CONDUCTIVE COATING OF POLYETHER ETHER KETONE (PEEK) FILAMENT YARN

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Abstract: The aim of this work is to develop the electric conductivity on inert Polyether ether ketone (PEEK) filament surface by applying metallic layers with the help of wet chemical procedure. The atmospheric pressure corona plasma modification and wet-chemical functionalization of PEEK filament surface is done before it is metalized by using polyamine with coating procedure. The wet chemical procedure of metal coating in this work is based on the use of aliphatic amines, which consist of five amine groups, and which are well-suited to form a silver diamine complex. The PEEK filament is coated by cationic silver. After the chemical reduction, the cationic silver turns into metallic silver nanoparticles on the surface of PEEK filament. The wettability of plasma treated PEEK is investigated by means of contact angle and surface free energy measurement. The measurement of electrical resistance is also done of silver coated PEEK filament yarns.

Key Words: **Plasma, wet-chemical method, electric conductivity.**

1. INTRODUCTION

Since ancient times, humans have exploited metallic material to produce decorative textiles. It can be proven by the study of cultural relics that the production of golden yarns developed in China in the third millennium BC. Flattened thin wires or sheets of noble metals like gold and silver were incorporated into textile fabrics in Roman era [1, 2]. However, today's metallic yarns are used to create fashionable as well as E-textiles, also known as electronic textiles or smart textiles, those are enable to computing digital components and electronics embedded in them. They are the part of development of wearable technology, and also known as 'intelligent clothing' because they allow technological elements in everyday textiles and clothes [3]. With the help of conductive textile structure it becomes possible to build complete switching circuits to construct textile-based sensors and to produce self-luminous textiles. Even textile solar cells are under way [4].

In this work, conductive coating of PEEK is reported. This is achieved by applying silver coating on PEEK filament yarns. PEEK is a high performance thermoplastic polymer possessing the service temperature -250°C to +300°C, tensile strength 90 to 120 MPa [5] and elongation of 16% to 80% [6] is gaining significant interest in aerospace and automotive industries. Taking the advantage of its high temperature resistance and higher elongation properties, the silver coated PEEK filaments yarn can be used apart from thermoset composites especially in the textile reinforced thermoplastic composites as a functional component. The possible uses of such silver coated PEEK include electricity conductance, heat, signal transfer and as an interphase strain sensor.

However, before silvering of PEEK filaments it is essential to modify the surface of it. An important point for surface treatment of polymer is that only its surfaces should be modified so as no change occurs in its bulk properties. Formic acid and atmospheric pressure corona air plasma have been used for the surface modification of PEEK filaments. Plasma acts on the PEEK filaments surfaces and does not change their internal structure. For this reason, plasma treatment is suitable surface treatment method prior to the metallization of polymer like PEEK filaments using silver. The influence of surface modification is investigated by measuring the wettability of individual filament.

After surface modification of PEEK filaments surface, metallization by silver has been done with the help of wet chemical procedure. The developed wet chemical procedure [7] in this work is based on the use of long chain aliphatic amines, which consist of five amine groups, and which are well-suited to form a silver di-amine complex. The silvered PEEK filaments are coated with cationic silver. After the chemical reduction, the cationic silver turns into metallic silver particles on the surface of PEEK filaments. This method of silver coating is applied successfully on PES for the manufacturing of antibacterial filter fabric [8, 9].

2. EXPERIMENTAL

2.1 Plasma treatment of PEEK filaments

The plasma treatments are carried out using atmospheric pressure plasma (APP) system "Corona pretreatment system-AS Coating star (ASCS)", Ahlbrandt, Germany. The working principle of this plasma system is based on the dielectric barrier discharge (DBD) system.

2.2 Contact angle and surface energy measurement

The contact angle and surface energy of single PEEK filament is measured by the instrument Tensiometer (K100), Kruess, Germany. Ten individual measurements are taken at randomly chosen filaments to calculate the mean value.

2.3 Silver coating on PEEK filaments

The PEEK filaments are coated with silver (Ag) with wet chemical process.

2.3.1 First silvering- one bath method

Plasma modified PEEK filaments are wrapped on a wrap reel. Then the wrapped filaments are tied with cotton threads in some places to avoid to and fro motion of the filaments. The tied filaments are withdrawn from the wrap reel and prepare them to dip in the first silvering solution by knotting again some places with cotton threads. The both types of filaments are then dipped in the 1st silvering solution for one day to grow the diamine silver seeds on the surface. The first silvering solution is consisted of Tetra ethylene Pentamine (50 ml TEPA) and silver diamine complex (5% $AgNO_3$ and 50 ml NH_4OH solution) (Equation 1).

$$AgNO_3 + 2\ NH_4OH \rightleftharpoons [Ag(NH_3)_2]^+ + NO_3^- + 2H_2O \quad (1)$$

Two amino groups and a silver ion form a silver diamine complex. In this manner, the ionic silver can be fixed with a wet chemical process to the fiber's surface and reduced to the metallic form with a suitable L (+) Ascorbic acid solution [8].

The first silvering on the surface modified PEEK filaments are carried out for one day at room temperature. The filaments contained solution jar is wrapped with Aluminum coated paper to avoid the reduction from the light.

2.3.2 Reduction of silvered PEEK filaments

After one day, the filaments samples are put out from the solution and properly dried at room temperature. The samples are then reduced with the 5% L (+) Ascorbic acid solution for 5 minutes to get the reduced metal seeds on the surface. This way, ionic silver in the wet-chemical process is fixed on the surface of filaments. The p^H value of the Ascorbic acid solution is made 11 by using some drops of NH_4OH solution.

2.3.3 2nd silvering and 2nd reduction of PEEK filaments

The second silvering step is carried out with silver diamine complex make with different (%) of $AgNO_3$ and 50 ml Ammonia. 1%, 2%, 2.5%, 3%, 4%, 5% $AgNO_3$ solution and 50 ml NH_4OH solution are used for the second silvering. The samples are dipped in 2nd silvering solution and continuously stirring to grow more silver on the surface. The stirring is done for 5 minutes then the samples are taken out from the 2nd silvering solution and dipped into the same reduction solution of L (+) Ascorbic acid to get metallic silver layer on the surface of PEEK filaments. The reduction is done for 5 minutes with continuous stirring and taken out from the solution. The ionic silver are reduced to metallic silver (Equation 2) [7]

$$2Ag^+ + C_6H_8O_6 \rightleftharpoons 2Ag^0 + C_6H_6O_6 + 2\ H^+ \quad (2)$$

2.3.4 Thermofixing of silver coated PEEK filaments

After the second silvering and second reduction, the samples are kept at room temperature for a day. Then rinsed with cold water properly and dried at room temperature and thermofixed in oven dryer at 120°C for 3 minutes for multifilament and. 200°C for 2 minutes is used for monofilament PEEK.

The surface modified PEEK filaments are also wound onto the spools then the same procedure is applied for silvering. These two ways of silvering method will be termed as hank and spool methods respectively.

2.4 Resistance (Ω) measurement of silver coated PEEK filaments

The direct current (DC) Resistance of silver coated PEEK filaments is measured by Fluke 8846A, precision multi-meter, USA.

3. Results and Discussion

3.1 Results of contact angle

The Figure1 represents the graphical comparison among different types of modification of PEEK filaments. It reveals that the contact angle is highest on untreated PEEK filaments and with water and diiodo methane, which is 83.4° and 41.1° respectively. Due to acetone treatment the contact angle of water and diiodo methane decreases to 64.2° and 21.0° respectively. The change in contact angle by formic acid treatment is insignificant on the original multifilament PEEK. Due to the surface modification of PEEK filaments by atmospheric pressure plasma the contact angle in both water and diiodo methane solution decreases significantly. The contact angle of untreated PEEK filaments with water has decreased due to the plasma modification from 83.4° to 49.9°, 47.9°, 51.7° at 2kW, 3kW and 4kW plasma treatment for 2 minutes respectively. However, the difference in wetting properties for different discharge power is relatively insignificant. Though the contact angle after acetone wash reduces by about 20°, however, due to plasma modification on the desized sample, the change in contact angle is less compared to that of plasma modified sample on original multifilament PEEK. In case of plasma treated monofilament the contact angle with water and diiodo methane is 60.5° and 50.2° respectively. As plasma treated surface becomes more oxidized, or has more ionizable groups introduced to it, hydrogen bonding with water becomes easier and the droplet spreads along the hydrophilic surface, resulting in a lower contact angle [10]. Lower contact angle of polar liquids means a higher amount of hydrophilic groups formed on the surface of PEEK and increased wetting properties.

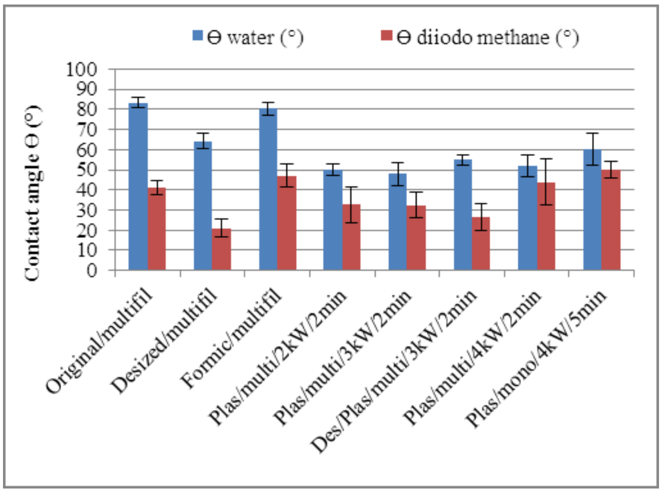

Figure 1: Graphical representation of contact angle measurement

3.2 Results of surface energy

Figure 2 shows the total surface free energy including polar and dispersive parts of differently surface modified filaments. Formic acid treatment does not increase polar parts significantly. It can be seen that the polar parts and surface energies increase simultaneously by plasma treatment on undesized PEEK multifilaments at 2kW, 3kW and 4kW for 2 minutes. The polar parts increased to 16.8, 17.7, and 18.2 mN/m respectively. 3kW plasma for 2 minutes has also been applied on desized PEEK multifilaments but the polar parts are less increased than that in undesized filaments and the value is 13.1 mN/m. In terms of plasma treated monofilament the polar part is 14.2 mN/m. The higher surface energy results in stronger adhesion between two surfaces. Generally, plasma treatments introduce unpaired electrons and create new polar groups (especially when using oxygen containing atmospheres) on the surface, which leads to an increase in the surface energy and a decrease in water contact angle. From this experiment it can be concluded that the PEEK filaments with plasma treatment at different power can increase the polar and dispersive parts as well as the free surface energy on the surface of PEEK filaments.

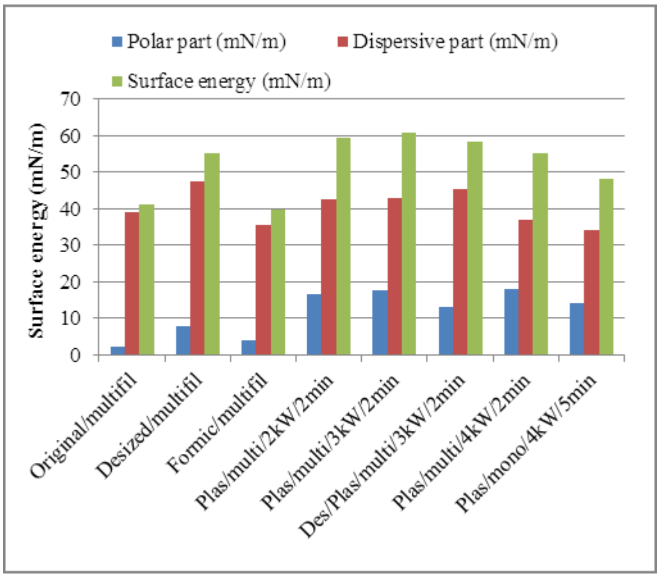

Figure 1: Graphical representation of surface energy measurement

3.3 Silver coating of PEEK filament

PEEK filaments are coated with silver in two methods by winding the filament yarn (i.e. mono and multifilament PEEK) on spool and wrap reel. As the coating is done by dipping in coating solution, in spool method the silvering solution does not spread into the internal layer of the multi-filaments evenly. The solution cannot enter into the internal layer and results are uneven or irregular silvering in lower layer of the PEEK on the spool. Furthermore, a periodic uneven coating pattern is created on monofilament PEEK by coating in spool method (Figure 3e). But in wrap reel method, the silvering solution distributes evenly on the surface of PEEK filaments and results in comparatively even coating. However, it is difficult to unwind multi-filament PEEK after coating using hank method. It is possible to obtain better coating on monofilament PEEK using hank method.

Figure 3: a) Original monofilament, b) silver coated monofilament, c) original multifilament, d) silver coated multifilament and e) unevenness in monofilament in spool winded silvering method.

3.3 Results of electrical resistance measurement

At first the variation of the silver content is investigated. Figure 4 depicts the dependence of electrical resistance of monofilament PEEK on the silver percentage. The change of electrical resistance with the increase of coating content of PEEK monofilament is observed.

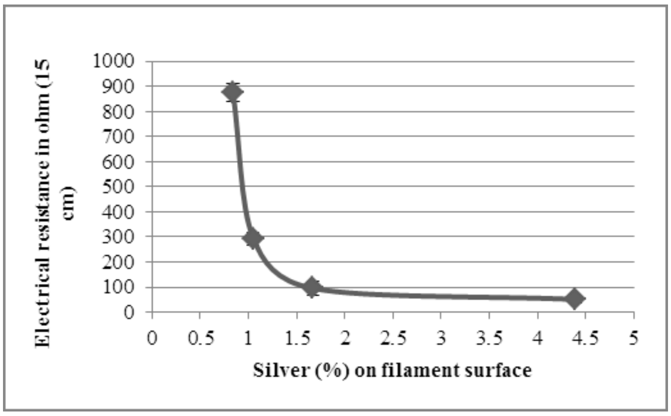

Figure 4: Influence silver content on electrical resistance of monofilament PEEK

The pronounced change in resistance for every variation in filament coating can be seen. However, the difference in resistance of the monofilament PEEK with the lower silver content (i.e. from 0.84% to 1.67%) is much higher than that with the higher silver content (i.e. 4.39%). This is related to the interconnected areas of silver coating on the surface. With the increase of cross sectional area due to the coating, resistivity decreases (Equation 3).

$$R_{yarn} = \rho_{coating} \frac{L}{A_{coat}} \quad (3)$$

R_{yarn} indicates the resistance, $\rho_{coating}$ indicates specific resistivity coated yarn, L length, and A_{coat} is cross sectional area of coated yarn.

In Figure 5 the dependence of the silver coated monofilament PEEK resistance on its length is illustrated for varying amount of silver (%). The monofilaments are modified by 4kW plasma discharge for 5 minutes. The monofilaments which are modified by 2 kW and 3 kW plasma discharge, show no conductivity after silver coating due to the lack of compact silver network on the PEEK monofilament.

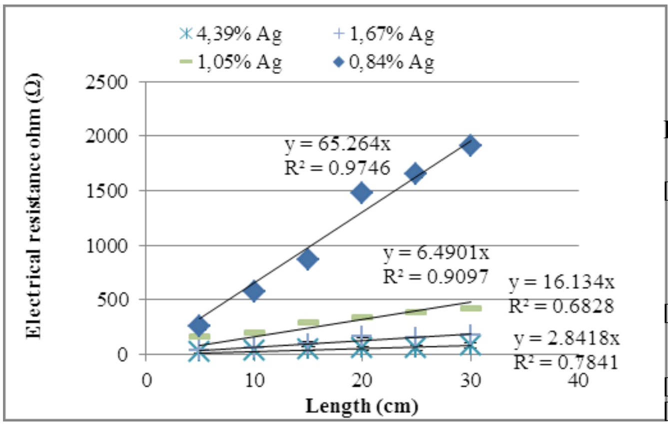

Figure Error! No text of specified style in document.**: Graphical representation on the resistance of silver coated PEEK monofilament in respect to length**

From Figure 5, firstly one can observe that for an identical filament length the resistance decreases with the increase of silver content on the filament. This is expected since the resistance of yarn is given by Equation 1.

Furthermore, a pronounced linear dependence on the resistance on the yarn length can be observed as predicted by Equation 1. A linear least square fit through the origin is performed in order to derive the different slopes of the data sets. As expected, the smallest slope is found for the filament with highest silver content and a clear trend to steeper slopes with decreasing amount of silver on the filament is observed.

4 CONCLUSIONS

The ultimate target of this work is to flow the electron through the network of silver particles on the surface of PEEK filaments. To fulfill this target the inert surface of PEEK is modified by the application of atmospheric pressure corona plasma to increase the surface free energy as well as increase the adhesion between PEEK surface and silver particles. The test results of contact angle measurement and surface free energy of surface modified PEEK show that due to plasma treatment, polar parts can be increased significantly which is most important for the wettability of PEEK in wet chemical method of silvering. Wet chemical method of silvering is used to bring silver particles on the modified surface by winding on spool and wrap reel (in hank form). With spool method, it is not possible to obtain regular coating layer on PEEK. However, hank method shows the results of avoiding the irregularities of coating on the surface. Better coating is obtained on monofilament PEEK by hank method. The test results of electrical resistance of silver coated PEEK filament shows that with the increase of silver (%) on surface of monofilament PEEK, electrical resistance decreases. A pronounced linear dependence of resistance on the yarn length can be also observed on the silver coated monofilament PEEK.

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