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SURFACE MODIFICATION OF CYCLIC OLEFIN POLYMERS: INTEGRATION OF AIR ATMOSPHERIC PRESSURE IN MICROFLUIDIC DEVICES

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ABSTRACT

The thesis makes extensive use of the design and development of the plasma pressure jet throughout its whole. The several essential components of the plasma jet are addressed. For the purpose of investigating the surface activation and bonding of cyclic olefin polymers, plasmas consisting of helium, argon, nitrogen, and air were utilized. Because the plasma gas had a temperature that was lower than fifty degrees Celsius, it was ideal for the processing of polymers. A distance of three to twenty millimeters from the plasma exit was used to treat the substrates. A surface wettability of less than 10 degrees is produced by air, which serves as the feeding gas for the plasma jet. For the purpose of determining the characteristics of the substrate surface, various techniques such as water contact angle (WCA), scanning electron microscopy (SEM), atomic force microscopy (AFM), and infrared spectroscopy (IR) were utilized. The results of this research demonstrate that atmospheric pressure plasma is a technology that is both cost-effective and capable of producing cyclic olefin polymers that are both hydrophobic and hyper hyderophilic. Furthermore, design expert V12 software was utilized in order to optimize the APPJ operating settings in order to get the lowest coefficient of performance (COP) water contact angle at the most affordable price. It is necessary to do additional research in order to improve the surface of the polymer and cut down on the number of trials that are repeated. Because of this, the plasma jet was described in greater depth in order to make it easier to comprehend. Electrical measurements were carried out with the assistance of voltage and current probes, while optical characterisation was carried out with the assistance of optical emission spectroscopy. In many different applications, the hydrophobic recovery of polymers is an issue. Microfluidic devices are the most prominent example of this worry. Following the completion of the work described in Chapter 5, a stable surface was produced. This surface stayed stable for more than sixty days and was partially stable for roughly one hundred eighty days. Lastly, in order to utilize disposable glass for biosensor applications, we changed the surface of the glass. In this work, the characteristics of the plasma jet may be altered to produce gold of variable thicknesses, which can then be used to accomplish the goal of improving the optical qualities. Scanning electron microscopy and ultraviolet-visible spectroscopy were utilized in order to characterize the surface that was treated. The experiment was valuable, despite the fact that the results did not meet the requirements for applications involving biosensors.

Keywords:- *cyclic olefin polymers, microfluidic devices.*

INTRODUCTION

In the process of creating a new material with specific physical properties, a polymer blend is a mixture of two or more polymers that have been blended together to generate the new material. The technique of polymer blending is one that is not only straightforward but also economical, and it has attracted a growing amount of interest in the process of producing polymeric materials that have the potential to be beneficial for commercial purposes. In order to adjust the properties of the blends for their final use, it is necessary to make an appropriate selection of the constituent polymers. Blends offer the essential flexibility to customize a particular material to a particular application, and in certain instances, they offer enhanced qualities in comparison to the materials that they are intended to replace. In addition to being extremely costly, the process of developing and commercializing new polymers takes a significant amount of time. On the other hand, the polymer blending process is quite inexpensive to run, and it frequently has the potential to shorten the amount of time required for the incorporation of commercialization.

Now that a large number of commercial polymer blends are accessible, there is a continual effort being made to generate new materials with superior chemical or mechanical performance. This endeavor is being projected persistently. Numerous more recent research have focused their attention on the alteration of the performance of polymer systems as a main topic of investigation. The process of blending also results in the production of materials that possess remarkable combinations of morphological, thermal, barrier, chemical, and mechanical properties.When it comes to developing polymeric materials with desirable qualities, blending is a procedure that is not only simple but also relatively cost-effective. In addition, the blending of polymers offers a straightforward and practical method for the reuse and recycling of waste polymer products.

Overview of Cyclic Olefin Polymers (COPs)

Cyclic olefin polymers (COPs) are a class of thermoplastic materials that have garnered significant attention in various high-tech applications due to their unique properties. These materials are characterized by their high optical clarity, low birefringence, excellent chemical resistance, and good dimensional stability. COPs are synthesized through the polymerization of cyclic olefins such as norbornene, often using metallocene catalysts, which results in a polymer with a cyclic structure contributing to its superior performance characteristics.

Importance of Surface Modification

Surface modification of COPs is crucial for enhancing their applicability, especially in the field of microfluidics. Microfluidic devices, which manipulate small volumes of fluids in channels with dimensions of tens to hundreds of micrometers, rely heavily on the surface properties of the materials used. Surface characteristics such as hydrophilicity, chemical functionality, and biocompatibility can significantly influence fluid flow, molecular interactions, and device performance. Therefore, modifying the surface of COPs to tailor these properties is essential for optimizing the functionality of microfluidic devices.

Atmospheric Pressure Plasma Treatment

One of the effective methods for surface modification of COPs is atmospheric pressure plasma (APP) treatment. This technique involves the generation of plasma at atmospheric pressure, which is then used to modify the surface of the polymer. The APP process can introduce various functional groups onto the polymer surface, enhance wettability, and improve adhesion properties without the need for high vacuum systems typically required in other plasma treatments. The use of air as the working gas in APP treatments is particularly advantageous due to its availability, cost-effectiveness, and environmental friendliness.

Cyclic olefin polymers

However, because of their limited wettability, the COP cannot be utilized with certain hydrophobic liquid reagents that are typically utilized. This is despite the fact that the COP have a number of advantages. The surface adjustments that are pertinent to the situation are still required as a consequence. As an illustration, Roy and his colleagues evaluated the hydrophilicity of the surfaces of COP by applying a plasma treatment to those surfaces. In order to achieve this goal, we made adjustments to the amounts of different gases, the power levels, and the amount of time that was spent. In addition, the surface morphologies of COP as well as its wettability were investigated and compared under a number of different circumstances. Furthermore, the effects of surface modification on the bonding strength of COP chips were examined at the same time. It was shown that the processing of COP surfaces through plasma treatment can not only make them hydrophilic but also boost the bonding strength associated with them. This was demonstrated by the experimental data that were presented alongside the study. It was demonstrated by the fact that the plasma treatment was successful. In addition, Balamurugan and colleagues looked at the surface fluorination modification of a number of different polymer materials, such as polycarbonate (PC), polymethyl methacrylate (PMMA), and COP. The researchers made the discovery that increasing the hydrophobicity of the materials' surfaces led to an improvement in the dimensional uniformity of the microdroplets that were generated. For the purpose of achieving both bonding and the endowment of hydrophobicity in a single phase, Su et al. adopted a technique that consisted of concurrently bonding with a solvent and fluorinating the surface. This allowed them to accomplish both of these activities simultaneously.

The current research, on the other hand, is primarily concerned with the intuitive augmentation of the uniformity and stability of water-in-oil droplets that are produced by a chip hydrophobic treatment in a laboratory environment. Nevertheless, in the process of industrial manufacturing, there are other much more significant factors that need to be addressed. Changes in microdroplet sizes can be induced by a wide range of causes, including, but not limited to, variations in the microchannels that occur during the bonding of various batches, pressure fluctuations that are brought about by the continuous operation of the pressure pump in droplet generating devices, and a variety of other reasons. Factors such as variations in the microchannels, pressure fluctuations brought on by the continuous operation of the pressure pump, and the slight variations in the microchannel diameters of the chips that occur during mass production are included in this category.

Research methodology

The fields of chemistry, biology, and medicine have, in recent years, committed a significant portion of their research efforts to the creation of microfluidic devices for a variety of tasks that are performed on a regular basis. This is because the small format leads in a reduction in the amount of time necessary for analysis as well as the volume of reagents that are required. This is the reason why this is the case. It has been demonstrated that microfluidics can be effectively utilized in the domains of genomics (the process of genotyping or sequencing DNA), proteomics (the identification of proteins), and clinical diagnostics (the detection of viruses or other infections). The substrate materials, on the other hand, need to be chosen with great care, taking into consideration a wide range of features, including but not limited to cost, biocompatibility, mechanical properties, chemical properties, optical properties, and feasibility of manufacture.

For a substantial chunk of the early research and development on microscopic chemical analysis systems, the standard lithographic manufacturing approach, in conjunction with the utilization of glass or silicon substrates, has been the primary focus of attention. Polymers are an appealing material that is perfectly suited for single-use disposable devices due to the fact that they are easy to construct, have good biocompatibility, and are inexpensive. This is in contrast to glass and silicon, which are very expensive materials. The application of polymeric materials in chip-based systems has been the focus of an increasing number of research endeavors in recent years. A variety of in-depth evaluations have been conducted to investigate the various production techniques of polymer microfluidic devices. These techniques include casting, laser ablation, imprinting, hot embossing, and injection molding. Additionally, the applicability of these techniques for genetic research have been extensively investigated. When it comes to the process of producing microfluidic devices, a number of polymeric materials have been utilized. These materials include poly(dimethylsiloxane) (PDMS), poly(methyl methacrylate) (PMMA), and polycarbonate (PC).

When it comes to microfluidic applications, the vast majority of hydrophobic polymers are already accessible on the market for use. A few examples of the materials that are included in this category are polycarbonate (PC), poly (PMMA), polydimethysiloxane (PDMS), and copolymer of 2-norbornene ethylene (often referred to as "cyclic olefin copolymer," or COC). It may be challenging to work with the substance in microfluidic devices when it comes to liquids because of the hydrophobic nature of the substance. The use of an external pump is required in order to wet hydrophobic channels. This is in contrast to the use of capillary force, which is employed in order to load materials into hydrophilic channels. It is possible that the surfaces, as a result of the hydrophobic interactions, will be able to capture particular compounds from the solution as it moves through the channels. The concentration of particular substances in the solution shifts as a consequence of this, which in turn has an impact on the dependability of quantitative tests. Not only would the right functionalization of the surface of the polymer microchannels make it feasible to govern the flow and adsorption processes, but it would also significantly boost the dependability of the microchips in general.

A number of examples of surface modifications that have been performed on a wide range of polymers are provided by the corpus of research that is currently being conducted. The majority of these techniques are not suitable for usage with microfluidic chips and should be avoided. This is due to the fact that they rarely give selective patterning on the device during the process. As a result of this requirement, processes that are triggered by UV light have a competitive advantage. The cyclic olefin copolymer is one of the polymer materials that is used the most frequently. It possesses a high level of optical clarity in the ultraviolet light spectrum that is comparable to that of glass and PDMS (more than 80 percent transmission at 320 nm wavelength), in addition to having a low background fluorescence. As a result of the fact that it exhibits a remarkable combination of optical clarity, mechanical strength, and a low cost, this material has been exploited in the production of microfluidic devices for clinical diagnostics. The behavior of fluids in surface-modified polyolefin microchannel networks was the primary focus of our research. After being manufactured using a technique that required hot embossing, these devices were subjected to a process that involved UV-mediated grafting in order to modify their surface. We investigated the imbibing flow that was driven by capillary force, pulsed drop motion, contact angle hysteresis, and loading of separation medium. All of these different types of flow were investigated. Through the utilization of the polymer devices, it was established that these devices may be utilized for the separation of nucleic acids after they have been constructed.

Increasingly, atmospheric-pressure low-temperature plasma jets (APPJ) are being utilized for a variety of applications, including surface activation, wound therapy, and sterilizing, among others. In order to build practical applications that make use of these systems, it is vital to have the capability to adjust the active species that are formed in the plasma jets in order to make them compatible with the treatment requirements. The objective of this study is to provide an optimization of the impact that APPJ has on cyclic olefin polymers (COPs), which is the substance that is being studied. There was a correlation found between the geometry of the water contact angle and the wettability of the surface of COP, as demonstrated by the findings. The utilization of historical data that met the D-optimal criterion was done with the intention of optimizing the process. The influence that plasma characteristics have on the surface of the COP was investigated. These parameters include the input voltage, the frequency of the plasma power source, the air flow rate, and the distance between the nozzles. According to the results of the analysis of variance (ANOVA), the model that was proposed has the potential to play a significant role in traversing surface wettability in a manner that is very efficient. After careful consideration, it was found that it was possible to forecast the best operating conditions that would result in the least water contact angle. In accordance with the findings, the COP surface modification is affected by each and every one of the parameters that were tested; nonetheless, it seems to be more sensitive to the plasma frequency and distance, in addition to the air flow rate.

Result and discussion

Surface modification

The fabrication procedure that is utilized in the production of silicon master and polyolefin plastic chips is depicted in this diagram. The selection of silicon as a candidate for the position of master material was brought about by the development of techniques for micromachining silicon on its surface and in bulk. As a result of the ease with which three-dimensional silicon molds may be manufactured, not only is it possible to readily produce planar structures, but it is also possible to easily achieve three-dimensional topology. both the silicon mold and the devices that were made using the silicon mold are displayed in this demonstration. An excellent crosssection profile of the microchannels that are formed as a result of dry etching is achieved due to the anisotropic nature of the process. If the surface of the polymer is subjected to ultraviolet radiation, it is possible for the surface to undergo a change, which will result in the surface becoming hydrophilic rather than hydrophobic.

In contrast to the lowered contact angle that surrounds a treated COP surface, the static contact angle of water on a native COP that is present in the environment. Using this method, it is possible to generate a hydrophilic surface that is reasonably constant after the grafting process has been completed. We monitored the contact angle for a period of one week, and throughout that time, we did not observe any obvious signs of aging in the contact angle. Other approaches, such as the oxygen plasma treatment, offer the advantage of enabling the hydrophilicity of the surface to be altered by modifying the reaction conditions (for instance, the gas for the plasma, the power, and the time). This is a significant advantage. These methods have a number of benefits, and this is one of them. The range of our research was fairly limited, ranging from ten to twenty minutes of exposure to a continuous source. Despite this, we did not discover any difference in the hydrophilicity of surfaces as a function of UV irradiation. According to findings from recent studies, the contact angle can, in fact, be altered by modifying the duration of time that ultraviolet radiation is present. If it is possible to better optimize the UV conditions, then it would be possible to use the UV grafting processes to a larger variety of applications.

Fluidic handling

It is possible that the capillary force will be loaded onto the surface with greater ease as a consequence of the surface treatment. displays the location of the meniscus as a function of time after a drop of DI water has been placed on the intake of the microchannel before the microchannel was used. Comparatively speaking, the fluidic behaviors of capillary-driven flow in untreated and treated COP devices, glass chips that are naturally hydrophilic, and oxygen plasma treated PDMS microchannels are all relatively comparable to one another.

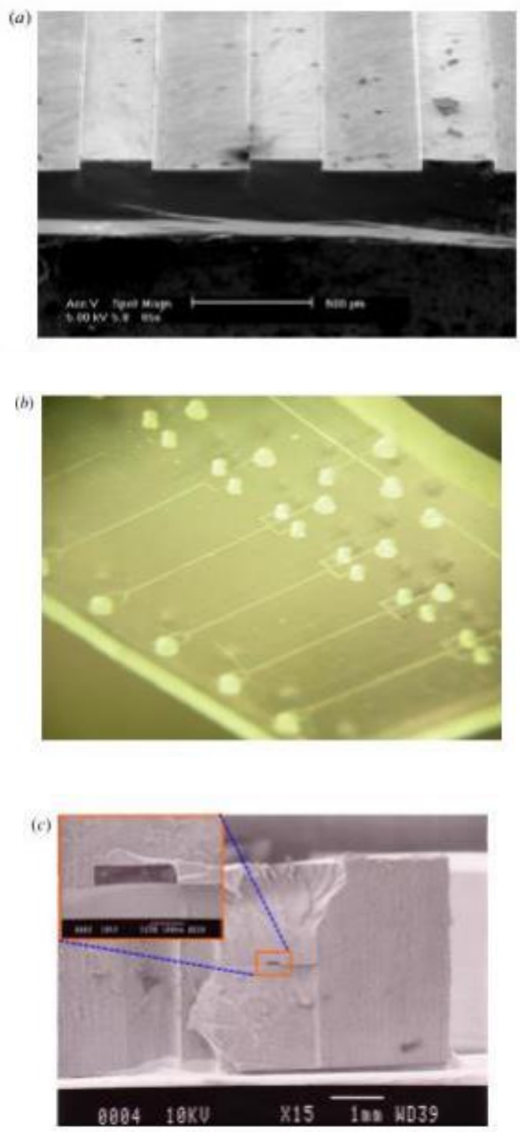

Figure 1. (a) Scanning electron micrograph of the microfabricated silicon mold. (b) Pictures of hotembossed plastic devices. (c) Scanning electron micrograph of the rectangular cross-section of the plastic microchannel.

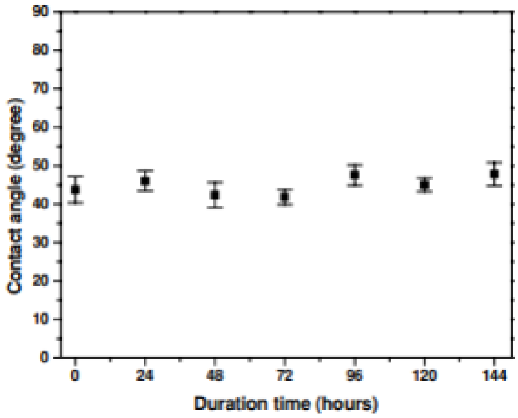

Figure 2. Contact angle of the photo-grafted COP surface as a function of duration time in the air at room temperature.

CONCLUSION

We provide a comprehensive description of the experimental setup and methodology that was applied in order to accomplish surface alteration. The characterization of altered surfaces was accomplished by the utilization of contact angle measurements, atomic force microscopy, and X-ray photoelectron spectroscopy as part of this methodology. The results of these research offer significant information on the changes that are occurring at the surface of the COP and the effect that those changes have on the behavior of the fluid. The purpose of this work is to demonstrate the practical applications of air atmospheric pressure-modified COPs in microfluidic devices. Specifically, we demonstrate better performance in areas such as droplet production, mixing, and analyte collection. A wide range of microfluidic applications, such as chemical synthesis, drug discovery, and diagnostics, could potentially be expanded as a result of these advancements. Using air atmospheric pressure as the driving force behind the process, this work provides a novel and effective approach for surface modification of cyclic olefin polymers in microfluidic devices. The method is based on the utilization of air. It is possible that the implementation of this technology will result in an improvement in the performance of COP-based microfluidic devices in a wide range of scientific and medicinal applications.

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