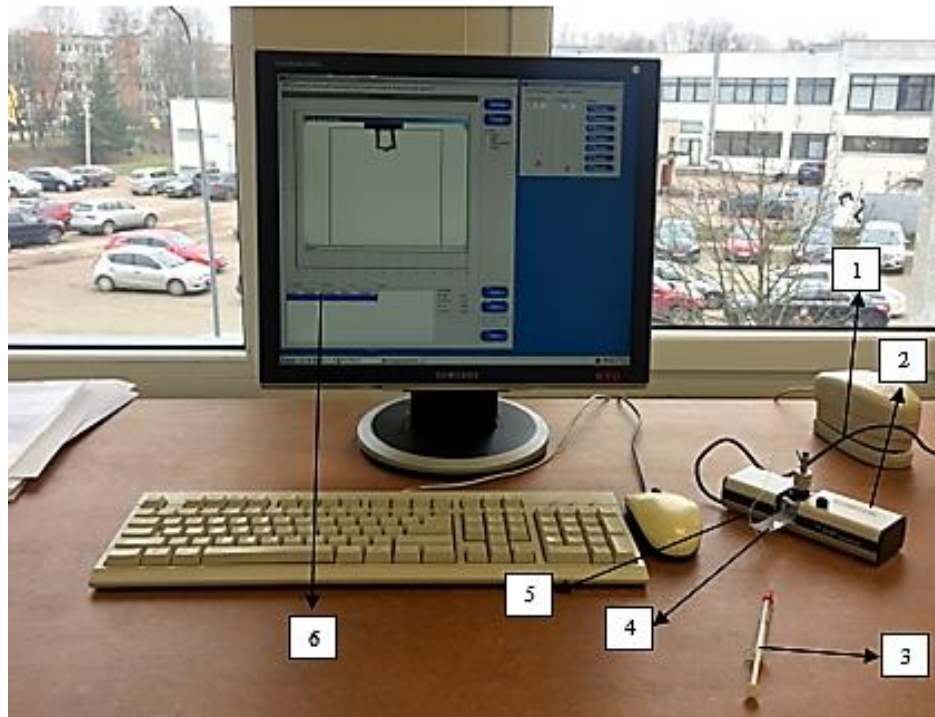


Fig. 15. Experimental setup of contact angle measurement technique: 1- USB cable; 2- pocket goniometer 3 (PG3); 3- syringe (1 ml); 4- tailored specimen (15 mm × 100 mm); 5- micro connecting tube; 6- “PG” application

The same method is followed by replacing ethylene glycol as the secondary wetting liquid. Before adding it is made sure to clean the syringe with an ethanol solution to remove the remains of water moisture for accurate results. A different micro connecting tube between the syringe and pocket goniometer is used for the ethylene glycol wetting liquid. The contact angle measurements are noted and every single capture of the image is saved and later examined. The measurements for modified boiled and non-boiled Polyamide PA6 with water and ethylene glycol are determined individually. The measured surface wetting angle influence of water and ethylene glycol to the dependency of abrasion disc rotations and the influence of plasma and chemical treatment was presented as a graph.

3. Results and discussion

3.1. Surface roughness measurement

1. Non-boiled PA6 with R_a , μm

The averaged surface roughness R_a to different abrasion disc rotations for the non-boiled surface is presented in Fig. 16. The scatter chart examines the correlation relationship and the linear propagation with two different variables.

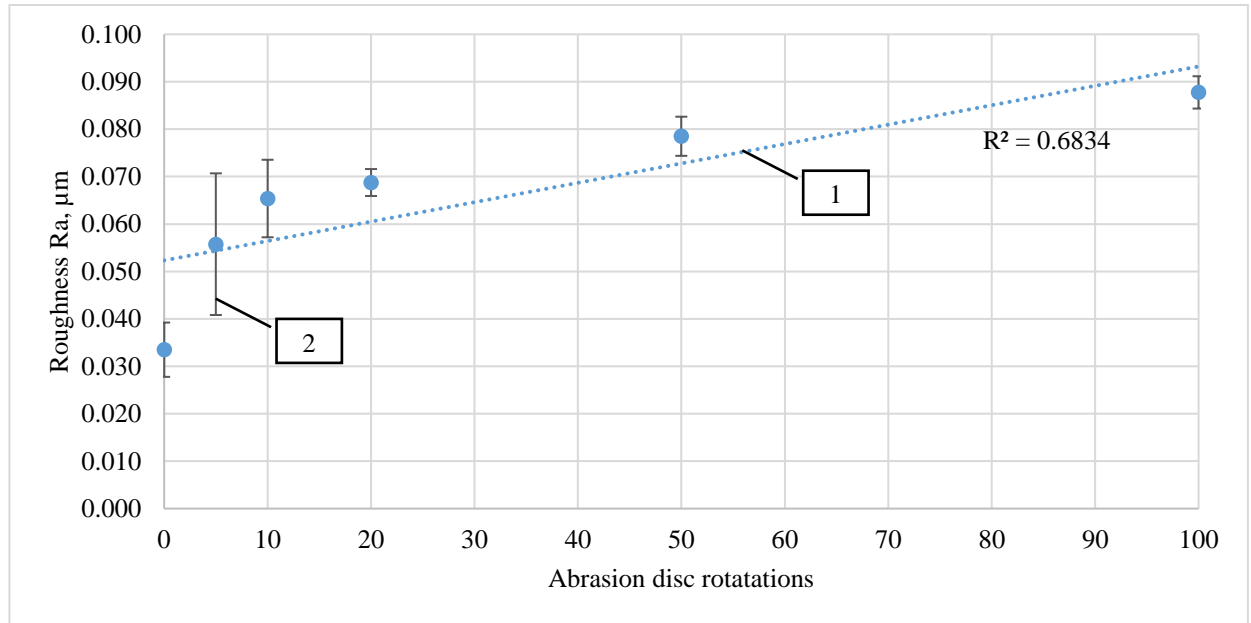


Fig. 16. Dependency of the abrasion disc rotations to surface roughness (R_a , μm) on non-boiled PA6: 1- linear regression with the coefficient of determination; 2- confidence interval

From the chart, the mean roughness of R_a on both sides of the non-boiled surface for different rotations is presented as the actual value. The tendency results of R_a are linear because the roughness on each surface increases for 0, 5, 10, 20, 50, and 100 abrasion disc rotations. It is observed that the mean R_a roughness on the non-boiled surface is between 0.034 μm to 0.088 μm . During increased rotations, the R_a results in an average measured non-boiled surface roughness of 0.065 μm from 0 to 100 abrader disc rotations. The coefficient of determination (R^2) for R_a is 0.6834, which means that the probability to determine the intermediate surface roughness is 68%. The intermediate roughness predicts that the rougher the surface is, the larger the material area is covered. The upper and lower limit between each mean measurements shows that the roughness lies within the range considered by the confidence interval. Thus, the expected roughness results in 68% of the actual mean roughness fitted to it.

2. Non-boiled PA6 with R_z , μm

The averaged surface roughness R_z to different abrasion disc rotations for the non-boiled surface is presented in Fig. 17. The scatter chart examines the correlation relationship and the linear propagation with two different variables.

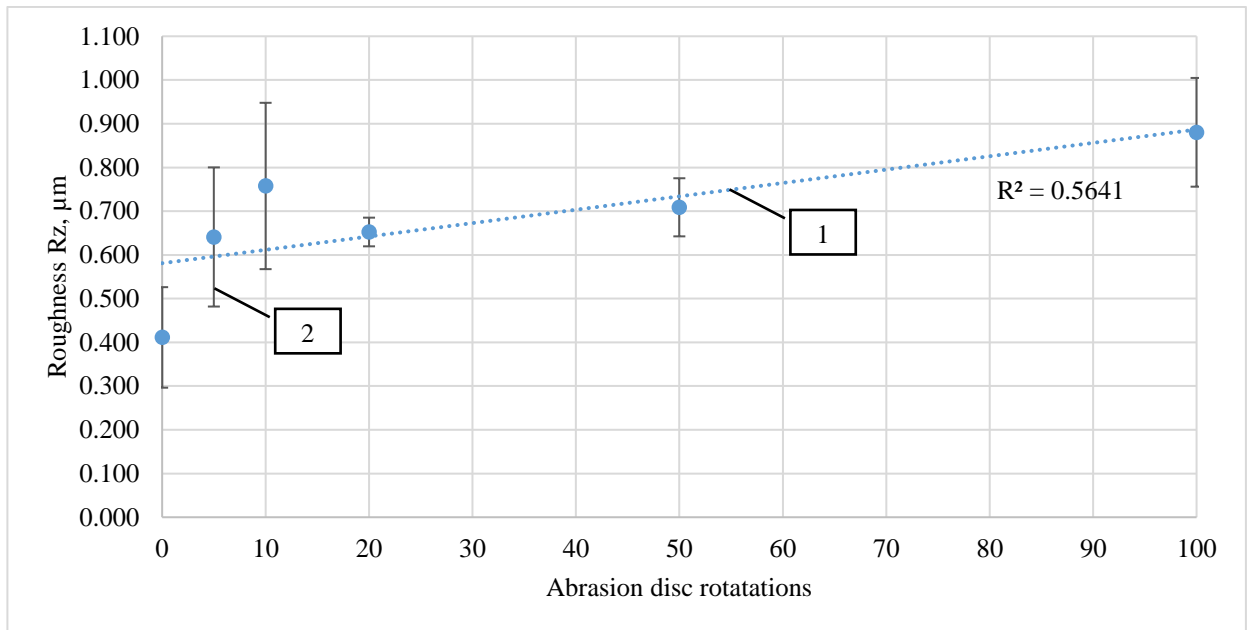


Fig. 17. Dependency of the abrasion disc rotations to surface roughness (R_z , μm) on non-boiled PA6: 1- linear regression with the coefficient of determination; 2- confidence interval

From the chart, the mean roughness of R_z on both sides of the non-boiled surface for different rotations is presented as the actual value. The tendency results of R_z are linear because the roughness on each surface increases for 0, 5, 10, 20, 50, and 100 abrasion disc rotations. It is observed that the mean R_z roughness on the non-boiled surface is between 0.411 μm to 0.880 μm . During increased rotations, the R_z results in an average measured non-boiled surface roughness of 0.675 μm from 0 to 100 abrader disc rotations. The coefficient of determination (R^2) for R_z is 0.5641, which means that the probability to determine the intermediate surface roughness is 56%. The intermediate roughness predicts that the rougher the surface is, the larger the material area is covered. The upper and lower limit between each mean measurements shows that the roughness lies within the range considered by the confidence interval. Thus, the expected roughness results in 56% of the actual mean roughness fitted to it.

3. Boiled PA6 with R_a , μm

The averaged surface roughness R_a to different abrasion disc rotations for the boiled surface is presented in Fig. 18. The scatter chart examines the correlation relationship and the linear propagation with two different variables.

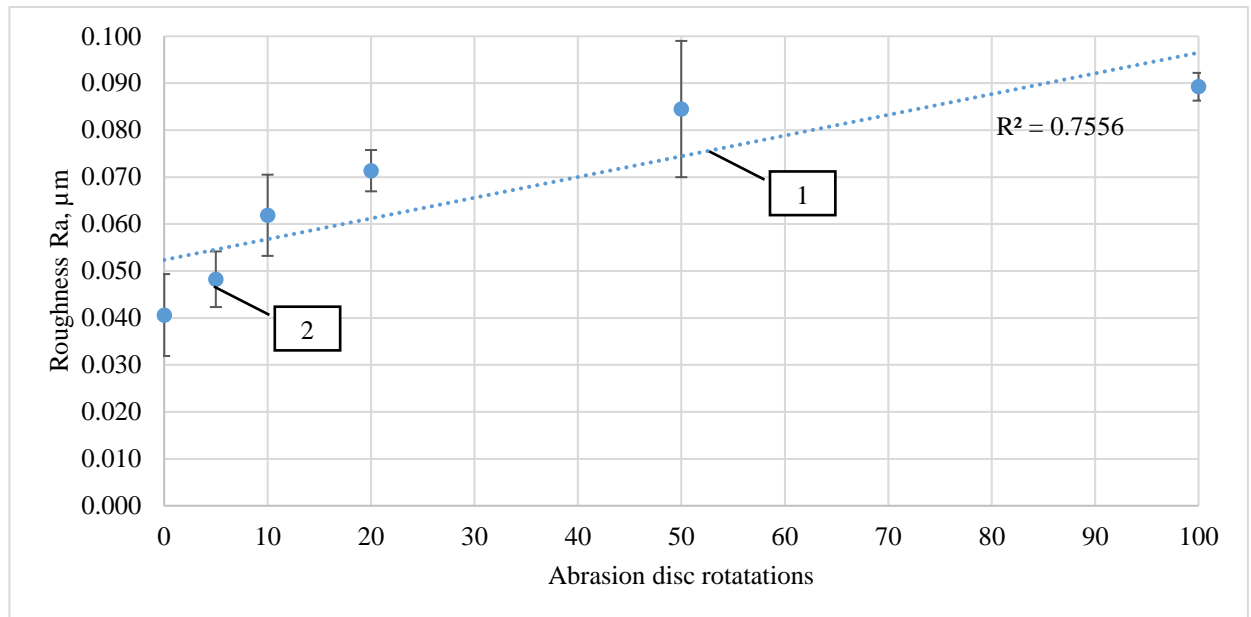


Fig. 18. Dependency of the abrasion disc rotations to surface roughness (R_a , μm) on boiled PA6: 1- linear regression with the coefficient of determination; 2- confidence interval

From the chart, the mean roughness of R_a on both sides of the boiled surface for different rotations is presented as the actual value. The tendency results of R_a are linear because the roughness on each surface increases for 0, 5, 10, 20, 50, and 100 abrasion disc rotations. It is observed that the mean R_a roughness on the boiled surface is between $0.041 \mu\text{m}$ to $0.089 \mu\text{m}$. During increased rotations, the R_a results in an average measured boiled surface roughness of $0.066 \mu\text{m}$ from 0 to 100 abrader disc rotations. The coefficient of determination (R^2) for R_a is 0.7556, which means that the probability to determine the intermediate surface roughness is 75%. The intermediate roughness predicts that the rougher the surface is, the larger the material area is covered. The upper and lower limit between each mean measurements shows that the roughness lies within the range considered by the confidence interval. Thus, the expected roughness results in 75% of the actual mean roughness fitted to it.

4. Boiled PA6 with R_z , μm

The averaged surface roughness R_z to different abrasion disc rotations for the boiled surface is presented in Fig. 19. The scatter chart examines the correlation relationship and the linear propagation with two different variables.

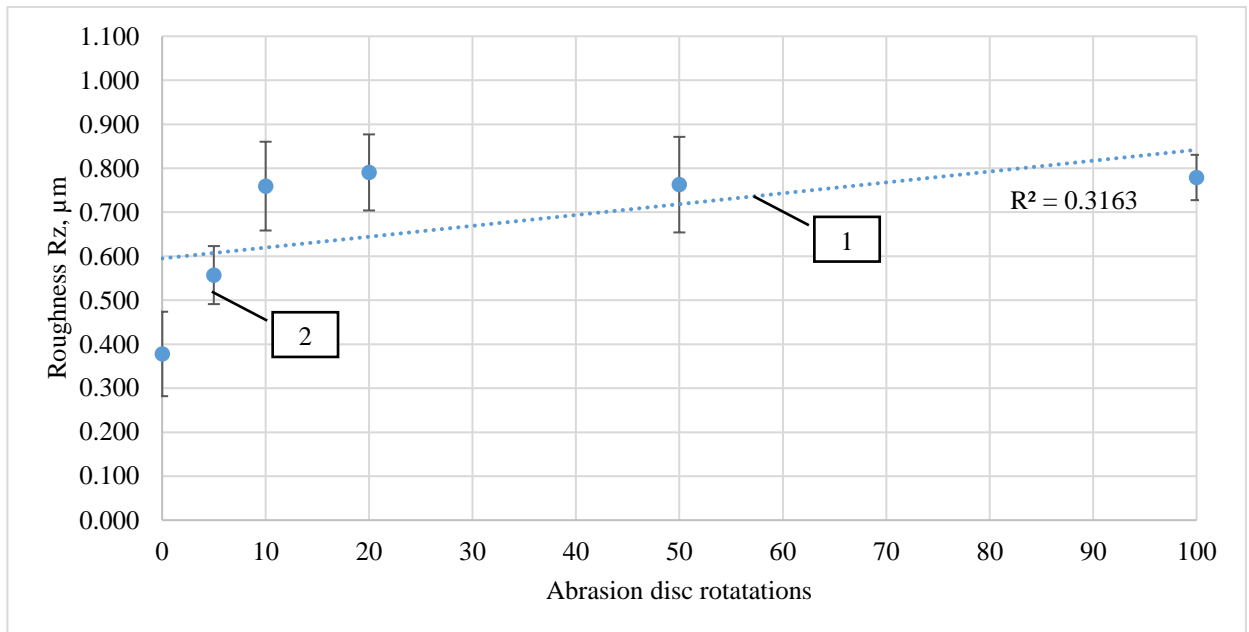


Fig. 19. Dependency of the abrasion disc rotations to surface roughness (R_z , μm) on boiled PA6: 1- linear regression with the coefficient of determination; 2- confidence interval

From the chart, the mean roughness of R_z on both sides of the boiled surface for different rotations is presented as the actual value. The tendency results of R_z are linear because the roughness on each surface increases for 0, 5, 10, 20, 50, and 100 abrasion disc rotations. It is observed that the mean R_z roughness on the boiled surface is between $0.378 \mu\text{m}$ to $0.779 \mu\text{m}$. During increased rotations, the R_z results in an average measured boiled surface roughness of $0.671 \mu\text{m}$ from 0 to 100 abrader disc rotations. The coefficient of determination (R^2) for R_z is 0.3163, which means that the probability to determine the intermediate surface roughness is 31%. The intermediate roughness predicts that the rougher the surface is, the larger the material area is covered. The upper and lower limit between each mean measurements shows that the roughness lies within the range considered by the confidence interval. Thus, the expected roughness results in 31% of the actual mean roughness fitted to it.

3.2. Abraded surface contact angle

1. Non-boiled PA6 with water wetting

The contact angle droplet view in Fig. 20 shows the low and high non-boiled surface wetting with water.

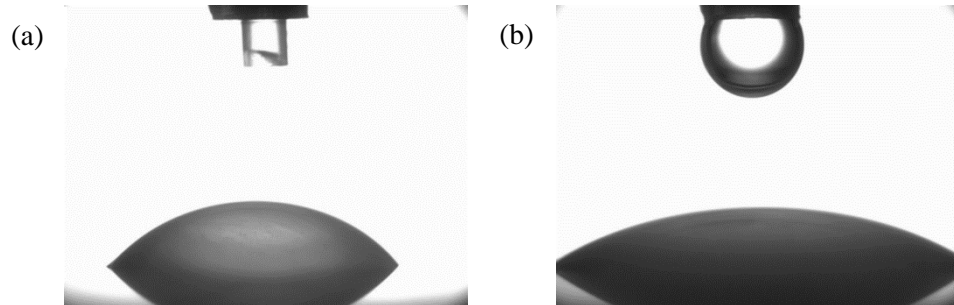


Fig. 20. Abraded non-boiled surface wetting with water: (a) low wetting for 0 rotation; (b) high wetting for 100 rotations

The averaged water wetting angle to different abrasion disc rotations for the non-boiled surface is presented in Fig. 21.

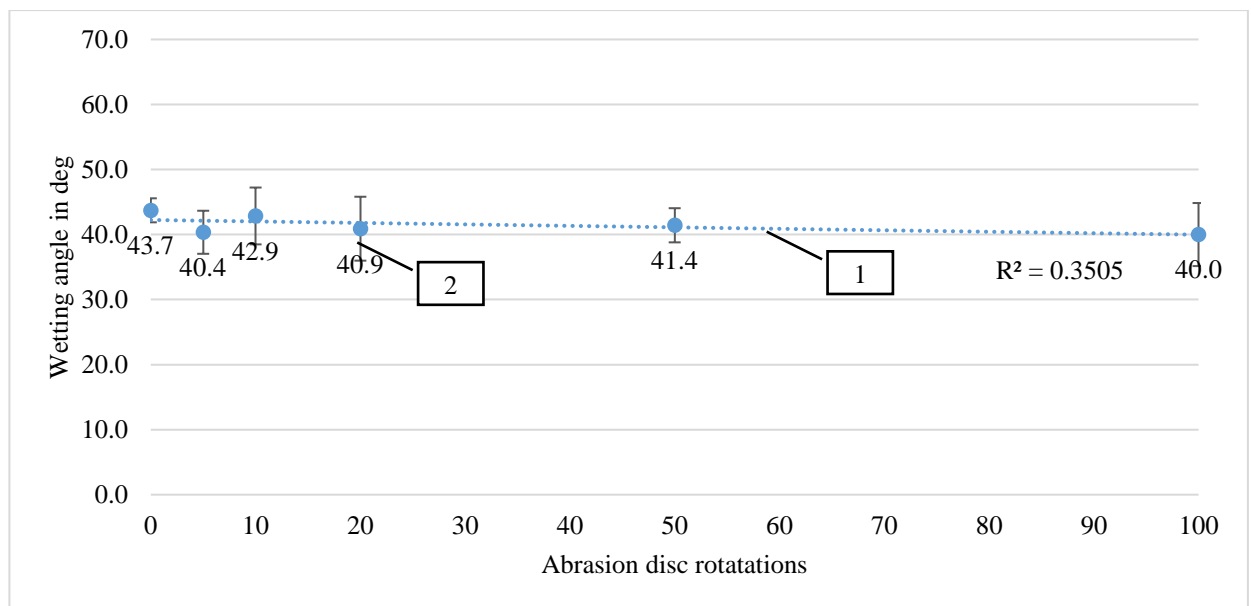


Fig. 21. Dependency of the abrasion disc rotations to water wetting angle on non-boiled PA6. 1- linear regression with the coefficient of determination; 2- confidence interval

From the scatter chart, the mean wetting angle on both sides of the non-boiled surface for different rotations is presented as the actual value. The obtained results of the water wetting angle are linear and decreases for 0, 5, 10, 20, 50, and 100 abrasion disc rotations. It is observed that the mean water wetting angle on the non-boiled surface is from 43.7° to 40° . During increased rotations, the non-boiled surface results in an average measured wetting of 41.5° from 0 to 100 abrader disc rotations. The coefficient of determination (R^2) for water is 0.3505, which means that the probability to determine the intermediate non-boiled surface wetting is 35%.

2. Non-boiled PA6 with ethylene glycol wetting

The contact angle droplet view in Fig. 22 shows the low and high non-boiled surface wetting with ethylene glycol.

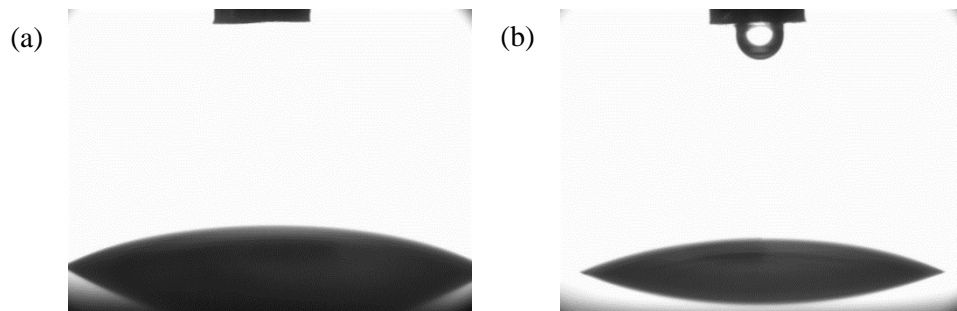


Fig. 22. Abraded non-boiled surface wetting with ethylene glycol: (a) high wetting for 0 rotation; (b) low wetting for 10 rotations

The averaged ethylene glycol wetting angle to different abrasion disc rotations for the non-boiled surface is presented in Fig. 23.

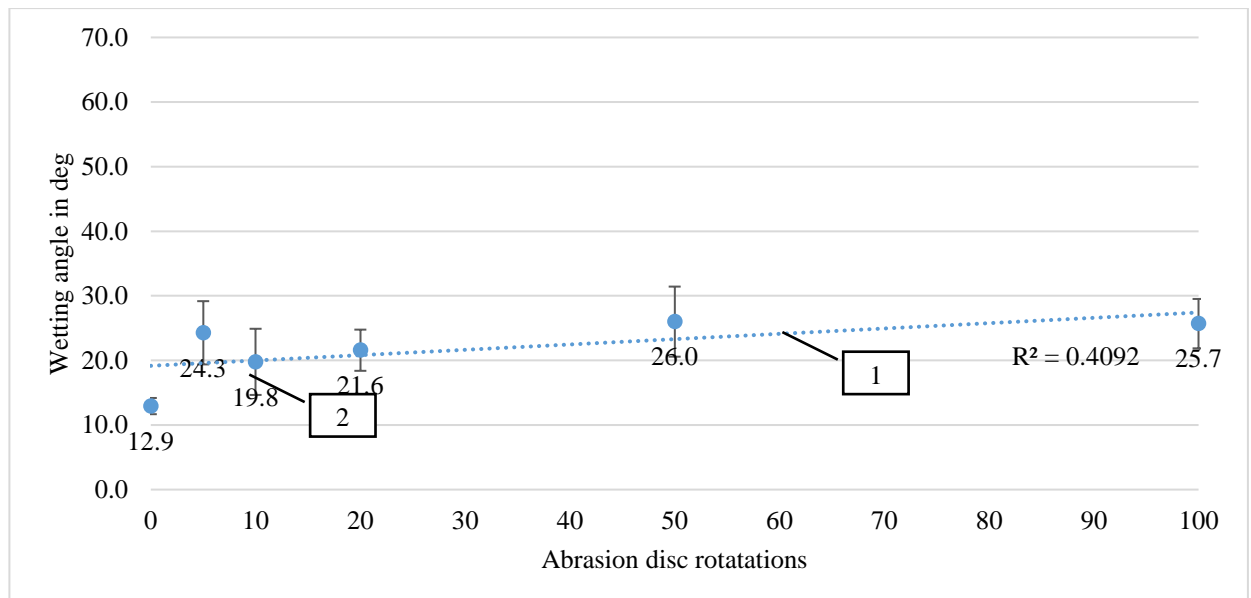


Fig. 23. Dependency of the abrasion disc rotations to ethylene glycol wetting angle on non-boiled PA6. 1- linear regression with the coefficient of determination; 2- confidence interval

From the scatter chart, the mean wetting angle on both sides of the non-boiled surface for different rotations is presented as the actual value. The obtained results of the ethylene glycol wetting angle are linear and increase for 0, 5, 10, 20, 50, and 100 abrasion disc rotations. It is observed that the ethylene glycol wetting angle on the non-boiled surface is from 12.9° to 26° . During increased rotations, the non-boiled surface results in an average measured wetting of 21.7° from 0 to 100 abrader disc rotations. The coefficient of determination (R^2) for ethylene glycol is 0.4092, which means that the probability to determine the intermediate non-boiled surface wetting is 40%.

3. Boiled PA6 with water wetting

The contact angle droplet view in Fig. 24 shows the low and high boiled surface wetting with water.

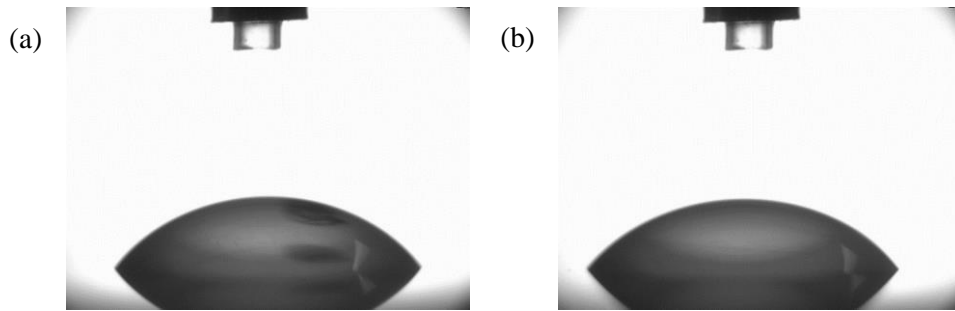


Fig. 24. Abraded boiled surface wetting with water: (a) low wetting for 20 rotations; (b) high wetting for 50 rotations

The averaged water wetting angle to different abrasion disc rotations for the boiled surface is presented in Fig. 25.

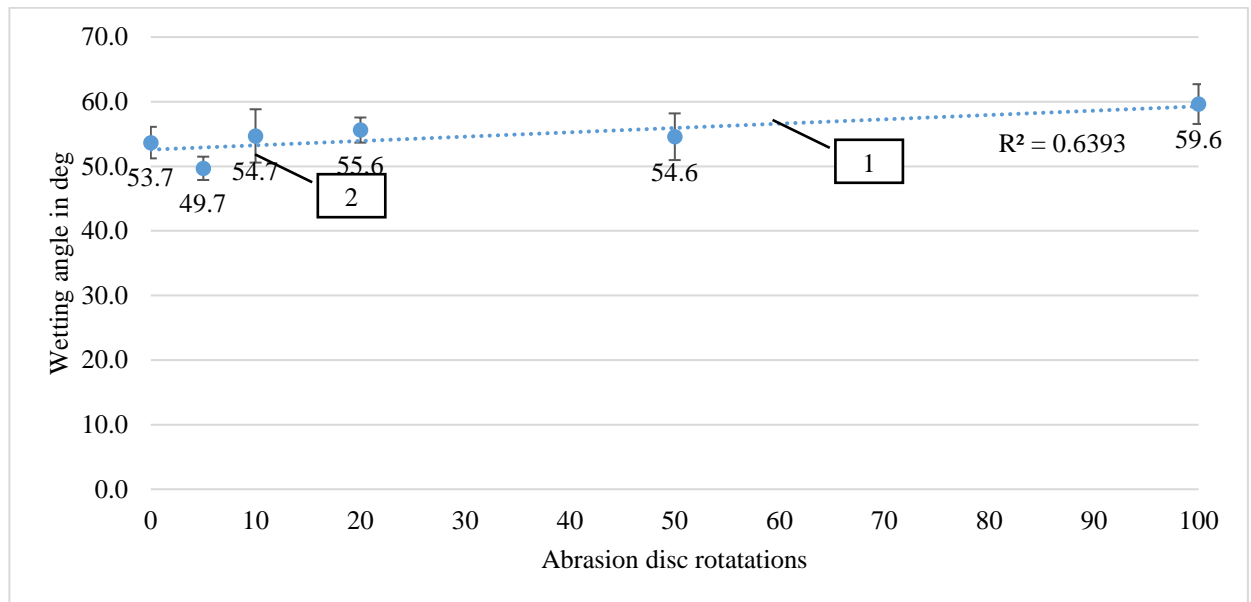


Fig. 25. Dependency of the abrasion disc rotations to water wetting angle on boiled PA6. 1- linear regression with the coefficient of determination; 2- confidence interval

From the scatter chart, the mean wetting angle on both sides of the boiled surface for different rotations is presented as the actual value. The obtained results of the water wetting angle are linear and increase for 0, 5, 10, 20, 50, and 100 abrasion disc rotations. It is observed that the mean water wetting angle on the boiled surface is from 49.7° to 59.6°. During increased rotations, the boiled surface results in an average measured wetting of 54.6° from 0 to 100 abrader disc rotations. The coefficient of determination (R^2) for water is 0.6393, which means that the probability to determine the intermediate boiled surface wetting is 63%.

4. Boiled PA6 with ethylene glycol wetting

The contact angle droplet view in Fig. 26 shows the low and high boiled surface wetting with ethylene glycol.

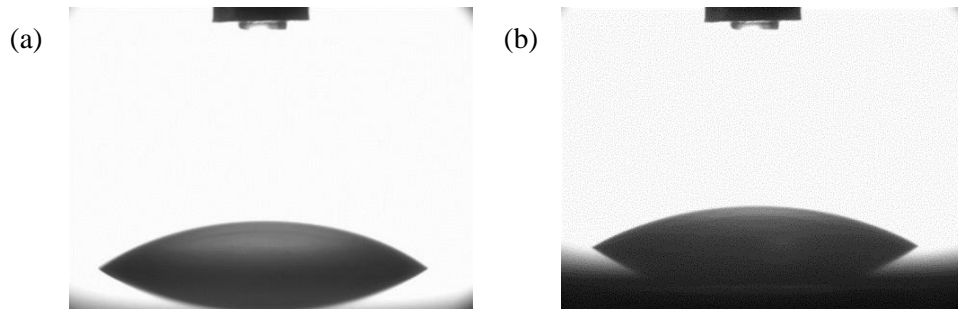


Fig. 26. Abraded boiled surface wetting with ethylene glycol: (a) low wetting for 20 rotations; (b) high wetting for 50 rotations

The averaged ethylene glycol wetting angle to different abrasion disc rotations for the boiled surface is presented in Fig. 27.

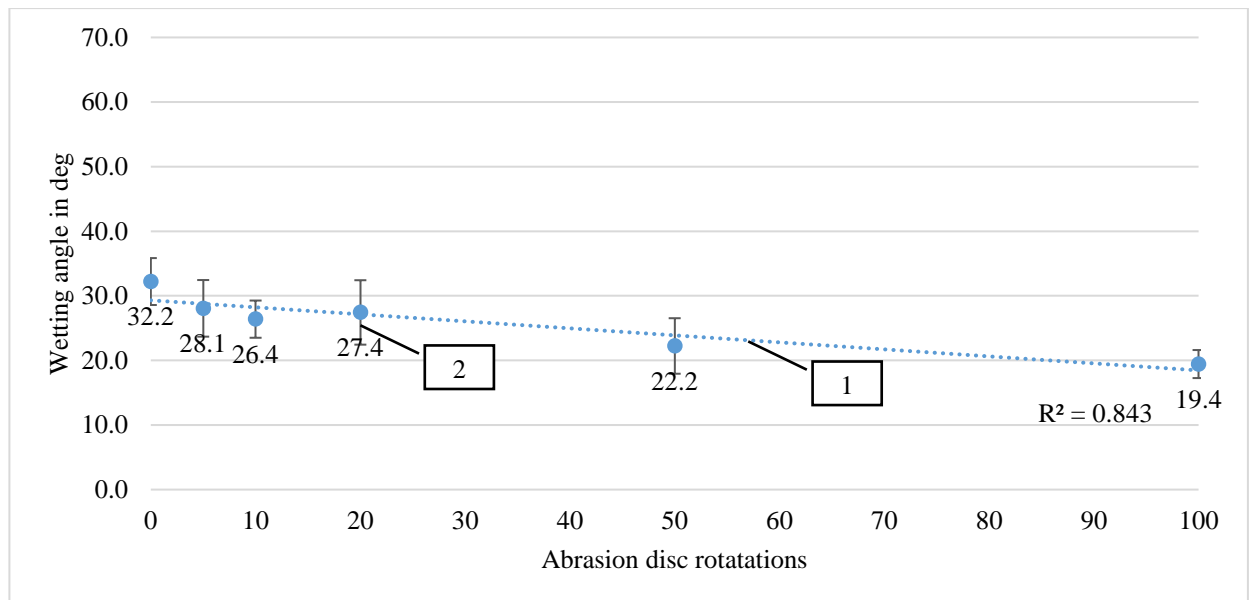


Fig. 27. Dependency of the abrasion disc rotations to ethylene glycol wetting angle on boiled PA6. 1- linear regression with the coefficient of determination; 2- confidence interval

From the scatter chart, the mean wetting angle on both sides of the boiled surface for different rotations is presented as the actual value. The obtained results of the ethylene glycol wetting angle are linear and decrease for 0, 5, 10, 20, 50, and 100 abrasion disc rotations. It is observed that the mean ethylene glycol wetting angle on the boiled surface is from 32.2° to 19.4° . During increased rotations, the boiled surface results in an average measured wetting of 26° from 0 to 100 abrader disc rotations. The coefficient of determination (R^2) for ethylene glycol is 0.843, which means that the probability to determine the intermediate boiled surface wetting is 84%.

3.3. Plasma treatment contact angle

1. Boiled and non-boiled PA6 with water wetting

The contact angle droplet view in Fig. 28 shows the low and high boiled and non-boiled plasma surface wetting with water.

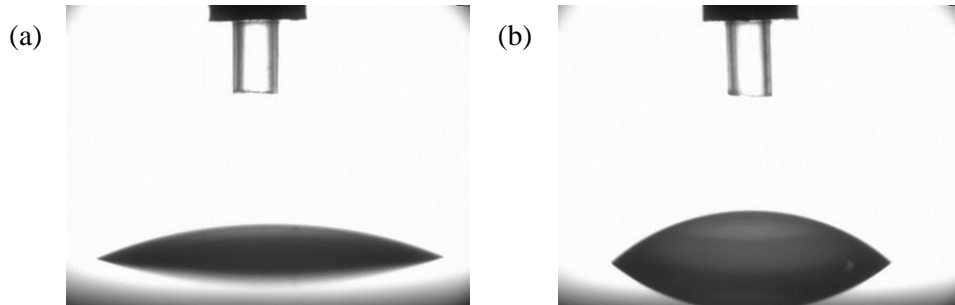


Fig. 28. Plasma surface wetting with water: (a) high wetting on boiled surface; (b) low wetting on non-boiled surface

The influence of plasma treatment on the boiled and non-boiled surface to water wetting angle is presented in Fig. 29.

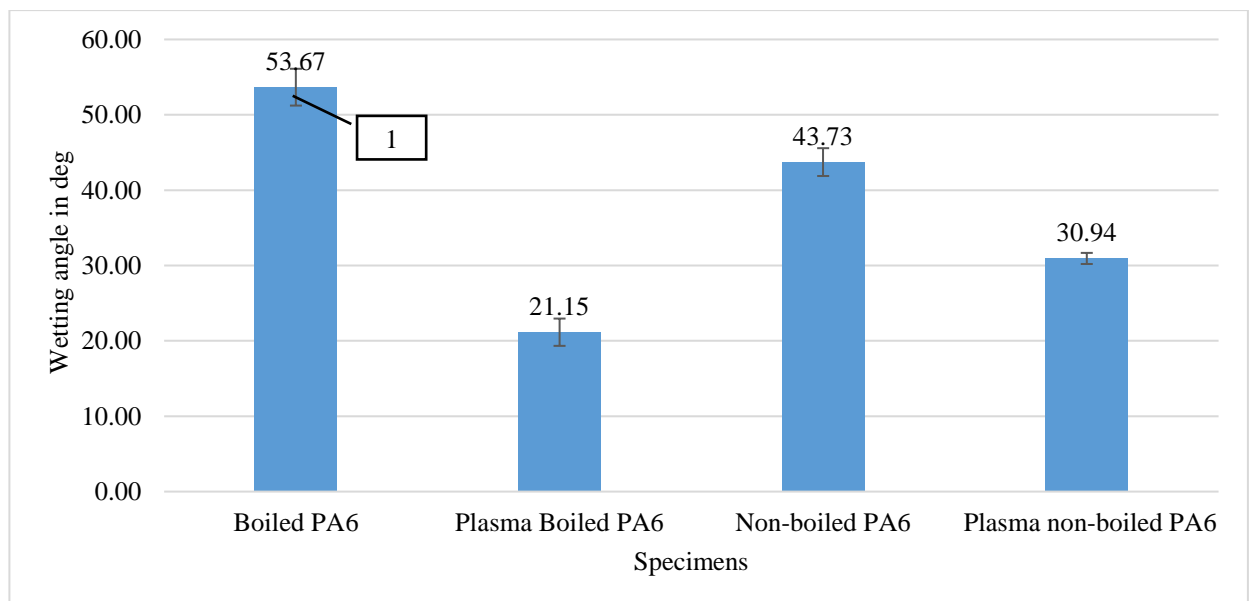


Fig. 29. Influence of PA6 surface plasma treatment to water wetting angle: *1*- confidence interval

The bar graph is utilized to show the comparison of water wetting influence on plasma-treated specimens. The observed results show that the averaged plasma boiled and non-boiled surface wetting with water is 21.15° and 30.94° . The water surface wetting of the boiled PA6 affected a decreasing difference of 30.41% with plasma boiled PA6 surface and the not boiled PA6 affected a decreasing difference of 70.76% with plasma non-boiled PA6 surface. For plasma boiled surface it had an increasing difference of 31.64% with the plasma non-boiled surface. Thus with water, the plasma boiled surface has better wetting compared to other specimens.

2. Boiled and non-boiled PA6 with ethylene glycol wetting

The contact angle droplet view in Fig. 30 shows the low and high boiled and non-boiled plasma surface wetting with ethylene glycol.

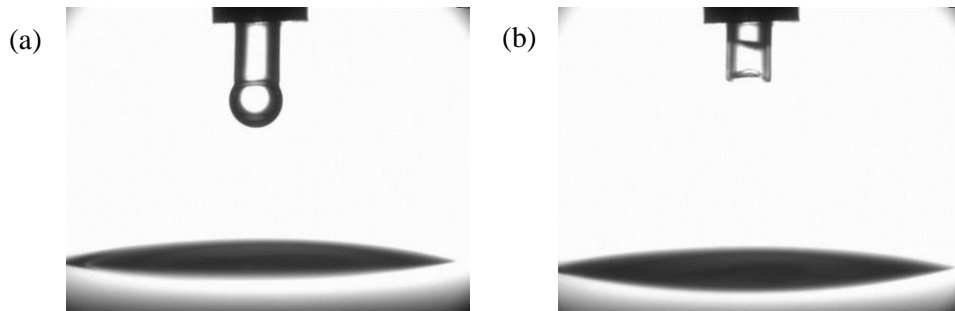


Fig. 30. Plasma surface wetting with ethylene glycol: (a) low wetting on boiled surface; (b) high wetting on non-boiled surface

The influence of plasma treatment on the boiled and non-boiled surface to ethylene glycol wetting angle is presented in Fig. 31.

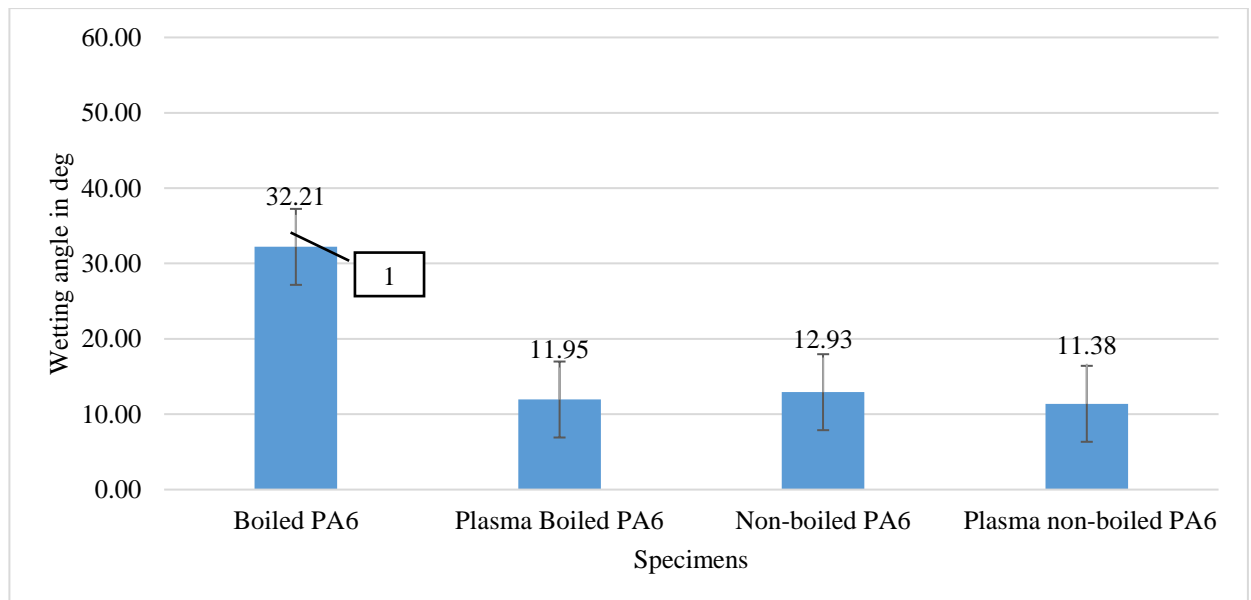


Fig. 31. Influence of PA6 surface plasma treatment to ethylene glycol wetting angle: 1- confidence interval

The bar graph is utilized to show the comparison of ethylene glycol wetting influence on plasma-treated specimens. The observed results show that the averaged plasma boiled and non-boiled surface wetting with ethylene glycol is 11.95° and 11.38° . The surface wetting of the boiled PA6 affected a decreasing difference of 37.10% with plasma boiled surface and the non-boiled PA6 affected a decreasing difference of 88.05% with plasma non-boiled surface. For plasma non-boiled surface it had an increasing difference of 4.77% with the plasma boiled PA6 surface. Thus with ethylene glycol, the plasma non-boiled surface has better wetting compared to other specimens.

3.4. Chemical treatment contact angle

1. Boiled and non-boiled PA6 with water wetting

The contact angle droplet view in Fig. 32 shows the low and high boiled and non-boiled chemical surface wetting with water.

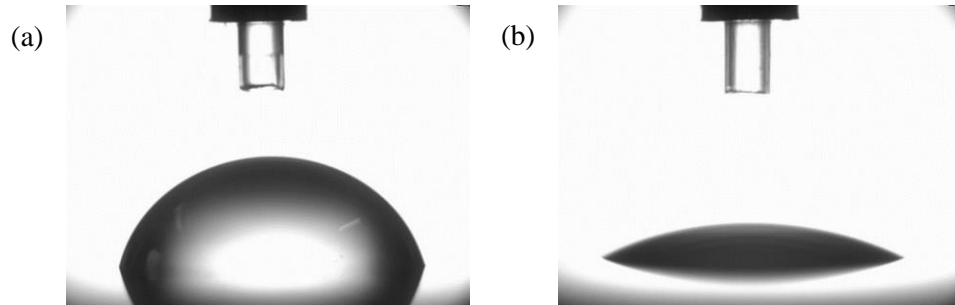


Fig. 32. Chemical surface wetting with water; (a) low wetting on 0.5M HCl of non-boiled PA6; (b) high wetting on 3M KOH of boiled PA6.

The influence of chemical treatment on the boiled and non-boiled surface to water wetting angle is presented in Fig. 33.

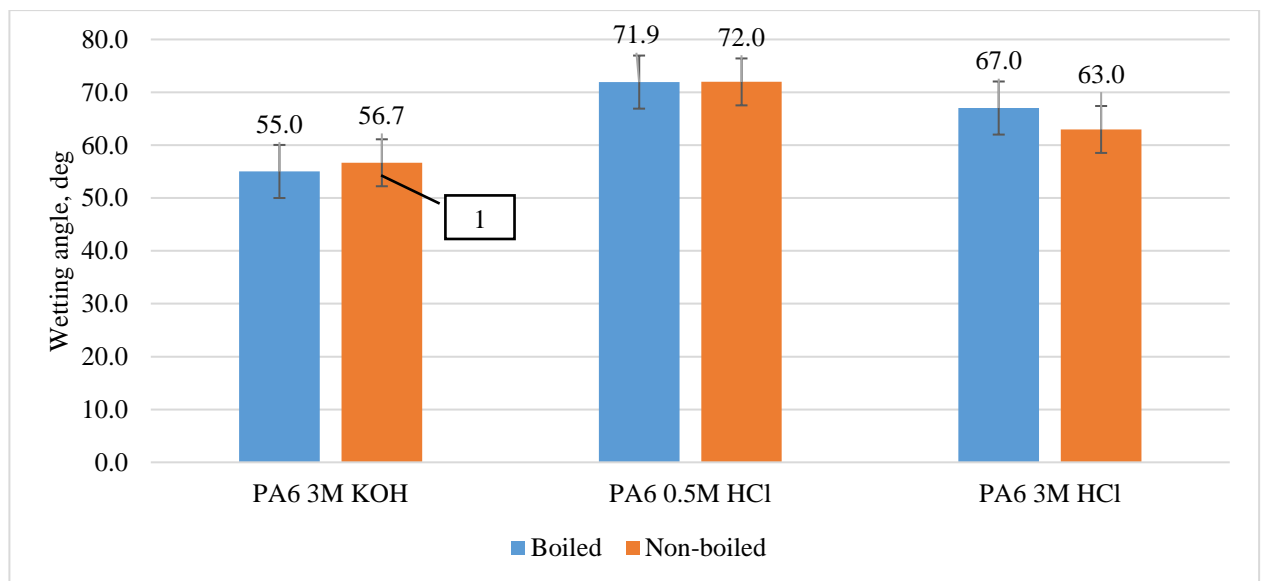


Fig. 33. Influence of PA6 surface chemical treatment to water wetting angle: 1- confidence interval

The bar graph is utilized to show the comparison of water wetting influence on the types of chemicals treated for the boiled and non-boiled surface. The observed results show that the averaged water wetting angle for 3M KOH, 0.5M HCl, 3M HCl treated on the boiled surface is 55°, 71.9°, 67°. Similarly, for 3M KOH, 0.5M HCl, 3M HCl treated on the non-boiled surface is 56.7°, 72°, 63°. For the types of chemicals used, the non-boiled surface has a lesser decreasing difference for 3M KOH, 0.5M HCl, and increasing difference for 3M HCl compared to the boiled surface. The non-boiled surface wetting of 3M KOH and 0.5M HCl is decreased by a lesser difference of 3% and 0.14%. Thus with water, 3M KOH treated on the boiled surface has better wetting compared to other chemicals.

2. Boiled and non-boiled PA6 with ethylene glycol wetting

The contact angle droplet view in Fig. 34 shows the low and high boiled and non-boiled chemical surface wetting with ethylene glycol.

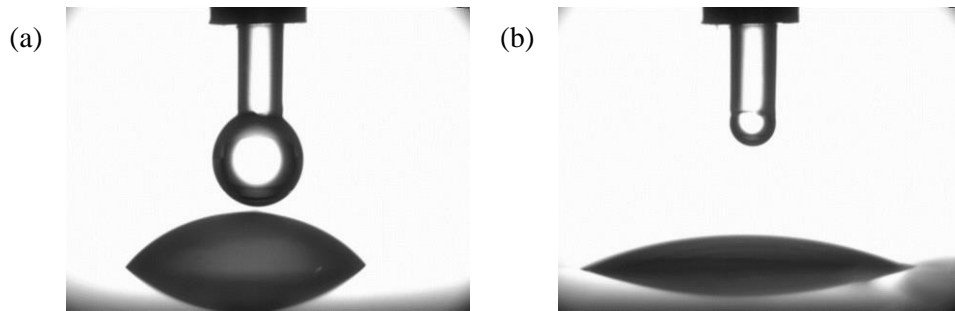


Fig. 34. Chemical surface wetting with ethylene glycol; (a) low wetting on 0.5M HCl of boiled PA6; (b) high wetting on 3M HCl of non-boiled PA6.

The influence of chemical treatment on the boiled and non-boiled surface to ethylene glycol wetting angle is presented in Fig. 35.

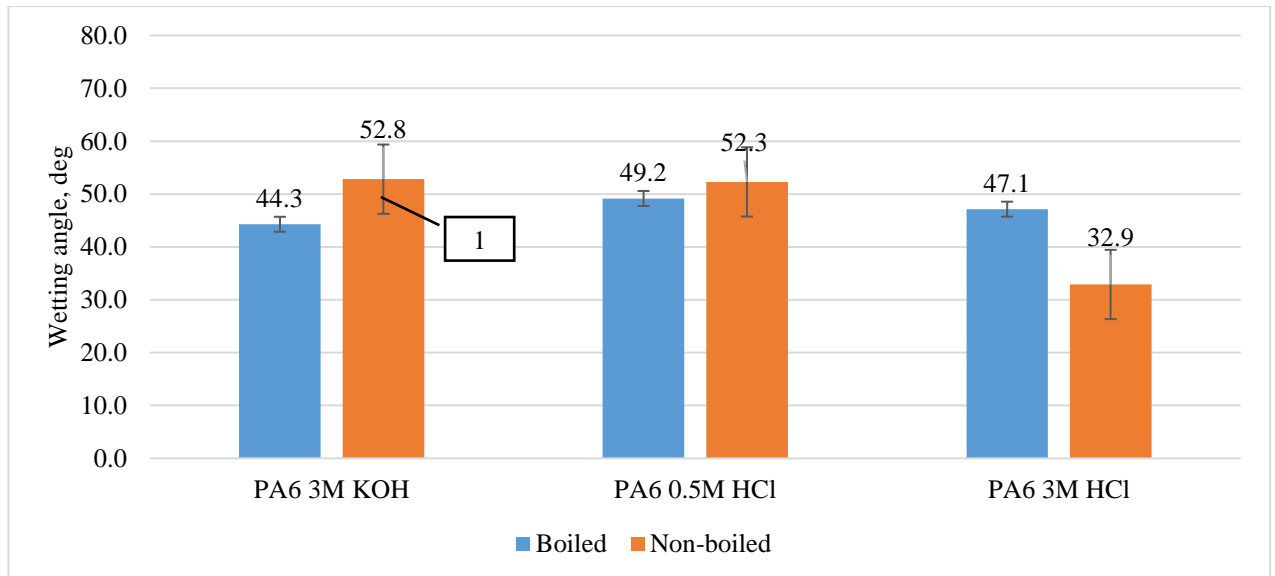


Fig. 35. Influence of PA6 surface chemical treatment to ethylene glycol wetting angle: 1- confidence interval

The bar graph is utilized to show the comparison of ethylene glycol wetting influence on the types of chemicals used for boiled and non-boiled surface. The observed results show that the averaged ethylene glycol wetting angle for 3M KOH, 0.5M HCl, 3M HCl treated on the boiled surface is 44.3°, 49.2°, 47.1°. Similarly, for 3M KOH, 0.5M HCl, 3M HCl treated on the non-boiled surface is 52.8°, 52.3°, 32.9°. For the types of chemicals used, the non-boiled surface has a decreasing difference for 3M KOH, 0.5M HCl, and an increasing difference for 3M HCl compared to the boiled surface. The non-boiled surface wetting of 3M KOH and 0.5M HCl is decreased by a difference of 16.10% and 5.93%. Thus with ethylene glycol, 3M HCl treated on the non-boiled surface has better wetting compared to other chemicals.

4. Managerial aspects

The polymer industry has grown rapidly in the past few decades with more than 360 million tonnes of plastics being produced and manufactured across the globe. Polymers have been widely used and favored because they are strong, elastic, and extremely durable. Such polymers include thermosets like epoxy resins, silicone, polyurethane, elastomers, and thermoplastics like polyamides (PA), polyethylene (PE), polyvinyl-chloride (PVC), etc. They can be shaped and reshaped when treated with additional physical and chemical changes. So far, the industry has revolutionized our lives through daily usage and indirect consumption owing to the significant environmental impacts and economic changes. Plastics in any form is causing a detrimental impact on a global scale and has given rise to countermeasures and the practice of safer choices.

4.1. Environmental limitations of Polyamide PA6

Among various polymers, polyamides are one of the predominantly used materials. Since the invention, polyamides are being extensively used and have contributed to monetarily more viable options than in the past. Coal and petroleum are subjected to a high pressure heated environment where a chemical reaction occurs forming large sheets of polyamides. With the constant need for production of polyamides, there is also continuous depletion of natural resources, coal, and petroleum. The production process creates nitrous oxide (N_2O) a greenhouse gas that is 300 times more powerful than carbon dioxide (CO_2). This means that the atmosphere will retain 300 times more heat due to the presence of CO_2 more than N_2O and results in global warming. While producing a polyamide, there is a considerable amount of water used for cooling purposes due to which contaminated and chemically polluted water is discharged. Polyamide material has high durability and it is a cheaper option, so as much as it is in demand the products made with this material should be disposed of as well. Due to the strong interchain interactions caused by the hydrogen bonds in a polyamide, it is resistant to degradation and has a low decay rate. According to a retail sustainability website “good on you“, a moderate nylon fabric takes approximately 30 to 40 years to decompose. In most instances, after a certain period of the garbage in landfills will get buried deeper into the earth’s soil which becomes the part of water bodies that result in environmental degradation and animals eating them.

It is important for us as humans as well to understand the toxicity that materials like Polyamide PA6 are causing in our habitat. Implementing circular economy models to ensure the inclusivity of end products in a second-life stage as resources to create more new products. For example, the World Society for the Protection of Animals published that, more than 600,000 tons of fishing gear is dumped into oceans every year and this includes nylon fishing nets. These nets are usually dumped into the ocean because fishers find this to be a better alternative than paying someone else to discard them. Since nylon is non-biodegradable and cannot be decomposed, it settles on the bed or deep in the ocean and becomes part of the food chain when ocean animals consume them. There is a loss in ocean life along with harmful effects for secondary and tertiary consumers. Bureo, a Los Angeles based company, initiated a campaign to pay fishers in Chile for the nets that will be thrown away and recycle them into skateboards and sunglasses. The world is gradually starting to be more aware to inculcate sustainable choices in their daily lives. The sports brand Speedo launched more than 50 products made of recycled nylon threads called econyl. Choices, like avoiding single-use plastic products and to use cloth bags instead of plastic bags, will go a long way. We must implement fundamental changes at the point of production rather than after consumption.

There have been recent efficient approaches to chemically decompose the PA6 polyamide through glycolysis and amino glycolysis processes. As the purpose of the recycling process is to recover monomers and reuse them, this could be an effective way to reduce the amount of waste. Both the process require a decomposing agent, catalyst, and no use of elevated pressure. This method can be used for polyamides, polyurethanes, and polyesters. The decomposing agent (ethylene glycol for glycolysis process and a mixture of ethylene glycol with triethylenetetramine for amino glycolysis process) will help in the depolymerization of Polyamide PA6 to help obtain caprolactam and hexamethylenediamine which have standard graded properties (commercial reagents). However, these experimental procedures don't have concrete proven statistics yet.

4.2. Economical views of Polyamide PA6

The contribution of Polyamide PA6 towards production and consumption shares a foremost expanding demand compared to other polyamides. PA6 and PA66 are two types of polyamides used across a wide range of industries and majorly by the end market users. They are used in the automotive industry due to their temperature and chemical resistance, for electrical and electronics applications, in industrial goods due to their mechanical resistance and moldability, in food packaging, and sports products. Polypropylene is a material that is less receptive to impact and scratches, instead, polyamides like PA6 and PA66 that are resistant to dirt and aging can be used in the manufacture of furniture goods as well. Since PA6 and PA66 have more adaptable and practical characteristics, they are the most commonly consumed amongst all types of polyamides. The increased price of raw materials used to produce PA66 made a massive shortage, thus increasing the demand for PA6 globally. Geographically, the rapid development of the PA6 market is still been controlled by the Asia Pacific region due to the rising of many industrial fields. The cost-effectiveness of PA6 has been a remarkable growth in the market for production. The majority of growth in production was due to the rising demand in the PA6 resin sector.

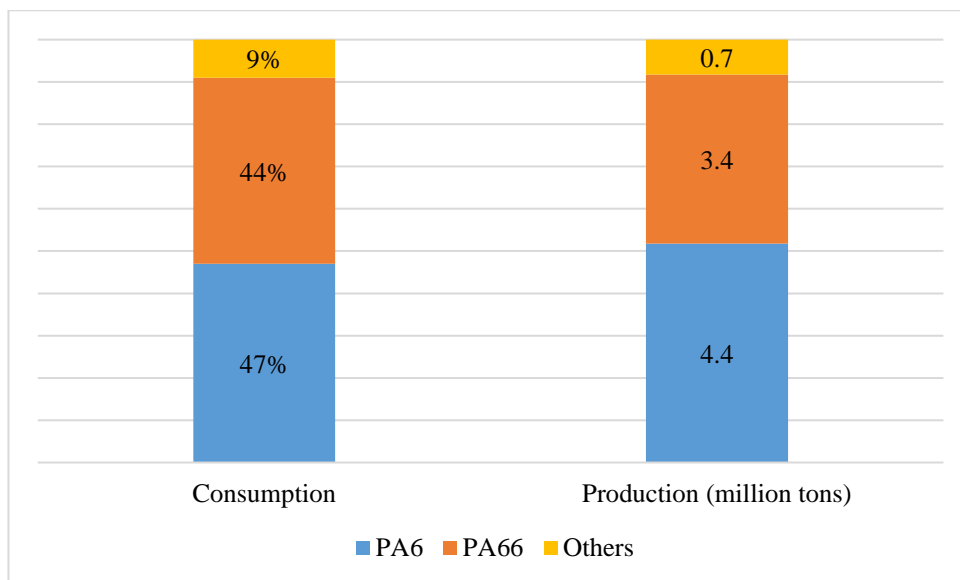


Fig. 36. Global consumption and production of polyamides

As of 2016, the collective global consumption of the two materials is 91 percent, as shown in Fig. 36. Since the other polyamides constitute only 9 percent, they are produced in less quantity. Polyamide PA6 is marginally produced and manufactured more than Polyamide PA66 due to two main factors; PA6 is highly versatile to dye and the chemical structure enables for a lustrous finish so it is

marginally produced and manufactured more than PA66 at 47 and 44 percent respectively. The second factor is, though both polyamides have their specific applications, PA6 is comparatively cost-efficient than PA66. Also, the global production of PA6 generated upto 4.4 million tons for a year is increased by 6.38% compared with PA66.

Globally, the estimated value of the Polyamide PA6 market was at US\$ 25.14 billion. The increasing trademark was because of different applications strengthening the consistent benefits in pricing and performance. Based on their applications, the PA6 market was raised by utilizing a variety of products in various industrial networks. The primary sector growth of rapid and improved technology from automobiles, electrical and electronics, films and coatings, and textile industries increases the global demand of the PA6 market. Compared to the industrial shares, automobile sectors own a huge market because of their increased consumption of PA6 in vehicle manufacturing. Fig. 37 presents the worldwide industry-wise application of PA6 material. A majority of the application, 33 percent is in the automobiles industry. Automobile goods should be able to withstand against and perform in extremely vacillating weather conditions, exposure to harsh chemicals, and higher temperatures. The most common applications are coolant pumps, engine cover components, heat shields, high voltage bushings, fuel line connectors, and headlight components. This also means that it can be used for similar heat resistant purposes to make electronic and general household appliances.

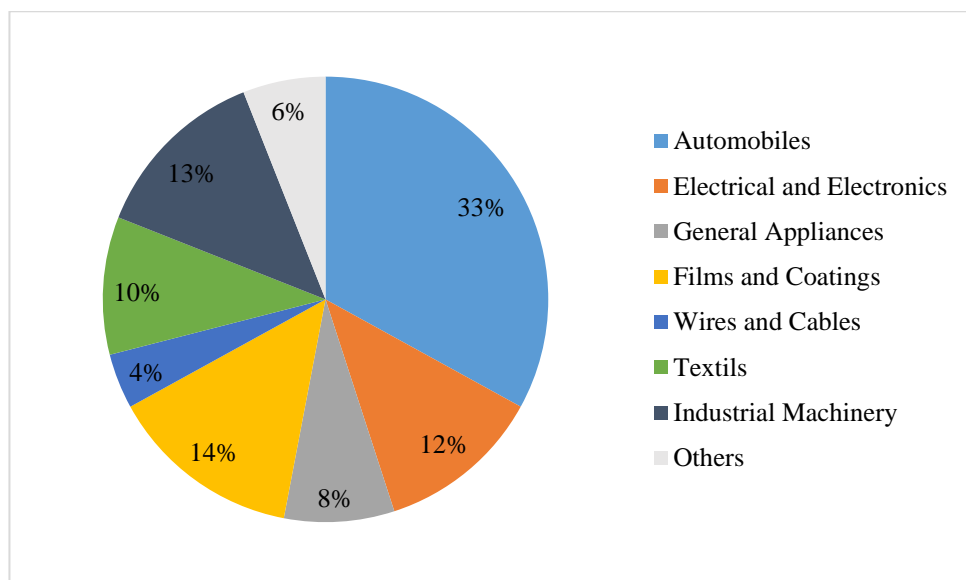


Fig. 37. Market shares of Polyamide PA6 utilized globally

The unique combination of properties makes it ideal for 14% of the total PA6 produced to be used in the films and coatings industry. The polymer is used to create thin coatings over solid edibles like pharmaceutical drugs, granules, and crystals. PA6 has heat sealing properties, low permeability values to oxygen, carbon dioxide, and nitrogen. So, it can form an adsorbate layer on the surface as a barrier against gas, moisture, and light. This ensures odor and taste masking, increases the shelf life of the tablets, improves product appearance and thereby allows for branding and trademarking of the product, increases the mechanical resistance, and improves ease of swallowing of the tablet. It also has a bi-axial structure along with high toughness which can be used for packaging purposes. The ability to use the material for multilateral reasons and versatility has opened the market for new and more innovative products. In the upcoming world of shares, the global market may also include the

field of growing research and development that have huge funding in their activities. Also, the market factors are driven by increasing demand in automobiles, electronics, and the coating industry.

The rising demand for long-lasting superior grades of PA6 satisfies the global need for the polymer market. The trade stability of PA6 polyamides turn down from 2012 to 2016 as the number of exports were less than the imports. Therefore the trade balance remains negative. This made a significant impact on the prices and trade between different countries. For instance, there was a shortage of imports from Asia to Europe and consequentially there has been an increase in demand for lightweight products in Europe. According to data published by the website “plastics insight“, two of the five biggest PA6 exporters and importers in the world are in Europe; Germany and Belgium showed in Fig. 38. The other countries are China, the USA, and Japan. Germany being the largest exporter of PA6 in the polyamide market values an export cost of US\$ 606.2 million. The later comes from China and the United States with an export value of US\$ 542.1 million and US\$ 496.8 million. Similarly, the import sector applies to the same segment from Germany being the largest importer of the PA6 market followed by China and the United States. Hence, the other major countries of exports and imports in the global market were Belgium and Japan.

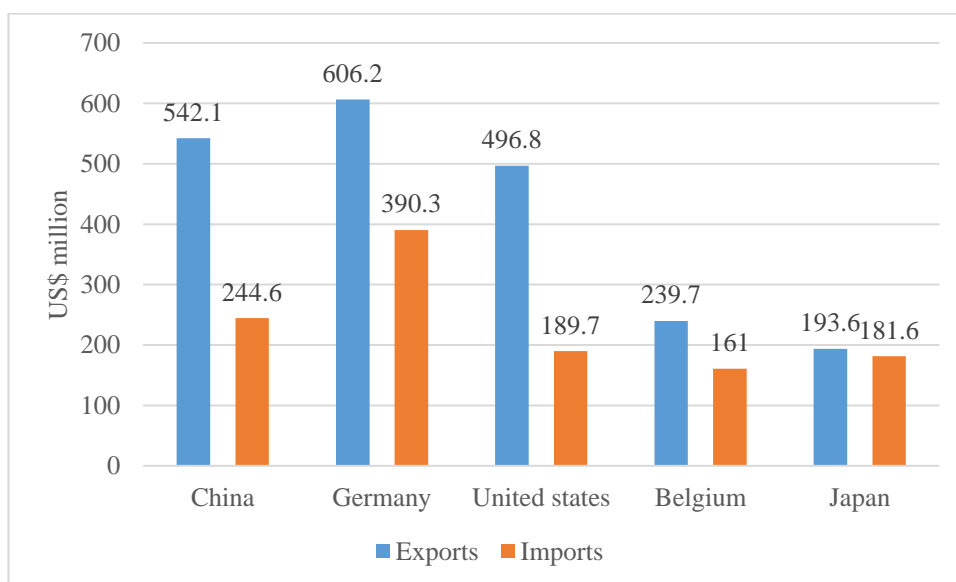


Fig. 38. Market trade comparison of polyamides

The global market is still controlled by Asia-Pacific, Europe, and North American regions by the usage of PA6 applications in major industries. So far, there has been a constant surge in the need for the Polyamide PA6 material and very few alternatives have been suggested. Since there are no drastic changes in the demand for the material, the consumption and production capacity can likely increase. If the chemical recycling process is successful and becomes a common practice, the caprolactam derived from this process will also be inclusive in the consumption and production numbers.

Conclusions

This research has provided a systematic methodology of surface improvement by conducting different experiments on the boiled and non-boiled Polyamide PA6 material. A minimum of six specimens was used for different treatment methods under atmospheric conditions. The adhesion behavior of water and ethylene glycol as wetting liquids was set to measure the wettability on the modified boiled and non-boiled surface. Based on the performed task, it was observed that;

1. The roughness R_a and R_z on the boiled and non-boiled surface for different Taber Abrader disc rotations was measured. The measured surface roughness R_a is from $0.034 \mu\text{m}$ to $0.089 \mu\text{m}$ and R_z is from $0.378 \mu\text{m}$ to $0.880 \mu\text{m}$. It was noticed that the roughness for R_a and R_z was increasing and parallel during increased abrader disc rotations. Therefore, no significant influence has been visually noticed as the roughness was raised.
2. The Taber Abrader disc rotations to boiled and non-boiled abraded surface wetting angle were measured. The ethylene glycol wetting angle was decreased from 32.2° to 19.4° for the boiled abraded surface and increased from 12.9° to 26° for the non-boiled abraded surface. The tendency with ethylene glycol wetting is linear and intersecting that showed a significant influence compared with water wetting. The tendency occurred because of the properties of ethylene glycol and the abraded surface.
3. The plasma-treated boiled and non-boiled surface to wetting angle was measured. For water and ethylene glycol wetting angle, the difference of the boiled surface with the plasma boiled surface has a wetting influence of 60.59% and 62.90%. Similarly, the non-boiled surface with the plasma non-boiled surface has a wetting influence of 29.24% and 11.95%. The plasma non-boiled surface with ethylene glycol showed better wetting because of the properties of ethylene glycol and the plasma-treated surface.
4. The chemical treatments of 3M KOH, 0.5M HCl, 3M HCl on the boiled and non-boiled surface wetting angle was measured. Different chemicals on the surface were used to measure the wettability influence of water and ethylene glycol. It was found that water had decreasing wetting influence compared with ethylene glycol for the concentration of chemicals used on the boiled and non-boiled surface. The ethylene glycol wetting influence of 32.9° after treatment with 3M HCl on the non-boiled surface is observed as the better wetting surface among the other chemically treated specimens.

List of references

1. R. Geyer, J. R. Jambeck, and K. L. Law, "Production, use, and fate of all plastics ever made," *Sci. Adv.*, 2017.
2. M. Chanda and S. K. Roy, *Plastics fabrication and recycling*. 2016.
3. E. Naveau *et al.*, "Effect of clay modification on the structure and mechanical properties of polyamide-6 nanocomposites," *Eur. Polym. J.*, 2011.
4. C. Silva, A. Cavaco-Paulo, and V. A. Nierstrasz, "Enzymatic hydrolysis and modification of core polymer fibres for textile and other applications," in *Advances in Textile Biotechnology*, 2010.
5. S. Begum, J. Wu, C. M. Takawira, and J. Wang, "Surface modification of polyamide 6,6 fabrics with an alkaline protease – Subtilisin," *J. Eng. Fiber. Fabr.*, 2016.
6. N. Mahmood, M. Islam, A. Hameed, and S. Saeed, "Polyamide 6/multiwalled carbon nanotubes nanocomposites with modified morphology and thermal properties," *Polymers (Basel)*., 2013.
7. P. Karami and A. Shojaei, "Improvement of dry sliding tribological properties of polyamide 6 using diamond nanoparticles," *Tribol. Int.*, 2017.
8. M. Asadollahi, D. Bastani, and S. A. Musavi, "Enhancement of surface properties and performance of reverse osmosis membranes after surface modification: A review," *Desalination*. 2017.
9. J. López-García, "Wettability Analysis and Water Absorption Studies of Plasma Activated Polymeric Materials," in *Non-Thermal Plasma Technology for Polymeric Materials*, 2019.
10. J. Schäfer, T. Hofmann, J. Holtmannspötter, M. Frauenhofer, J. Von Czarnecki, and H. J. Gudladt, "Atmospheric-pressure plasma treatment of polyamide 6 composites for bonding with polyurethane," *J. Adhes. Sci. Technol.*, 2015.
11. X. Bai, C. H. Xue, and S. T. Jia, "Surfaces with Sustainable Superhydrophobicity upon Mechanical Abrasion," *ACS Appl. Mater. Interfaces*, 2016.
12. B. V. Lingesh, B. N. Ravikumar, and B. M. Rudresh, "Mechanical and Sliding Wear Behavior of Polyamide 66 and Polypropylene (PA66/PP) Blends," 2016.
13. T. Irisawa, T. Takamura, S. Momozono, J. Kaneko, and M. Shioya, "Analysis on Abrasive Wear Rate of VGCF/Polyamide 6 Composite Fibers," *Tribol. Online*, 2011.
14. G. Zhao, I. Hussainova, M. Antonov, Q. Wang, and T. Wang, "Friction and wear of fiber reinforced polyimide composites," *Wear*, 2013.
15. C. Mandolino, E. Lertora, and C. Gambaro, "Influence of cold plasma treatment parameters on the mechanical properties of polyamide homogeneous bonded joints," *Surf. Coatings Technol.*, 2017.
16. R. Wolf and A. C. Sparavigna, "Role of Plasma Surface Treatments on Wetting and Adhesion," *Engineering*, 2010.
17. J. Hnilica, L. Potočňáková, M. Stupavská, and V. Kudrle, "Rapid surface treatment of polyamide 12 by microwave plasma jet," *Appl. Surf. Sci.*, 2014.
18. J. Kim, H. S. Kim, and C. H. Park, "Contribution of surface energy and roughness to the wettability of polyamide 6 and polypropylene film in the plasma-induced process," *Text. Res. J.*, 2016.
19. H. S. Salapare, T. Darmanin, and F. Guittard, "Reactive-ion etching of nylon fabric meshes using oxygen plasma for creating surface nanostructures," *Appl. Surf. Sci.*, 2015.
20. H. W. Ha, A. Choudhury, T. Kamal, D. H. Kim, and S. Y. Park, "Effect of chemical modification

- of graphene on mechanical, electrical, and thermal properties of polyimide/graphene nanocomposites,” *ACS Appl. Mater. Interfaces*, 2012.
21. M. Gilbert, “Aliphatic Polyamides,” in *Brydson’s Plastics Materials: Eighth Edition*, 2017.
 22. L. Gendre, J. Njuguna, H. Abhyankar, and V. Ermini, “Mechanical and impact performance of three-phase polyamide 6 nanocomposites,” *Mater. Des.*, 2015.
 23. Y. Zhang, R. Wang, S. Yi, L. Setiawan, X. Hu, and A. G. Fane, “Novel chemical surface modification to enhance hydrophobicity of polyamide-imide (PAI) hollow fiber membranes,” *J. Memb. Sci.*, 2011.
 24. S. Ebnesajjad, *Handbook of adhesives and surface preparation : technology, applications and manufacturing*. 2011.
 25. H. Wang, H. Shi, Y. Li, and Y. Wang, “The effects of leaf roughness, surface free energy and work of adhesion on leaf water drop adhesion,” *PLoS One*, 2014.
 26. H. Zhu, Z. Guo, and W. Liu, “Adhesion behaviors on superhydrophobic surfaces,” *Chem. Commun.*, 2014.
 27. F. Rupp *et al.*, “A review on the wettability of dental implant surfaces I: Theoretical and experimental aspects,” *Acta Biomaterialia*. 2014.
 28. J. B. Kim, J. K. Choi, I. W. Han, and I. Sohn, “High-temperature wettability and structure of the TiO₂–MnO–SiO₂–Al₂O₃ welding flux system,” *J. Non. Cryst. Solids*, 2016.
 29. K. L. Mittal, *Advances in contact angle, wettability and adhesion*. 2018.
 30. V. Takke, N. Behary, A. Perwuelz, and C. Campagne, “Surface and adhesion properties of poly(ethylene glycol) on polyester(polyethylene terephthalate) fabric surface: Effect of air-atmospheric plasma treatment,” *J. Appl. Polym. Sci.*, 2011.
 31. D. L. Williams and T. M. O’Byron, “Cleanliness Verification on Large Surfaces: Instilling Confidence in Contact Angle Techniques,” in *Developments in Surface Contamination and Cleaning*, 2013.
 32. A. Fathi-Azarbayjani, A. Jouyban, and S. Y. Chan, “Impact of surface tension in pharmaceutical sciences,” *Journal of Pharmacy and Pharmaceutical Sciences*. 2009.
 33. A. Kozbial *et al.*, “Study on the surface energy of graphene by contact angle measurements,” *Langmuir*, 2014.
 34. D. X. Li, X. Deng, J. Wang, J. Yang, and X. Li, “Mechanical and tribological properties of polyamide 6-polyurethane block copolymer reinforced with short glass fibers,” *Wear*, 2010.
 35. S. Korkut and M. Budakci, “The effects of high-temperature heat-treatment on physical properties and surface roughness of rowan (*Sorbus aucuparial.*) wood,” *Wood Res.*, 2010.
 36. A. B. Pop, M. A. Țițu, G. I. Pop, and S. Țițu, “Modeling the machined surface quality of an aluminum alloy using the active experiment type,” in *IOP Conference Series: Materials Science and Engineering*, 2019.
 37. K. Fricke *et al.*, “Atmospheric pressure plasma: A high-performance tool for the efficient removal of biofilms,” *PLoS One*, 2012.

Appendices

Appendix 1. Article for publishing in upcoming International Young Researchers Conference 2020.

KTU Faculty of Mechanical Engineering and Design May 14, 2020, Kaunas, Lithuania

The International Young Researchers Conference
“INDUSTRIAL ENGINEERING 2020”

Influence of Polyamide PA6 Surface Modification on Wettability Properties

Ram Pramod MONIKANTAN*, Vaidas BIVAINIS**,
Aistė KUNCIŪTĖ***

* Kaunas University of Technology, Faculty of Mechanical Engineering and Design,
Studentų g. 56, 51424 Kaunas, Lithuania, E-mail: ram.monikantan@ktu.edu

** Kaunas University of Technology, Department of Production Engineering,
Studentų g. 56, 51424 Kaunas, Lithuania, E-mail: vaidas.bivainis@ktu.lt

*** Kaunas University of Technology, Department of Physics and Inorganic
Chemistry, Radvilėnų pl. 19c, 50254 Kaunas, Lithuania, E-mail:
aiste.kunciute@ktu.edu

Introduction

Polyamide 6 (PA6) is widely used in industrial applications due to its advanced properties such as lightweight, elasticity, stiffness, and ability to form high-performance composites [1]. The scope of their properties is applicable for wettability, adhesive joining, sealing, and coating influences on the surface layer.

Due to the consumption of low energy and easy processing, modification of surface is greatly involved in the present field of surface science. The influence of wettability on a hard surface has been a foremost application in various studies and Young's law was used as the main regulation in different wetting procedures. The surface treatment determination to wetting liquids was observed to be compelling by the upgrade of mechanical and thermal properties [2, 3].

The aim of the present study is to investigate the effect of the surface modification of PA6 sheets on its wettability properties. Attention towards PA6 surface

modification was focused on finding a method to reduce contact angle between water or ethylene glycol and PA6 surface.

Materials and methods

The white 1 mm thickness transparent PA6 specimens; the size of 100 mm × 100 mm was utilized. The surface properties by mechanical and thermal modifications were used with density 1.09 - 1.10 g/cm³ [4], coefficient of thermal expansion 95 × 10⁻⁶ K⁻¹, and 24-hour water absorption stability of 0.4 - 0.6 %. Boiled (100 °C in distilled water for 120 min using the laboratory heating device) and non-boiled specimen under transparent and heat stabilized conditions were used in this investigation. For all the experimental investigations, the same side of PA6 sheets was used.

The material mechanical surface abrasion was performed using the Taber Abrader 5131 device, according to the ISO 5470-1: 2016 [5] Rubber - or plastics-coated fabrics - Determination of abrasion resistance - Part 1: Taber abrader, conditions. The specimen size for abrasion wearing test was 100 mm × 100 mm, for the fixing in the device the hole of 5 mm diameter in the square specimen center was cut out. The investigation was performed using boiled and not boiled PA6 sheets; the abrader rotations were: 5, 10, 20, 50, and 100 rotations (in the paper result part 0 abrasion disk rotations means the specimen without surface wearing). The selection of these rotations values was made by the visual differences of each set of those test rotations. A set of standard Taber CS-10 rubber abrading wheels of thickness 12 mm and the radius 23 mm was used to make vertically contact with the surface. The pressing of wheels was 250 g for each and the standard specimen 60 revs/min. rotating speed was used.

The surface roughness for different abraded rotations was measured by the Mitutoyo SJ-210 device. The R_a, μm, and R_z, were set as the roughness parameters. The points were randomly marked on each tailored 15 mm × 100 mm size sample surface and the drive unit moved vertically over the abraded surface. The dependency of the surface abrader disc rotations to the measured roughness parameters was presented as a graph.

The plasma treatment was set up by the JSC Kvarzt Plasma-600T device. The method involved the treatment of 100 mm × 100 mm boiled and not boiled PA6 surface for 60 seconds. Within 2 hours of the treatment, the contact angle measurements were executed. The influence of plasma treatment for the sample surface tension was presented.

Contact angle measurements of the modified surface were carried out by a pocket goniometer PG3 device connected to the computer. Measurements were performed under static conditions; for the modified surface wettability measurements distilled water and ethylene glycol were used. Table 1 shows the surface tension comparison of wetting liquids. The selection of ethylene glycol is related to the future experiments of PA6 coating with a semiconductor layer. Each modified specimen is

tailored to a size of 15 mm × 100 mm for contact angle measurements. The measured surface contact angle to the abrasion disc rotations and plasma treatments was presented as a graph. A minimum of six PA6 specimens was used for all experiments. Before conducting experiments, specimens were kept in an environmental conditions (23 ± 1 °C temperature and 50 ± 2 % relative humidity) for 48 hours.

Table 5

The surface tension of wetting liquids [6]

| Wetting liquid | Surface tension (mJ/m ²) |
|-----------------|--------------------------------------|
| Water | 72.8 |
| Ethylene glycol | 47.7 |

Results and discussion

Average values of surface roughness parameters (R_a and R_z) are presented in Fig. 1. Analysing the surface roughness results, It was not found any significant difference between boiled and not boiled specimens, accordingly that, in this chart was presented averaged the data of both specimens.

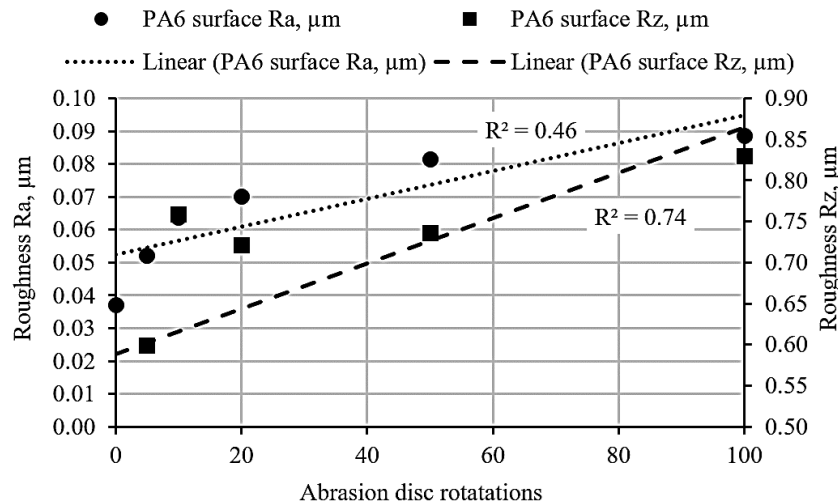


Fig. 1 Dependency of boiled and not boiled Polyamide PA6 abrasion disc rotations to surface roughness R_a , and R_z

The tendency results of R_a , and R_z , is close to linear and parallel because the roughness on each surface increases for 0, 5, 10, 20, 50, and 100 abrasion disc rotations. During increased rotations, the R_z is steeper compared to R_a , which results in an average

measured boiled and not boiled surface roughness difference of 0.61 % from 0 to 100 abrader rotations. The coefficient of determination for R_a and R_z is 0.46 and 0.74, which shows 46 % and 74 % probability to determine intermediate surface roughness values. Therefore, the results clearly show the possibility to achieve PA6 surface roughness R_a $0.037 \div 0.089 \mu\text{m}$ and R_z $0.395 \div 0.830 \mu\text{m}$.

Ethylene glycol contact angle to different abrasion disc rotations of boiled and not boiled PA6 sheets is presented in Fig. 2.

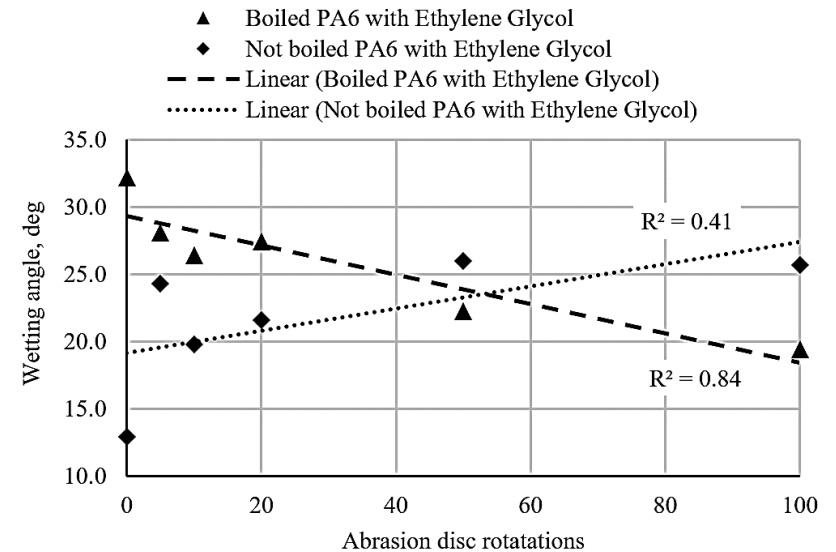


Fig. 2 Dependency of boiled and not boiled Polyamide PA6 abrasion disc rotations to ethylene glycol wetting angle

From the chart, the obtained results of the boiled and not boiled abraded surface showed the visual difference of contact points with the ethylene glycol contact angle. The tendency results of ethylene glycol wetting are close linear and wetting angle for not boiled intersecting and for boiled PA6 decreasing for increasing abrasion disc rotations. Those wetting changes occur because of the properties of ethylene glycol and modified surface properties of the boiled PA6 sheets surface. The coefficient of determination for the contact angle of ethylene glycol is 0.84 (boiled PA6) and 0.41 (non-boiled PA6).

There are a few differences in tendencies of contact angle of water. It was found, that changes in surface roughness do not have a significant influence on the contact angle of water. The contact angle of water was 54.6 ° (boiled PA6) and ~ 41.1 ° (non-boiled).

The influence of plasma treatment for contact angle of water and ethylene glycol is shown in Fig. 3.

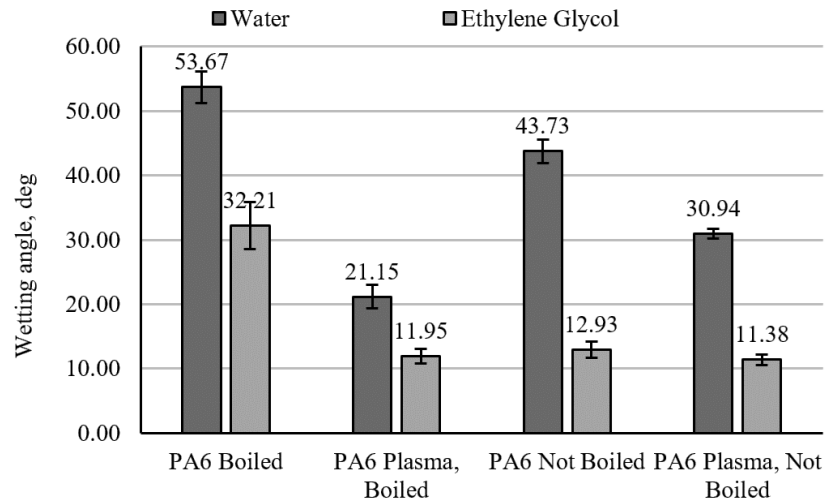


Fig. 3 Impact of surface plasma treatment on boiled and not boiled PA6 to surface water and ethylene glycol wetting angle

For the plasma treatment surface, the water surface contact angle of the boiled PA6 affected a decreasing difference of 30.41 %, and the non-boiled PA6 affected a decreasing difference of 70.76 %. Similarly, the ethylene glycol surface wetting of the boiled PA6 sheets had an effect on decreasing difference of 37.10 % but the non-boiled PA6 affected a low decreasing difference of 91.84 %. The low wetting difference was because of the properties of ethylene glycol and non-boiled PA6 surface. Comparing plasma and non-plasma treatment for boiled and non-boiled PA6 sheets (Fig. 3), it was found that the contact angle of water was lower than the contact angle of ethylene glycol. Therefore, After plasma treatment difference between contact angle of ethylene glycol for boiled and non-boiled PA6 sheets is 4.77 %. Plasma or mechanical treatment increases surface energy of PA6 sheets, due to this value of contact angle decreases. Because surface tension of ethylene glycol is lower than water, contact angle between ethylene glycol and PA 6 surface is also lower compared with contact angle between water and PA6.

Conclusions

Surface roughness parameters R_a ($R^2 = 0.46$) and R_z ($R^2 = 0.74$) increased in linear tendency by increasing of Taber Abrader disc rotations.

The contact angle of ethylene glycol decreased from 32.0 ° to 19.4 ° for boiled PA6 abraded surface but increased from 12.9 ° to 26 ° for non-boiled PA6 abraded surface by increasing of Taber Abrader disk rotations from 0 to 100.

The plasma treatment on not boiled surface with ethylene glycol have better a wetting influence of 11.38°. In specific, the plasma treatment is considered as the better wetting tendency method of contact angle influence among other surface changes.

References

1. **Karami P.; Shojaei A.** 2017. Improvement of dry sliding tribological properties of polyamide 6 using diamond nanoparticles. *Tribology International*, 115, pp.370-377.
2. **Canal C.; Molina R.; Bertran E.; Erra P.** 2004. Wettability, ageing and recovery process of plasma-treated polyamide 6. *Journal of adhesion science and technology*, 18(9), pp.1077-1089.
3. **Novák I.; Popelka A.; Valentín M.; Chodák I.; Špírková, M.; Tóth A.; Kleinová A.; Sedliačik J.; Lehocký M.; Marônek M.** 2014. Surface behavior of polyamide 6 modified by barrier plasma in oxygen and nitrogen. *International Journal of Polymer Analysis and Characterization*, 19(1), pp.31-38.
4. **Li M.; Wan Y.; Gao Z.; Xiong G.; Wang X.; Wan C.; Luo H.** 2013. Preparation and properties of polyamide 6 thermal conductive composites reinforced with fibers. *Materials & Design*, 51, pp.257-261.
5. Determination of abrasion resistance rubber or plastics coated fabrics. Part 1: Taber Abrader. ISO 5470-1:2016.
6. **Mittal, K.L. ed.** 2018. *Advances in Contact Angle, Wettability and Adhesion* (Vol. 3). John Wiley & Sons.

Ram Pramod MONIKANTAN, Vaidas BIVAINIS, Aistė KUNCIŪTĖ

Influence of Polyamide PA6 Surface Modification on Wettability Properties

Summary

The research carries out the surface modification of polyamide 6 by abrasion wearing test and plasma treatment. The abraded surface roughness for different abrasion disc rotations and the contact angle of water and ethylene glycol was measured to determine the influence on the modified material.

Keywords: Polyamide PA6, Taber abrasion, surface roughness, plasma treatment, wetting angle.