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Surface analysis, hydrophilic enhancement, ageing behavior and flow in plasma modified cyclic olefin copolymer (COC)-based microfluidic devices

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ABSTRACT

Radio frequency (RF) argon and argon-oxygen plasma were used to improve hydrophilicity and increase wettability of the COC (Topas) surface to enhance its surface properties for applications in microfluidic devices. This is necessary because the hydrophobic nature of COC can lead to adsorption of specific compounds from biological fluids in the channel which can impair precise quantification and cause clogging. The significant loss in hydrophilicity during ageing was found to be associated with the decrease in –OH groups on the plasma modified surface. A correlation was found between the surface oxygen/carbon ratio and hydrophobicity of the treated surface. Plasma power ratings of 60 W and 100 W with exposure times from 15 s to 240 s were carried out. The surface roughness was characterized using atomic force microscopy (AFM) and wettability was determined using contact angle measurements. The oxygenated-argon plasma treatment improved surface wettability more effectively as compared to the argon treatment. The changes in surface properties due to treatment and during ageing were characterized using FTIR and XPS (X-ray photoelectron spectroscopy) revealing the presence of polar species such as carbonyl, carboxyl and hydroxyl groups. The probable chemical surface mechanisms were identified. The study indicates that plasma modified COC-based microfluidic devices ought to be vacuum-packed for storage to ensure that their performance will not be impaired.

1. Introduction

Most synthetic polymers have chemically inert hydrophobic surfaces, which restrict their applications as adhesives, coatings, printing inks and other areas [1]. The hydrophobic polymer surfaces usually adsorb biological molecules when they come into contact with biological fluids (blood, serum, proteins, DNA, etc.) resulting in cell attachment, thrombosis and coagulation. Therefore, surface modification of the polymer surface is essential for generating new functionalities in the polymers in order to improve its hydrophilicity, biocompatibility, conductivity, surface roughness, and antistatic adhesion [2–4].

Several methodologies have been employed for improving the surface characteristics of polymers and RF plasma is one potential [5–7] technology with wide industrial applications [8,9]. The reasons behind this are that in the RF plasma treatment: (i) only a thin surface layer of polymer is modified and the mechanical properties of the polymer bulk [10,11] are retained, (ii) the procedure is safe and environmentally benign as the process is chemical free, (iii) the need for sterilization of the products is eliminated, and (iv) the surface can be treated homogeneously and the surface chemistry can be tailored for the required end use. Another added advantage is that RF plasma can be used to modify the characteristics of non-uniform contoured surfaces including plastic substrates that contain micro and nanochannels. Hence, it can be readily adapted for mass fabrication of disposable biochips in industry.

Microfluidic systems have many potential industrial applications especially in the pharmaceutical, food, medicine [12–15], biotechnology, chemistry, and analytical sectors. The key advantage of using a microfluidic device is the ability to integrate successive steps in analytical processes on a single microchip to create a miniaturized total analytical system known as a Lab-on-chip. Polymer based microfluidic devices have attracted great interest due to their light weight, low cost, optical transparency and chemical resistance. Furthermore, they can be fabricated using established techniques such as hot embossing and injection molding. Although polymeric microfluidic devices has brought remarkable changes in recent diagnostic applications, several critical issues such as controlling hydrophilicity, repeatability and the development of low-cost bonding techniques have to be addressed.

Cyclic olefin copolymer (COC) Topas is considered as a suitable substrate for microfluidics because of its high glass transition tem-

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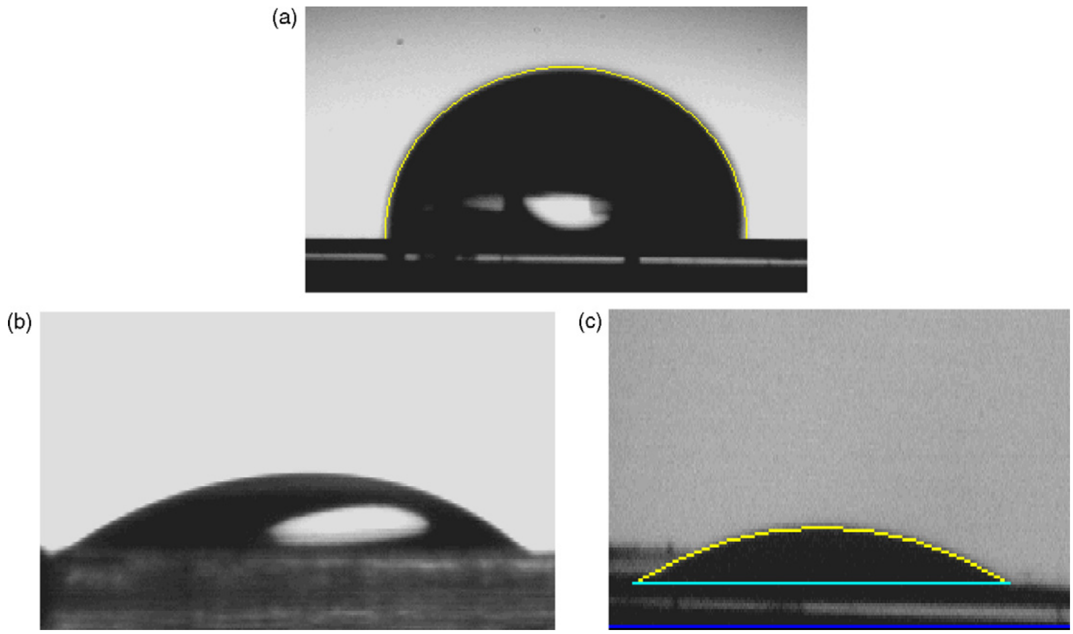

Fig. 1. Typical images of droplets in contact angle measurements for both untreated and plasma treated COC: (a) untreated COC [88°]; (b) argon plasma treated specimen [20°] at 100 W, 70 sccm Ar, and $t = 120$ s (c) oxygenated-argon plasma treated [15°] at 100 W, 70 sccm Ar + 50 sccm O_2 and $t = 120$ s.

peratures (Tg), low moisture uptake, high chemical resistance and excellent optical properties [16,17]. However, a microfluidic device made by COC [18] may have undesirable characteristics due to its strong hydrophobic interactions towards biological molecules. This is because biomolecules that are deposited on the wall of the channel can alter the character of the surface, and hence affect both adsorption of other molecules and the reliability of the quantitative assay. Therefore, proper functionalization of the microchannel surface is necessary to eliminate this undesired adsorption process in order to enhance the reliability of COC-based chips. The surface wettability of a polymer surface is an important characteristic which relates to the biocompatibility for biomaterials.

It has been reported [19] that the radicals, ions and electrons that are formed during RF treatment interact with the polymer to produce a hydrophilic surface leading to improved bond strength. Oxygen is probably the most commonly used process gas for plasma surface modification because it aids in the formation of polar groups that improves wettability, which in turn enhances adhesion and control biocompatibility. The specific chemical reaction mechanisms that occur are dependent on the structure of the virgin polymer and RF plasma process parameters including the type of plasma gas, the plasma pressure, the plasma power and the treatment time (dose).

The reactive chemical species (radicals) formed during plasma treatment may induce surface etching through degradation of polymer [20–22] molecular chains. During this process, some derivative chemical particles are released which are mixed with the plasma. These active chemical species are responsible for the formation of new functional groups [23] formed by molecular chain scissions [24,25], substitution and recombination. Some of the free radicals are also responsible for polymerization and crosslinking. It is interesting to note that studies with 1,3-diamino propane [26] and fluorocarbon [27] films have revealed that chemical reactions can continue in the plasma-deposited films for ageing under ambient conditions from several months to two years.

Although there have been some studies [28–32] on the argon and oxygenated-argon plasma treatments on different types of COC, there has not any detailed study on the effect of ageing on

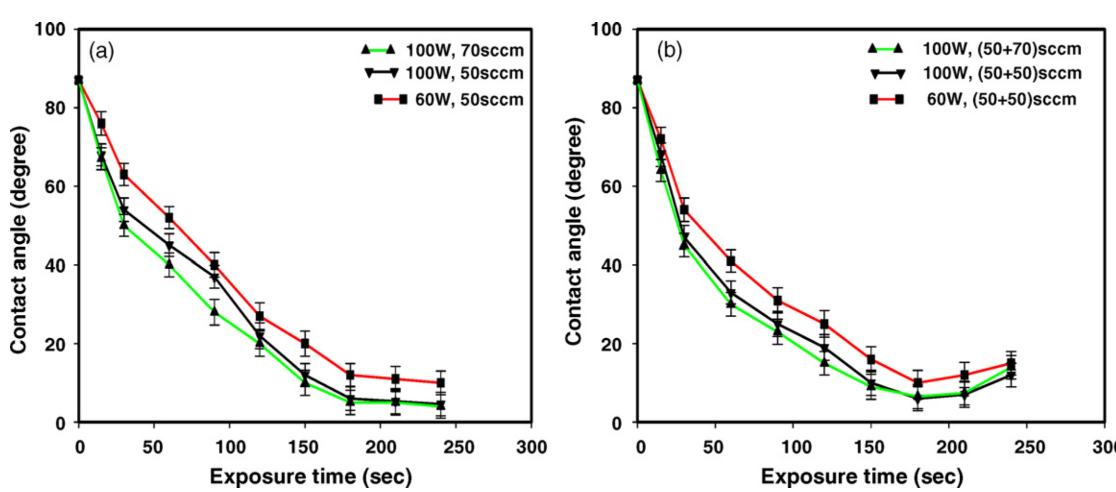

Fig. 2. Variation of contact angle (using DI water) with exposure time for different plasma power ratings in (a) argon plasma treated COC and (b) oxygenated-argon plasma treated COC substrates. Each data point shows the average and standard deviation from eight measurements.