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Surface Modification of Natural Rubber by Sulfur hexafluoride (SF_6) Plasma Treatment: A New Approach to Improve Mechanical and Hydrophobic Properties

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Abstract: Plasma treatments have faced growing interest as important strategy to modify the hydrophobic/hydrophilic characteristics of materials. However, challenges related to the plasma modification of polymers are the improvement of the chemical resistance without decreasing the mechanical resistance. In this letter, we present for the first time a plasma treatment, using Sulfur hexafluoride (SF_6), analogous to vulcanization process, of natural rubber surface, which resulted in a chemical and tension resistance improvements. The natural rubber membranes were coated with glow discharge plasmas generated in sulfur hexafluoride (SF_6) atmospheres at a total pressure of 160 mTorr and applying 70 W of radiofrequency. Plasma treatment increases the contact angles from 64° to 125° i.e. leading to a hydrophobic surface. The tension at rupture increased from 3.7 to 6.1 MPa compared to natural rubber without plasma treatment demonstrated by stress-strain investigation. These results provide a fast alternative approach to improve mechanical and chemical properties of rubber-based products.

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1. INTRODUCTION

Recently, an increasing number of researchers are shifting their attention toward the use of plasma treatment shared with polymers properties in order to develop biosensors [1], microfluidic devices [2, 3], food packages [4], systems of drug delivery [5], and enhancing of biocompatibility properties [5, 6].

Currently, the natural rubber is of growing interest owing to its potential importance on biomedical applications. The plasma treatment of rubbers has become a strategic methodology in the development of new class of materials through graft copolymerization [7-9], fluorination [10], blending [11] and layer-by-layer [12] deposition. These methodologies have provided improvements on chemical resistance [13] and antibacterial properties of latex medical gloves [14] as well as on interfacial adhesion [15, 16]. Nevertheless, no improvements on mechanical properties are reported as consequence of plasma treatment and the best results related to improvements on hydrophobic properties report contact angles ranging from 103 to 119º [10, 13].

Natural rubber (NR) has been recently subject of several researches in order to develop gas barrier, [17] or gas recognition sensors [18, 19], shape memory polymers [20] as well as thermo-mechanical actuators [21]. We have recently introduced the concept of natural rubber-based microfluidic device [22], as well as its use as microreactor for the synthesis of Fe_3O_4-Au nanoparticles [23]. Here, we report improvements on hydrophobic properties of natural rubber surface and mechanical resistance (strength) achieved using Sulfur hexafluoride (SF_6) plasma treatment. The hydrophobic properties are an important request to reduce the interaction of the samples with the microfluidic devices walls as well as an essential property to improve the chemical resistance in biomedical applications.

MATERIALS AND METHODS

Natural Rubber Membranes Preparation

Natural rubber (NR) self-standing membranes were prepared using high ammoniated latex (industrial latex - 60wt% dry

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rubber content acquired from *DLP Indústria e Comércio de Borracha e Artefatos LTDA)*. The latex beneficiated was implemented based on the natural latex and presentsseveral differences comparing different extractions *i.e.*, the latex compound depends on the climate, year period, soil components, etc.NR membranes of 0.5 mm thickness were prepared by casting latex on glass and annealing for 10 hours at 65°C.

Surface Plasma Treatment

The treatments have been performed with glow discharge plasmas generated in sulfur hexafluoride (SF_6) atmospheres at a total pressure of 160 mTorr (base pressure at 55 mTorr and SF_6 parcial pressure at 105 mTorr), applying 70 W of radiofrequency (13.56 MHz) power to the substrate holder during 3 minutes.

Characterization

The mechanical strength of the natural rubber was evaluated by stress-strain tests in which the sample was stretched at 500 mm/min using an EMIC DL2000 digital universal testing machine and using an internal deformation transducer. The sample preparation was carried out according to ASTM D412 type C.The contact angle measurements were carried out using a *Ramé Hart* device, model 100-0. Distilled deionized water and diiodomethane (CH_2I_2) were used in a nominal volume of 3.0 µL.The surface energy has been evaluated from harmonic average method using deionized water and diiodomethane as probe liquids. FT-IR spectroscopy was recorded on a Vector 22 spectrometer from Bruker, with wave number that covers the range between600 and 4000 cm^{-1} with 4 cm^{-1} spectral resolution. The normalization for relative intensity measurement in the FT-IR spectra was carried out using the 1446 cm^{-1} peak as reference.

RESULTS AND DISCUSSION

Figure **1** presents images of water and diiodomethane drops deposited onpristine (left column) and SF_6 plasma treated (right column) natural rubber surfaces.

The SF_6 plasma treatment increased the water contact angle (Table **1**) from 64.4º to 124.8º. The dissociation of SF_6 molecules through collisions with plasma electrons results in the presence of fluorine atoms in the plasma. Chemical reactions involving species on the gas phase and on the polymer surface can result on the incorporation of fluorine to the material producing a highly non-polar and, consequently, hydrophobic surface. As reported on literature [7-9, 12], the natural rubber contact angle ranges from 75 to 90º. Schlögl

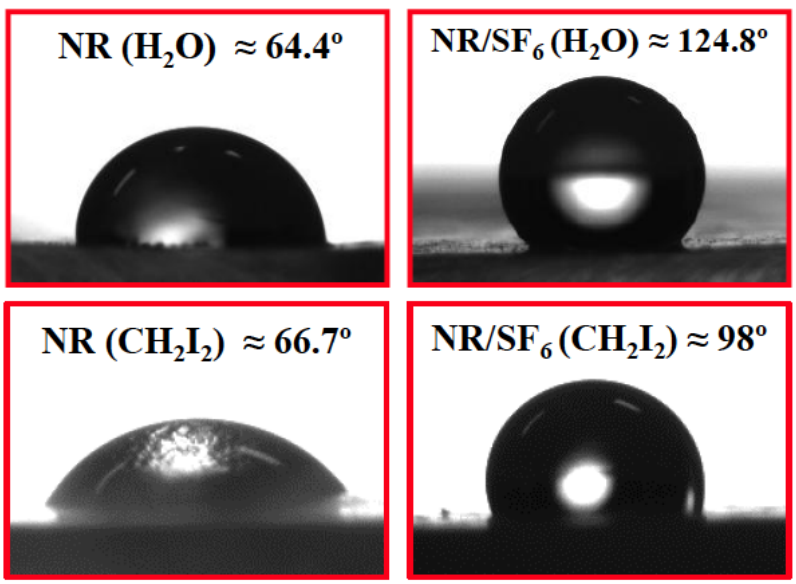

Figure 1: Images of water and diiodomethane drops on pristine and SF6 plasma treated natural rubber surfaces.

Table 1: Contact Angle and Surface Energy Measurements Comparing Natural Rubber and the NR/SF6 (Plasma Treated)

		NR		NR/SF_6	
		H_2O	CH_2I_2	H_2O	CH_2I_2
	Contact Angle	64.4º±2.9º	66.7º±2.6º	124.8º±1.5º	98.0º±4.2º
Surface Energy (dyn/cm)	***Polar Component***	16.39 ±0.37		0.04 ±0.01	
	Dispersive Component	24.74 ±0.27		9.40 ±0.29	
	Total	41.13 ±0.36		9.43 ±0.28	

and coworkers [10] reported the fluorination treatment of natural rubber surface, reaching the contact angle of 119º.

It has been reported that the contact angles of surfaces with comparable chemical resistance such as styrene-butadiene rubber (SBR) [24], latex medical gloves [13] and, ethylene propylene diene monomer (EPDM) [25] are round 108.5º, 103º, and 109º, respectively. The plasma treatment described here resulted in surfaces of natural rubber with contact angles higher than every type of rubber compared. Moreover, when diiodomethane (CH_2I_2) was used as test liquid, the contact angle increased from 66.7º to 98º as consequence of plasma treatment i.e. a significant improvement on chemical resistance for apolar reagents.

Regarding the surface energy (Table **1**), it is noticed that the NR is partially polar in nature since the polar component has considerable contribution on total surface energy. However, a polar surface is obtained after the SF_6 plasma treatment (total surface energy is quite similar to the dispersive component), resulting in an increase of hydrophobicity and a decrease on surface tension from the NR/SF_6.

Figure **2** shows results from stress-strain analysis comparing the untreated and natural rubber SF_6 plasma treated.

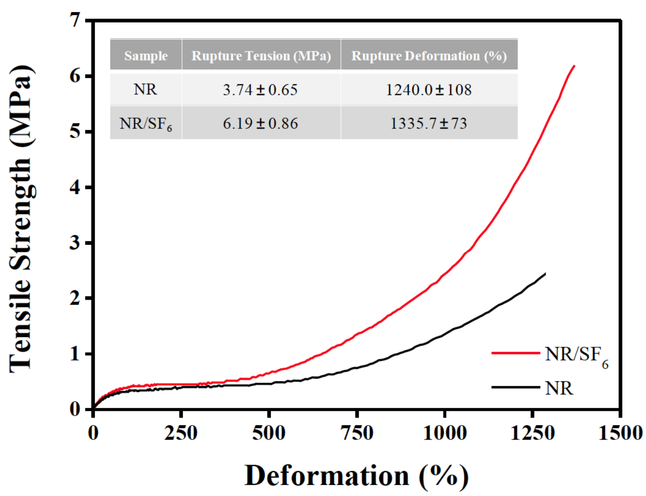

Figure 2: Stress-strain curves evaluating the mechanic properties of natural rubber (NR) and natural rubber SF_6 plasma treated (SF_6). The insettable presents the average values of tension and deformation at rupture.

It is noticed the increase of the strength resistance from 3.74 to 6.19 MPa after the plasma treatment, as well as the increase of the rupture deformation from 1240.0 to 1335.7 %. Schlögl and coworkers [10] reported an enhancement of the modulus at 500% elongation from 3.0 to 3.9 MPa attributed to the saturation of C=C bonds and the formation of fluorine groups on the rubber surface related to the fluorination treatment. Moreover, they reported the reduction of the tensile strength in 2.0 MPa as consequence of surface modification process. Since the effect of plasma is restricted just to the surface, the samples are not homogeneous and asymmetric i.e. there is a reinforced fluorine skin over the elastomeric material. However, due on porosity of natural rubber surface [26] it is possible that the plasma treatment reaching feels micrometers deep which improve the interaction of fluorine and rubber causing no differences of phases or double rupture points due the strain stress resistance from the two type of materials. Consequently, the increases on the mechanical resistance by 2.45 MPa is relevant comparing that the reported literature.

The FT-IR spectra of the NR and NR plasma treated samples are presented on Figure **3**.

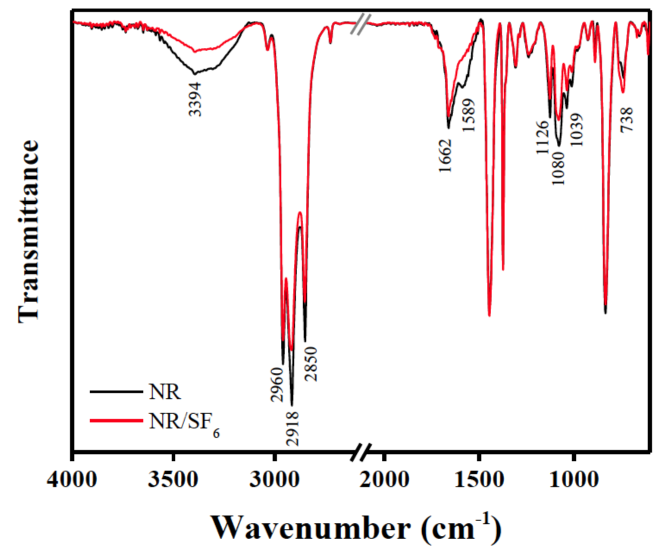

Figure 3: FT-IR/ATR spectra, comparing the structural properties of natural rubber (NR) and natural rubber SF_6 plasma treated (SF_6).

It is noticed the decrease on relative intensity of peaks related to natural rubber monomer (isoprene) at 834 cm^{-1}, associated to –CH compounds, as well as peaks at 1012, 1091, 1126, 2850 cm^{-1} associated to –$CH_2$and peaks at 1038, 2918, 2960 cm^{-1}, associated to –CH_3groups. (Table **1** - Supporting information). Shift on peaks at 2850 cm^{-1} and 2918 cm^{-1} from natural rubber to 2852 cm^{-1} and 2916 cm^{-1} for NR/SF_6, respectively can also be observed. However, it is noticed a shift of the peaks at 738 cm^{-1}(NR) to 742 cm^{-1} (NR/SF_6) and the decreasing of the relative intensity similar to the observed on the peak at 760 cm^{-1}, both attributed to the CH_2 rocking. Moreover, increasing of the relative intensity is observed at peak at 889 cm^{-1}, attributed to the -CH_3 wagging. The plasma treatment also resulted in changes on the vibrational modes from –CH_2 and –CH_3.Moreover, decreases on the relative intensity of the peaks at 1589 cm^{-1} and 1662 $cm^{-1}$are attributed to structural changes on amides or amines groups. The fluorine ions should interact with the rubber chain, mainly on hydrogen groups, generating volatile compounds and consequently creating radicals in adjacent chains. Those radicals could interact with each other resulting in reticulation (cross links formation) and, consequently creating a tridimensional structure. The reticulation process is similar to the used on peroxide vulcanization [27, 28]. Das *et al*. [29] have studied the recycling process of natural rubber vulcanized through mechanochemical devulcanization. They have associated the peak at 1540 $cm^{-1}$to stretching of CH=CH bond, which as increased conjugated double bond consequently deteriorates the mechanical properties of rubber compound. In our case, the decreasing on C=C bond could be associated to the interaction of fluorine ions with π bonds, generating radicals to the cross linking formation and, consequently, increasing the mechanical resistance. Considering the results, the peak 1540 cm^{-1} are overcome by 1589 cm^{-1} amides peak. We can attribute the modification on amides and amines groups as consequence of plasma treatment and the fluoride surface formation, which can interfere the vibrational modes measured at 3394, 2918, 1598, 1080 cm^{-1}.

CONCLUSION

This report describes a novel concept of surface modification through SF_6 plasma treatment in order to improve the natural rubber properties. The treatment lead the water contact angle of natural rubber surface to increase from 64º to 125º i.e. conferred a hydrophobic feature, as well as enhanced the strength resistance from 3.74 to 6.19 MPa. Consequently, the enhanced hydrophobic properties decreases the interaction of the samples with the microfluidic devices a recently new approach for microfluidic technology. Improves on chemical resistance, shown on contact angle increases from 67º to 98º testing by diiodomethane (CH_2I_2), could be essential in order to generate novel biomedical applications.

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SUPPORTING INFORMATION

The supporting information can be downloaded from the journal website along with the article.

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