

## The Influence of Plasma Surface Modification on Frictional Property of Natural Rubber Vulcanizates

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**ABSTRACT** : The plasma surface modification of natural rubber vulcanizate was carried out using chlorodifluoromethane in a radio-frequency (13.56 MHz) electrodeless bell type plasma reactor. The modification was qualitatively assessed by Fourier transform infrared spectroscopy. The frictional force of the plasma-treated surface was found to decrease with the time of plasma treatment. An increase in the surface polarity, as evidenced by the decrease in contact angle of a sessile drop of water and ethylene glycol on the natural rubber vulcanizate surface, was noted with the plasma modification. In the case of similar plasma treatment of glass surface, only a reduction in the polarity was observed. The use of geometric and harmonic mean methods was found to be useful to evaluate the London dispersive and specific components of surface free energy. Irrespective of the method used for evaluation, an increasing trend in the surface free energy was noted with increasing plasma treatment time. However, the harmonic mean method yielded comparatively higher values of surface free energy than the geometric mean method. The plasma surface modification was found to vary the frictional coefficient by influencing the interfacial, hysteresis and viscous components of friction in opposing dual manners.

요약: 라디오 주파수(13.56 MHz) 무전극 중형 플라즈마 반응기를 이용하여 천연고무 가교체의 표면을 클로로디플루오로메탄으로 처리하였다. FT-적외선 분광분석으로 표면개질 정도를 정성적으로 조사하였다. 플라즈마 처리표면의 마찰힘은 플라즈마 처리시간 증가에 따라 감소하였다. 고무표면에 에틸렌글리콜과 물을 떨어뜨려 접촉각을 측정된 결과 플라즈마 처리에 따라 감소하는 것으로 미루어 플라즈마 개질에 따라 표면극성이 증가하는 것을 확인하였다. 유리판 표면을 동일조건으로 플라즈마 처리할 경우는 극성의 감소만이 확인되었다. 표면자유에너지의 London 비극성 및 극성요소를 계산하는데 있어서 기하평균법과 조화평균법이 유용한 것으로 확인되었다. 평균방법에 관계없이 플라즈마 처리시간이 증가함에 따라 표면자유에너지는 증가하였다. 그러나 조화평균법으로 계산된 자유에너지가 기하평균법으로 계산된 값에 비해 상대적으로 높았다. 플라즈마 표면개질은 마찰의 계면, 히스테리시스, 점성요소들에 영향을 미침으로써 마찰계수를 변화시키는 것으로 나타났다.

*Keywords* : plasma surface treatment, natural rubber, frictional coefficient

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## I. Introduction

All elastomers have their own inherent bulk properties which make them most fit for a particular application, for example, the strain crystallizing ability of natural rubber, flame retardancy of chloroprene rubber, oil resistance of nitrile rubber, ozone resistance of ethylene propylene diene rubber, low air permeability of butyl rubber etc. Most of these elastomers, especially the natural rubber has the property of tear and wear during service. This arises from the adhering and peeling mechanism resulting from the adhesive nature of the elastomer.<sup>1,2</sup>

The simplest solution to reduce the wear may be to apply some lubricant such as silicone oil, but it cannot be considered as a safe and permanent solution to the problem of wear. In the case of rubber vulcanizates, a more reliable solution is the modification of their surface by depositing thin polymer films. This can be done by mainly two ways. The first method is to carry out wet processes like Langmuir-Blodgett, spreading, dipping or solvent casting methods. The second method is to adopt dry processes such as physical vapor deposition (PVD) and chemical vapor deposition (CVD). Among CVD methods, the plasma polymerization deserves a prominent place, as it can offer very thin films free of pin holes.<sup>3</sup>

Plasma polymerization involves a specific type of plasma chemistry with reactions between plasma species, between plasma and surface species and between surface species.<sup>4</sup> The starting gases need not necessarily contain certain functional groups that are usually required in conventional polymerization. In the plasma polymerization, deposition of a thin polymer film on the rubber surface reduces the coefficient of friction, resulting in an improvement in the wear characteristics of the material. Plasma-polymerized films are chemically inert, insoluble, mechanically tough and thermally stable. The films are highly coherent and they can adhere to a variety of substrates such as conventional polymers, glasses and metals. Plasma polymerization can be carried

out without any solvent. Thickness of the film can be very small as 500 Å to 1 μm. The thin polymer film formed in this technique is chemically bonded to the rubber surface and the film tribology can be tailored by altering the monomer gas and plasma treatment conditions. Another advantage of this method is that only the surface properties are changed while the rest of the bulk properties remain intact.<sup>5</sup>

The plasma polymerization of fluorocarbons<sup>6</sup> produces materials with low energy surface, which find applications such as hydrophobic, protective and biocompatible coatings.<sup>7-9</sup> Even though some initial works<sup>10</sup> reported the inability of saturated monomers to get involved in plasma polymerization, later works<sup>11</sup> with hexafluoroethane (HFE) revealed that even saturated monomers can be made to react if the substrate is capable of participating in the deposition process. The fluorocarbon plasmas can show a dual nature in which there is a balance between etching by highly reactive fluorine atoms and polymerization.<sup>12</sup> O'Keefe and Rigsbee<sup>10</sup> studied the mechanism using transmission electron microscopy and revealed that the initial phase in plasma polymerization occurs through a localized growth of islands of fluorocarbon on the substrate, thus supporting the activated growth model put forward by d'Agostino et al.<sup>13</sup> Therefore, it can be stated that ablation and polymerization (CAP) can occur in a competitive manner in plasma polymerization and the balance depends on the overall system conditions of the plasma.<sup>14</sup>

In this paper, the radio-frequency plasma polymerization coating of chlorodifluoromethane on to natural rubber vulcanizate sheets is described. The characterization of the plasma-polymerized film was done by Fourier transform infrared spectroscopy and the influence of plasma coating on the frictional forces of the vulcanizate surfaces was assessed.

## II. Experimental

The details of the materials and the experimental

**Table 1. Basic formulation**

Ingredients	Loading level, phr
NR (SMR CV60)	100
ZnO	3
Stearic acid	1
TDQ	1
TBBS	1
Sulfur	2

procedures used in the study are given below;

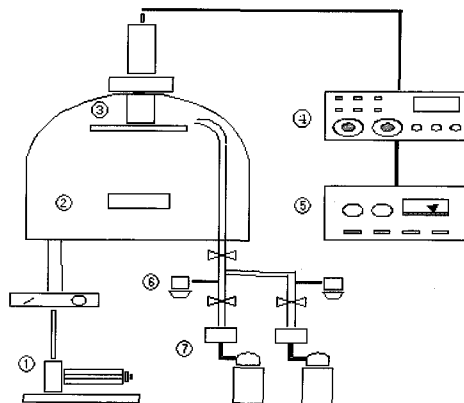
- Natural rubber (SMR 60CV) was obtained from Malaysia. Other rubber chemicals for compounding were obtained from various rubber chemical suppliers, such as Zinc oxide from Hanil Co. Korea, Polymerized 2,2,4-trimethyl-1,2-dihydroquinone (TDQ), N-t-butyl-2-benzothiazole sulfonamide (TBBS) from Flexsys, USA.
- Natural rubber compounding, as per the recipe given in Table 1, was carried out in an internal mixer (Haake Rheocord 9000, Germany) at a rotor speed of 50 rpm at 100 °C and then sheeted out in a two roll mixing mill (Farrel 8422, USA), according to ASTM D3182 and D-3184.
- Cure behavior of the mixed rubber compounds was studied using an oscillating die rheometer (ODR, Alpha Technologies, USA).
- The vulcanization to optimum cure was carried out in a heated press (Carver WMV50H, USA) for 30 min at a pressure of 3 MPa. Vulcanized rubber sheets of thickness 2 mm were obtained.

### 1. Plasma treatment procedure

The schematic diagram of the instrument used for plasma polymerization coating is given in Figure 1. The cured rubber sheets were dried at 50 °C for 48 hrs in a vacuum oven. Then the plasma surface modification of the cured rubber sheets was carried out in the presence of chlorodifluoromethane at 50 °C in a radio-frequency electrode-less bell type plasma reactor (HPPS-300, Hanat, Korea) at 13.56 MHz and a maximum instrument limit power of 150 W. The treatment time was varied as 0.5, 1, 2, 5,

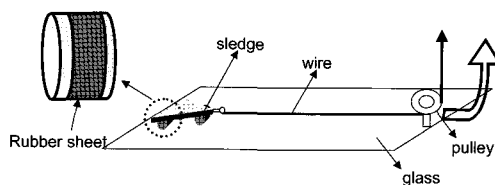
10 and 60 minutes. During the treatment, a vacuum of  $10^{-3}$  torr and a gas pressure of 40 mtorr and a plasma power of 20 W were applied according to the reported procedure.<sup>15</sup> The qualitative analysis of the plasma polymerization coating was done using FTIR (Jasco 300 E, Japan) spectroscopy at 64 scans under 2 torr pressure. Instead of directly taking the FTIR of the plasma-treated natural rubber vulcanizate, FTIR of plasma treated potassium bromide (KBr) powder (after drying in a vacuum oven at 100 °C for 12 h), was taken under optimized conditions of plasma polymerization.

Frictional characteristics were determined by using a friction tester, as depicted in Figure 2. It consisted of a triangular platform with wheel like structures in the three corners. The wheel at one corner is rotatable like wheel of a vehicle. A plasma modified rubber strip (one each) of dimension 10



**Figure 1.** Schematic diagram of plasma polymerization instrument

1. Vacuum pump
2. Rubber vulcanizate
3. Electrode
4. Impedance matching unit
5. Power supply unit
6. Pneumatic valve
7. MFC



**Figure 2.** Schematic diagram of friction tester

X 70 X 1 mm was attached to the bottom part of the other two remaining wheels. The whole instrument was dragged for 2 min over a glass surface with the help of an instron machine (STM-10, United, USA) keeping the plasma modified surface touching the glass surface. The speed of dragging used was 50 mm/min. The stress value recorded on the instron at the end of 2 minutes was taken as the frictional force. The experiment was repeated three times for each sample and the average value was accepted.

In order to elucidate the scientific reason for the variation in frictional forces resulting from plasma surface modification, the contact angle of a sessile drop of water and ethylene glycol on the unmodified and plasma modified natural rubber vulcanizate surface was analyzed at a temperature of  $20 \pm 1$  °C. A contact angle analyzer (Kyowa Inetrace Science Co Ltd) was used for this purpose. The sessile liquid drop size was 10  $\mu$ l and the measurement was done after giving three minutes as conditioning time. Contact angle measurement of the sessile drop of liquid was carried out on both natural rubber vulcanizate and glass surfaces. The results from three measurements were averaged to get the final value.

The hardness of the samples also was measured according to ASTM D-2240-81 using a Shore A type durometer (Kobunshi Keiki Co., Japan).

### III. Results and discussions

#### 1. Qualitative analysis of plasma modified surface

The FTIR spectrum of  $\text{CHClF}_2$  plasma-treated KBr is given in Figure 3. The absorption peaks at 600-800 and 1000-1400  $\text{cm}^{-1}$  reveal the presence of C-Cl bonds and the peak at 1173  $\text{cm}^{-1}$  can be attributed to the presence of C-F bonds. It is to be noted that these peaks are absent in the unmodified sample. Also, it is important to notice that the intensity of the respective peaks obtained from the modified samples increases with the increase in the

plasma treatment time. All these facts clearly confirm the occurrence of plasma surface modification using  $\text{CHClF}_2$ .

#### 2. Frictional force determination

The frictional forces observed for the untreated and plasma-treated samples are presented in Figure 4. It can be seen from the figure that the frictional force initially increases with travelling time and becomes constant. Also it is interesting to note that in the case of untreated samples, the fluctuation in the maximum frictional force is higher. This is due to the stick-slip phenomena which takes place during the frictional movement of elastomer vulcanizate on other surfaces. In the case of plasma-

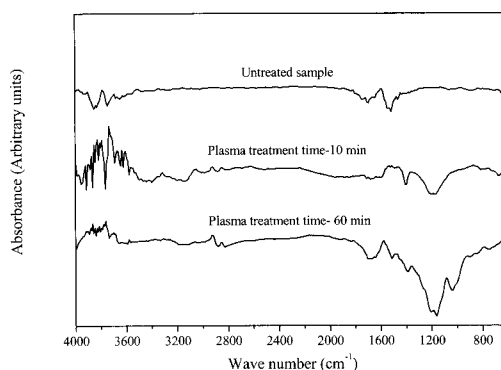


Figure 3. FTIR Spectra of plasma treated KBr samples

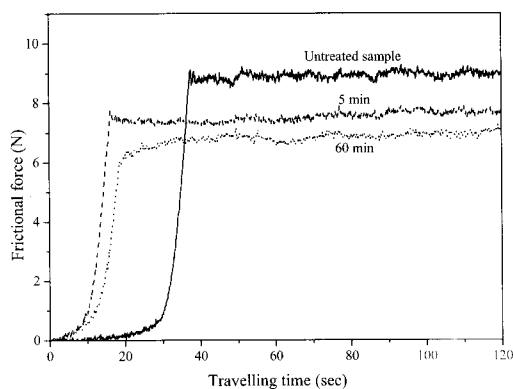


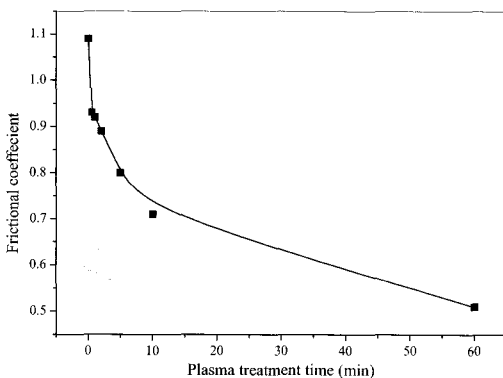
Figure 4. Variation of frictional force with travelling time for various plasma treated rubber vulcanizates

modified samples, the fluctuation in the maximum frictional force is comparatively less. This points out that the smoothed surface resulting from plasma modification considerably reduces the stick-slip phenomena. Also, the travelling time required for the stabilization of frictional force is less for plasma treated samples. In the case of untreated natural rubber vulcanizate, the stabilized frictional force is attained after a travelling time of 35 seconds while in the case of plasma-treated vulcanizate (treatment time- 5 min), this is achieved after 15 seconds. In the case of the natural rubber vulcanizate plasma-treated for 60 min, the stabilized frictional force is achieved after the travelling time of 20 seconds. These observations are also in agreement with our earlier studies<sup>16</sup> on the HCl treatment of natural rubber vulcanizate surface. A similar decrease in the maximum frictional force with HCl treatment time was observed.<sup>16</sup>

Another parameter called frictional coefficient ( $\mu$ ) can be calculated using the equation (1)

$$\mu = F / N \quad (1)$$

where, F is the maximum stabilized frictional force and N is the normal force which is kept constant (5 Newton) in these experiments. The variation of frictional coefficient ( $\mu$ ) with plasma treatment time is presented in Figure 5. Generally, it can be



**Figure 5.** Variation of Frictional Coefficient with plasma treated time

observed that the frictional coefficient reduces with plasma treatment time. This observation can be explained based on the concept of frictional force components.<sup>17</sup> The total frictional force experienced by a viscoelastic material such as vulcanized rubber sheet has contributions from three different components. These are the interfacial or adhesive component ( $F_i$ ), hysteresis component ( $F_h$ ) and the viscous component ( $F_v$ ). The equation describing this concept is given below.

$$F = F_i + F_h + F_v \quad (2)$$

The interfacial or adhesive component is determined by the polarity of the interface. More precisely, in the present case, it is determined by the change in the polarity of the natural rubber vulcanizate surface with plasma treatment relative to the polarity of the glass surface. The hysteresis component,  $F_h$  characterizes the energy losses associated with bulk deformation. The viscous component ( $F_v$ ) arises from the viscous dissipation in the lubricant. For the plasma-treated samples of natural rubber vulcanizates, as the plasma treatment time increases from 0 to 0.5 minute, a drastic drop in frictional coefficient can be observed. This has contributions from all the three components discussed above. Owing to the increased polarity of the plasma-treated natural rubber vulcanizate, its adhesion with the polar glass surface increases and this causes increase in the friction. On the other hand, the enhancement in the surface hardness of the vulcanizate due to plasma treatment (will be discussed later in the manuscript) reduces the deformation-recovery phenomena. This enhanced hardness reduces the hysteresis component of friction. In addition to this, the smoothed surface after plasma treatment creates a lubricating effect between the contacting surfaces. But due to the physical absence of a real lubricant in between the contacting surfaces, the concept of viscous dissipation in the lubricant becomes irrelevant and therefore the viscous component of friction also

decreases. As a result of the supremacy of hysteresis and viscous components at this plasma treatment time (0.5 minute), the total frictional force is decreased. When the plasma treatment time increases further, the contribution of hysteresis and viscous components of friction to the frictional coefficient again increases and therefore the value drops regularly.

The smoothed surface (or in other words the surface roughness) also has dual effect. The reduction in the surface roughness due to plasma treatment increases the true contact area between the rubber vulcanizate and glass surface. An increase in the friction coefficient can be expected from this phenomenon. But the reduction in surface roughness decreases the deformation tendency of the rubber and this finally results in the reduction of the visco-elastic loss of energy and ultimately, the frictional coefficient.

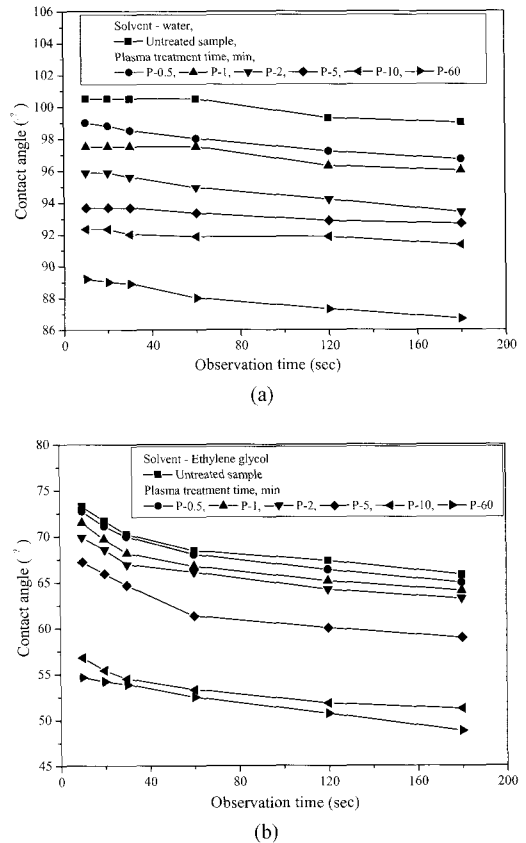
### 3. Wettability of a sessile drop of liquid

The quantitative assessment of the wetting characteristics of a liquid on a solid surface is made by measuring the contact angle of the liquid on the solid surface. If the liquid is polar and the surface modification of the solid increases the polarity of its surface, then the liquid will tend to wet the surface more and this leads to a reduction in the contact angle. A liquid which wets the surface extensively will readily spread on the surface resulting in a zero contact angle. In other words, the contact angle of the sessile drop of liquid on the solid surface is a measure of the hydrophobicity / hydrophilicity of solid surfaces. Water and ethylene glycol are often used for the measurement of contact angle and their surface energy characteristics<sup>18</sup> are given in Table 2. The variation in contact angle of water and ethylene glycol with the time of observation is presented in Figures 6a and b. As the observation time increases, a progressive decrease in contact angle values is observed in the case of ethylene glycol while in the case of water,

**Table 2. Surface free energy characteristics of liquids, measured at 20°C**

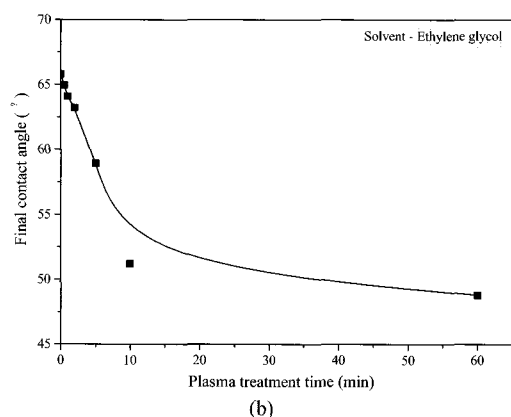
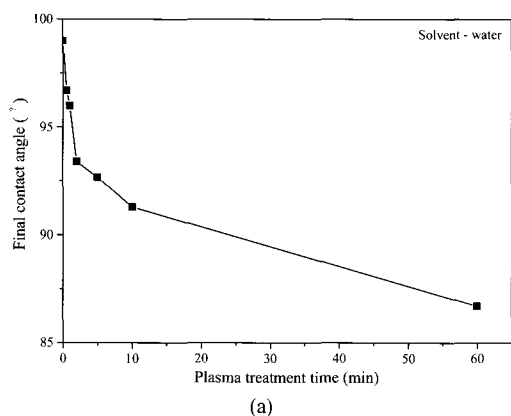
Liquid	$\gamma_L^L$ (mJ/m <sup>2</sup> )	$\gamma_L^{SP}$ (mJ/m <sup>2</sup> )	$\gamma_L$ (mJ/m <sup>2</sup> )
Water	10.8	61.2	72
Ethylene glycol	31	16.7	47.7

$\gamma_L^L$ - London dispersive component,  
 $\gamma_L^{SP}$ - Specific or polar component  
 $\gamma_L$ - Surface free energy (Total)



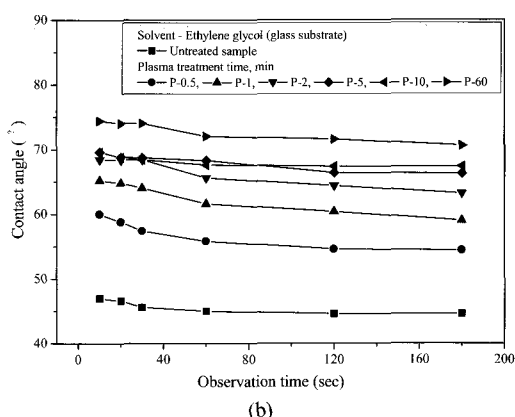
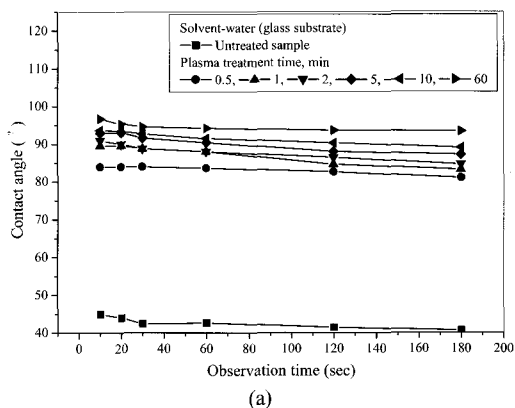
**Figure 6.** Variation of contact angle with plasma treatment time of rubber vulcanizates (a. sessile drop of water, b. sessile drop of ethylene glycol)

such an observation is not seen. The final value of contact angle at the end of 180 seconds is plotted as a function of plasma treatment time in Figures 7a and b. A regularly decreasing trend in the contact angle values is observed in the case of water and



**Figure 7.** Variation of final contact angle with plasma treated rubber vulcanizates (a. sessile drop of water, b. sessile drop of ethylene glycol)

ethylene glycol. The change in contact angle with the observation time and plasma treatment time indicates the increased wetting of these polar liquids on the newly created polar surface of plasma-treated natural rubber vulcanizate. These results give evidence for the successful plasma treatment process on the natural rubber vulcanizate. For a comparison with the plasma treatment on the glass surface, contact angle measurements on unmodified and plasma-modified glass surface also are carried out. These results are presented in Figures 8 (a&b) and 9 (a&b). Similar to the earlier observation with natural rubber vulcanizate, a decrease in the contact angle with observation time is noted in the case of glass surface also. But in the case of plasma modi-

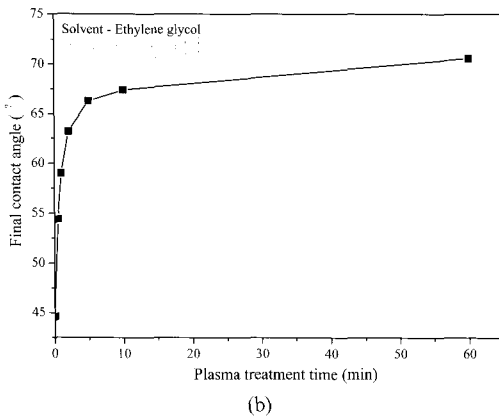
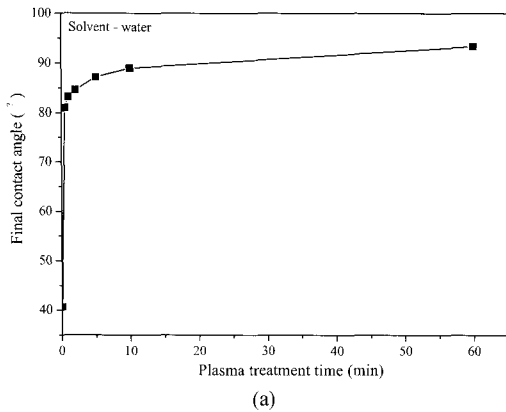


**Figure 8.** Variation of contact angle with plasma treated glass (a. sessile drop of water, b. sessile drop of ethylene glycol)

fied glass surface, an increase in contact angle is observed with plasma treatment time. This is different from the observation in the case of natural rubber vulcanizate and is due to the lowering of the high initial polarity of the glass surface. The decreased polarity of the glass surface with plasma treatment reduces the wetting of the liquids on the glass surface. This leads to an increase in contact angle values with plasma treatment time.

#### 4. Calculation of London dispersive and specific components of surface free energy-comparison of different procedures

London dispersive and specific components of surface free energy were calculated using the



**Figure 9.** Variation of final contact angle with plasma treated glass (a. sessile drop of water, b. sessile drop of ethylene glycol)

geometric mean method<sup>19</sup> reported by Owens and Wendt<sup>20</sup> and also by Fowkes.<sup>21</sup>

$$\gamma_L(1 + \cos \theta) = 2(\gamma_L^L \gamma_S^L)^{1/2} + 2(\gamma_L^{SP} \gamma_S^{SP})^{1/2} \quad (3)$$

The other method used is the harmonic mean method<sup>22</sup> as given by the equation;

$$\gamma_L(1 + \cos \theta) = 4[\gamma_L^L \gamma_S^L / (\gamma_L^L + \gamma_S^L) + \gamma_L^{SP} \gamma_S^{SP} / (\gamma_L^{SP} + \gamma_S^{SP})] \quad (4)$$

Here the two test liquids, water and ethylene glycol of known dispersive and polar components (as shown in Table 2) are used to measure their contact angles ( $\theta$ ) on the natural rubber vulcanizate

**Table 3a.** London dispersive and specific components of surface free energy from geometric mean equation

Sample	$\gamma_s^L$ (mJ/m <sup>2</sup> )	$\gamma_s^{SP}$ (mJ/m <sup>2</sup> )	$\gamma_L$ (mJ/m <sup>2</sup> )
Untreated sample	21.25	3.78	25.03
Sample-treated 0.5 min	20.29	4.72	25.01
Sample-treated 1 min	20.47	4.92	25.39
Sample-treated 2 min	19.28	6.17	25.45
Sample-treated 5 min	22.36	5.79	28.15
Sample-treated 10 min	28.08	5.16	33.24
Sample-treated 60 min	26.08	7.41	33.49

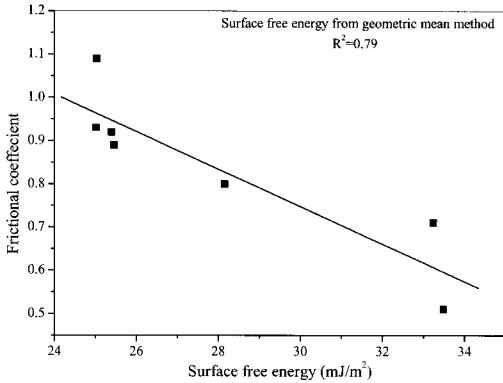
**Table 3b.** London dispersive and specific components of surface free energy by harmonic mean equation

Sample	$\gamma_s^L$ (mJ/m <sup>2</sup> )	$\gamma_s^{SP}$ (mJ/m <sup>2</sup> )	$\gamma_L$ (mJ/m <sup>2</sup> )
Untreated sample	15.80	10.23	26.03
Sample-treated 0.5 min	15.25	11.35	26.6
Sample-treated 1 min	15.38	11.63	27.01
Sample-treated 2 min	14.77	12.95	27.72
Sample-treated 5 min	16.61	12.88	29.49
Sample-treated 10 min	19.99	12.79	32.78
Sample-treated 60 min	19.17	15.12	34.29

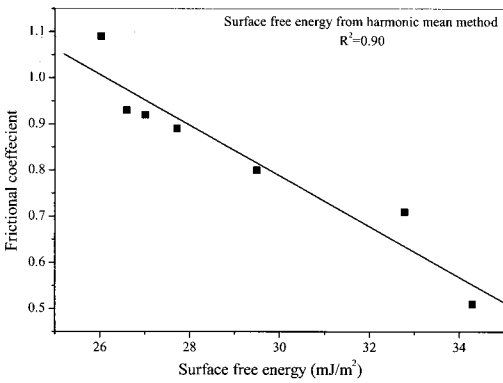
surface. The obtained data are substituted in the above equations (3) and (4) and the resulting two simultaneous equations are solved to get the dispersive and polar components of surface energy of the solid.

The values of London dispersive and specific components of surface energy calculated using the above two methods are shown in Table 3a and b. In the case of geometric and harmonic mean methods, even though an increasing behavior in London dispersive and specific components with plasma treatment time is observed, it is in an irregular manner. However, both methods present an increasing trend in the total free energy with plasma treatment time. A comparatively higher value of total surface free energy predicted by harmonic mean method is supported by the previous



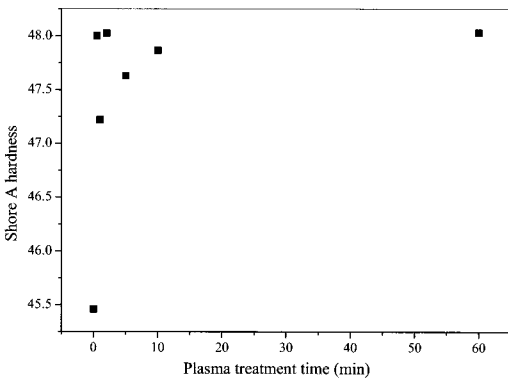


(a)

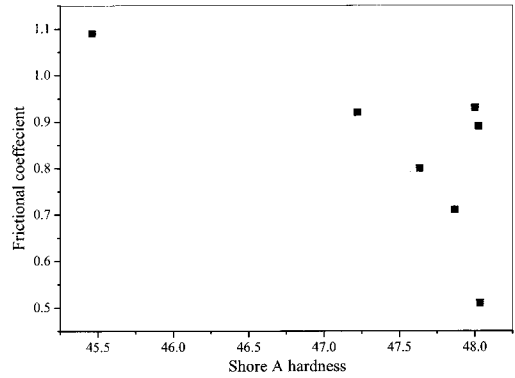


(b)

**Figure 10.** The relationship between frictional coefficient and surface energy (a. geometric mean method, b. harmonic mean method)



**Figure 11.** Change in Hardness of the rubber vulcanizates with plasma treatment time



**Figure 12.** Inverse relationship between frictional coefficient and hardness of the rubber vulcanizates

literature.<sup>23</sup>

In order to investigate the relationship between the frictional coefficient and surface energy, they are plotted in to a graph. It can be seen from Figure 10a and b that the frictional coefficient drops with surface free energy. Linearity can be claimed for the plots only to some extent, as supported by correlation coefficient values of 0.79 and 0.90 in the case of geometrical and harmonic mean methods respectively.

The relations between plasma treatment time, hardness and frictional coefficient are presented in Figure 11 and 12. With increasing plasma treatment time, an increase in Shore A hardness is observed (Figure 11), while an inverse relation between the hardness and frictional coefficient also can be seen in Figure 12.

#### IV. Conclusions

The plasma surface modification is a versatile tool to vary the surface characteristics of many materials in order to improve their performance in various uses. In this paper, the studies on the plasma surface modification of natural rubber vulcanizate using chlorodifluoromethane were reported. An electrodeless bell type plasma reactor at radio-frequency of 13.56 MHz was employed for the treatment. The plasma modification was confirmed by using Fou-

rier transform infrared spectroscopy. A reduction in the frictional force of the plasma-treated surface was observed with the time of plasma treatment. The trends observed in the variation of contact angles using sessile drop of water and ethylene glycol indicated the increased polarity of the natural rubber vulcanizate as well as the decreased polarity of glass surface due to plasma treatment. The total surface free energy, calculated from London dispersive and specific components of free energy using geometric and harmonic mean methods, showed a general increasing trend with increasing plasma treatment time. An inverse relation between frictional coefficient and surface free energy was also observed from the studies. The plasma treatment improved the hardness of the natural rubber vulcanizates. Also, the frictional coefficient was found to inversely vary with the hardness of the rubber vulcanizates.

### Acknowledgement

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