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R.F. 대기압 플라즈마를 이용한 소수성 표면처리 연구

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A research of hydrophobic surface treatment with RF atmospheric plasma

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Abstract - The importance of protecting people from harsh weather conditions cannot be over-emphasized and the way to do so should be sought vigorously. The most well known and widely used weather protection fabric in the current industry is Gor-Tex.[1] However, the Gore-Tex membrane cannot be attached to cotton or other natural fibers so it's use is not suitable for clothing such as underwear.

If the exterior of cotton fabric can be made to be hydrophobic without sacrificing the comfort and breathability, the result will be a cotton fabric with the weather protection capability equivalent to Gore-Tex as well as the ability to provide the best wear comfort. However, this should be done without using toxic and expensive gases to be environmentally friendly and cost effective.

Therefore, our approach for hydrophobic treatments of fabric and metal surfaces is to utilize a plasma-based technique. In general, plasma processes do not produce chemical wastes or waste disposal problems and they are fully automated.

1. Introduction

Deposition of hydrophobic coatings on various materials has many important applications such as protective garments, water repellent textiles, corrosion prevention, micro-device lubrication, microfluidics, barrier coatings in biomedical systems, etc.[2,3,4,5,6,7] There are many techniques that can be utilized for this purpose. However, a plasma-based process is very attractive in many aspects.

This paper demonstrates the CH_4 plasma polymerization deposition of stable hydrocarbon coating layers using an in-line atmospheric RF plasma process. Hydrophobic coating layers were produced by plasma polymerization of CH_4. Even though the plasma deposition process was operated in atmospheric conditions, the incorporation of oxygenated species was negligible. Ultra-hydrophobicity was attained on rough surfaces such as cotton.

Although the Gore-Tex technology is truly a breakthrough in fabric industry, there still exist the need for developments of hydrophobic treatments of other conventional fabrics. The Gore-Tex fabric consists of a nylon outer materials, a Gore-Tex membrane, and a nylon liner. Thus it is only used for outerwear and is unsuitable for underwear since the Gore-Tex membrane cannot be attached to cotton or other natural fibers. Cotton provides the best comfort in contact with human skins. Cotton has an excellent water absorption capability. The fine fiber texture of cotton fabric also provides a large surface area from which the absorbed water can evaporate. If the exterior of cotton fabric can be made to be hydrophobic selectively without sacrificing the comfort, water absorption and evaporation capability of the interior, it will render the weather protection capability equivalent to Gore-Tex along with the best wear comfort in a cost effective manner.

The surface texture of cotton fabric also imparts an additional advantage. If combined with hydrophobic coatings, the roughness of the fabric that naturally results from weaving of cotton fibers will enable ultra-hydrophovicity that can be found in lotus leaves or other engineered polymer surfaces.[8-10] This ultra-hydrophobicity leads to increased water repellency and reduced particle adhesion and is therefore the crucial factor for self-cleaning. The self-cleaning fabric can offer maximum protection to medial workers as well as soldiers from pathogenic contamination. An example of its immediate applications will be wound gauzes and bandages.

2. Experimental Section

2.1 Experimental Setup

The atmospheric RF glow-discharge plasma system was constructed with a custom-made plasma generator head and a 13.56 MHz RF power supply with a L-C matcher. A schematic of the plasma head and sample stage is shown in Figure 1.

The atmospheric plasma was operated in a glow discharge mode; so it could be directly applied to metallic substrates as well as non-conducting substrates without arc or streamer damage. Helium or argon was used as a carrier gas (3 ~ 15 lpm) and CH_4 was used as a reactive gas (10 ~ 100 sccm). The RF power was controlled in the range of 200 ~ 600 W. Figure 2 shows RF plasma with Ar and CH_4. Samples were mounted on a computer-controlled moving stage that traveled about 3 ~ 10 mm below the plasma source along the orthogonal direction to the plasma source head. In typical processes, the substrate was repeatedly passed back and forth across the glow discharge plasma region at a speed of 1 ~ 10 mm/sec. The substrates tested in this work were cottons(Oxford cloth, 20 thread counts per centimeter), slide glass, a Kimwipe paper, and printer paper(A4 paper).

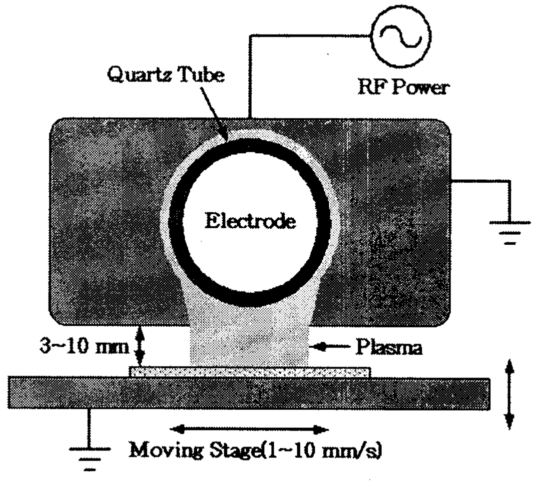

Figure 1 A Schematic diagram of the plasma head and sample moving stage.

Figure 2 Picture of RF plasma with Ar and CH_4.

2.2 Results and Discussion

Figure 3 shows the water droplets on a hydrophobic treated cotton fabric. The inset shows an apparent contact angle of ~135°.

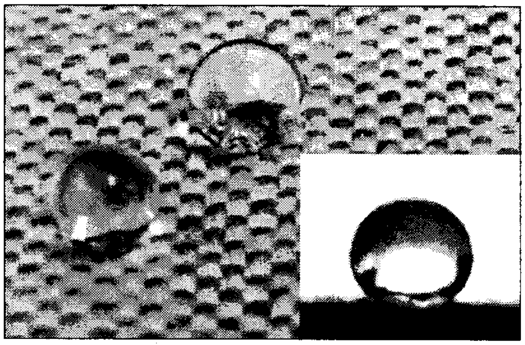

Figure 3 Picture of water droplets on a hydrophobic treated cotton fabric. The inset shows the water contact angle.

The surface texture of the cotton textile enables the ultra-hydrophobicity. It remains after several cycles of immersion in cold water and air drying. It should be noted that water completely wets the inner surface of the treated fabric.

As shown in Figure 4, the plasma system can be utilized for hydrophobic treatments of paper and even very thin Kimwipe tissues.

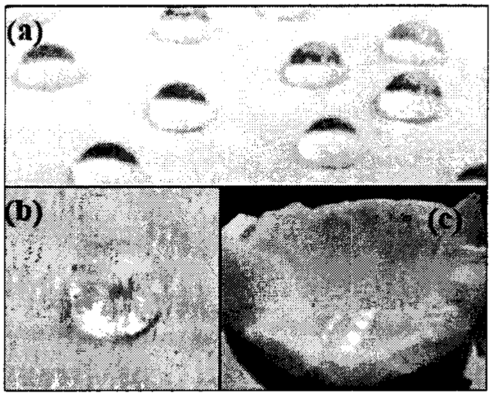

Figure 4 Pictures of water droplets on (a) a printer paper, (b) a Kimwipe and (c) a picture of the treated Kimwipe holding 200 ml water.

The hydrophobic treated Kimwipe can hold bulk water for many hours without any water dripping into the cup. In preliminary tests, we had to add water to keep the water level constant only due to water evaporation, and not from water leaking. This picture also clearly demonstrates the capability of treating a large surface area. It should be noted that all these hydrophobic treatments are done with He and CH4 gases, no fluorocarbons were used. Our plasma system can also be used for not only hydrophobic but also hydrophilic treatments of inorganic materials such as glass. Figure 5 compares the surfaces of slide glass after placing water droplets.

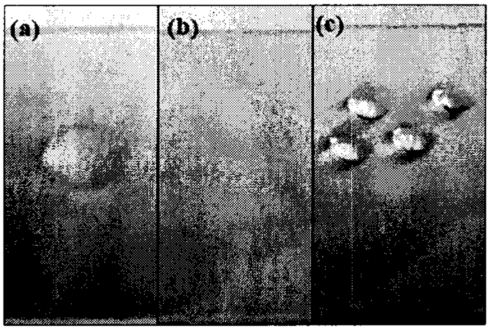

Figure 5 Picture of water drops on (a) untreated, (b) hydrophilic and (c) hydrophobic treated glass slides.

On untreated glass, water spreads to some degree, but not completely. The water contact angle is 34° without any treatments. When the same glass is treated with He/O_2 plasma, water droplets now completely wet the surface. When this surface is treated with He/CH_4 plasma, the water droplets do not spread at all. The water contact angle increases to 101°. We believe that even greater ultra-hydrophobicity can be achieved if the glass surface is roughened by pre-treatments with plasma under etching conditions.

Water contact angles on these coatings are plotted in Figure 6 as a function of the plasma deposition cycles. On flat surfaces such as glass slides, the contact angle increases to ~90° after only a single treatment with the CH_4 plasma. This value is very close to the water contact angle of polypropylene (93°). The contact angle remains unchanged upon further deposition. However, paper and cotton substrates require at least 3 deposition cycles to be hydrophobic. Until the third cycle, the water droplet is completely absorbed into the substrate. This probably arises from lower deposition yields on side walls present in rough surfaces, so repeated treatments are required for conformal coating. It should be noted that the contact angles on paper (110±3°) and cotton (150±3°) substrates are significantly higher than those on flat substrates.

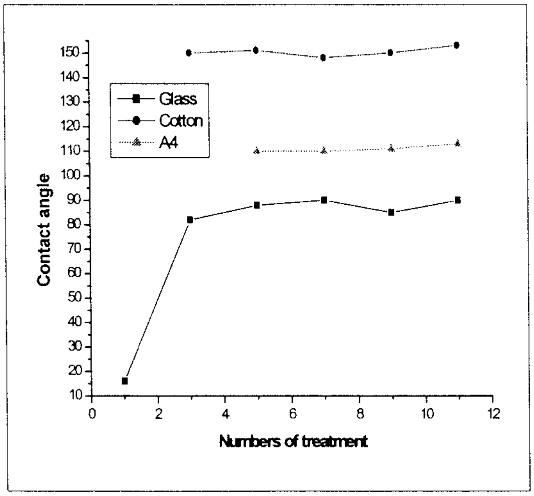

Figure 6 A function of the plasma deposition cycles.

The higher contact angle on these substrates is due to the surface roughness effect that amplifies the hydrophobicitiy.[11,12] In general, the water contact angle becomes larger on rough surfaces than on flat surfaces. On the treated cotton sample, the water droplet easily rolls off with only slight tilting of the substrate, showing a self-cleaning capability. It should be noted that the untreated side of the cotton sample still absorbs water readily. These properties will make the plasma-treated cotton fabric a good candidate for self-cleaning garments.

The atmospheric RF glow-discharge plasma described in this paper is suitable for continuous in-line manufacturing. It can be applied to any surface regardless of the surface chemistry of the substrate. The samples were exposed to air for long periods of time (we have tested up to 4 months). And the plasma-deposited coatings remain intact even in organic solvents such as hexane, and retain their hydrophobicity after the solvent is dried completely. The coating on the fabric does not degrade even after many cycles of cold water wash(without mechanical rubbing or laundry detergent).

3. Conclusions

A CH_4 atmospheric RF plasma treatment process is developed which can be applied to various substrates regardless of their surface roughness and chemistry. Since the plasma is operated in the glow discharge region, it can be applied directly to both metallic and insulating substrates. The atmospheric operation and use of stable hydrocarbon gas make it suitable for continuous in-line processing. Water contact angle of the produced coating is ~90° on flat surfaces and reaches up to 150° on rough surfaces such as cotton.

The proposed atmospheric RF plasma is a green process. It does not consume toxic gases nor generate any chemical liquid wastes that require special collections or treatments. The entire experiment can be done in an open lab without any special ventilation systems. The produced surface functional groups or coated films are slowly based on hydrocarbon and are not harmful upon contact with human skin. We have not attempted any specific allergy tests yet; but knowing the chemical inertness of the hydrophobic functional groups, any serious allergic response is not expected. Therefore, further research is necessary before we can apply this technique to the manufacturing process.

4. Acknowledgements

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