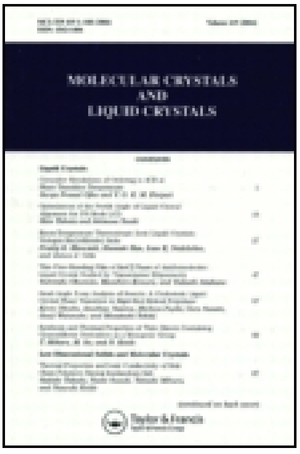

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Surface Modification of EPDM Rubber by Reactive Argon-Oxygen Plasma Process

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The ethylene-propylene diene monomer (EPDM) rubber is an important material for rocket engine technology due to its thermal and mechanical characteristics. The improvement of the adhesion characteristics of EPDM on other kinds of polymers, using plasma technology, has been the major subject of many research works carried out during the last years. In this work, the EPDM surface activation process was carried out in a reactive ion etching reactor (RIE) operated at 13,54 MHz using pure oxygen and a gas mixture of argon and oxygen. These essays were performed varying the process pressure from 70 mTorr to 1000 mTorr, process time from 1min to 10min and RF power input from 50W to 200W.The surfaces of the treated samples were analyzed by Fourier transform infrared attenuated total reflection spectroscopy (FTIR–ATR). The evolution of the C-OH, and C=O and R-O chemical groups were observed as a function of the plasma process parameters. The analysis of the IR spectra showed that there are experimental condition of the process in which the production of new radical groups on this rubber surface is maximized.

Keywords: EPDM rubber; Plasma treatment; FT-IR; RIE

1 - INTRODUCTION

Recently, many methods have been applied to alter the physical and chemical properties of polymer material surfaces [1,2]. The most widely used surface modification techniques involve either chemical treatments from solutions, photo-irradiation or treatments with many type of ionized gases produced by glow or corona discharges [3,4,5]. The plasma treatment as become increasing more important owing to their very high efficiency and operational simplicity, due to the absence of organic solvents or chlorinated products (in contrast with the use of primers) which no hazardous by-products createt [6], but the main disadvantage of this technique is that it requires a vacuum system, which increases the cost of operation [7].

One of the main interests of plasma treatment of polymers is to improve their adhesive properties. For this application, an ideal plasma treatment should only modify the polymer surface without affecting their bulk properties, specially the cohesion strength of bulk at the near surface sites. Therefore a good plasma treatment has to produce a suitable surface to enhance its adhesion without involving degradation of the surface inner regions. The optimal adhesion strength is limited by the smallest intrinsic cohesion strength of the bulk and the surface region of the polymer [8,9,10].

As often shown, the occurrence of active oxygen-containing groups on a polymer surface is essential for adhesion, specially in the case of an epoxy-containing adhesive [11]. The chemical composition and concentration of surface functional groups created by plasma assisted processes depend on the gas nature, the polymer substrate characteristics and the process parameters as electric power, gas flow, pressure and residence time [9]. The formed new functionalities improve the surface hydrophilicity, hydrophobicity, biocompatibility, antistatic, colorability, conductivity and adhesion characteristics of many types of polymers [12,13].

Although plasma aided methods require investment in equipments, is truly a scientific method which minimize the labor for surface preparation, i.e., it eliminates bond surface preparation as an art and make it a science. In addition, plasma surface treatment takes advantage in four major chemical aspects considering the substrate preparation ablation (micro-etching), surface cleaning, cross-linking, and surface activation [10,14]. A number of polymers, especially rubbers, requires special surface treatments to achieve a satisfactory level of adhesion, and more, the adhesion problems in rubber are usually related to the type of additives used during the rubber formulation (antioxidants, mold-release agents), which can migrate to the surface, and at the adhesive joint surface can contribute to form a lack of adhesion [15]. The surface of vulcanized EPDM rubber is highly hydrophobic and so it is not suited for a number of potential applications, in particular, for to the polyurethane liner of solid rocket propellants. In this case, plasma treatment can be a very attractive process, because it can efficiently increase the surface energy oxidizing the surface, introducing polar groups and producing or enhancing the surface roughness [10,16,17].

In this paper a reactive ion etching plasma system was used to promote the activation of the surface of EPDM rubber. The samples were analyzed by Fourier transform infrared attenuated total reflection spectroscopy (FTIR – ATR). The evolution of the C-OH, and C=O and R-O chemical groups were observed as a function of the plasma process parameters.

2 – EXPERIMENTAL SECTION

2.1. Material

The EPDM (ethylene-propylene norbonene rubber) used in this work had the relation ethylene/propylene: 60/40 and was vulcanized with sulfur, and contain carbon black as filler, as well as zinc oxide, stearic acid, antioxidant, plasticizer, accelerators of vulcanization also were introduced in this formulation. The ASTM D 3182 Standard procedure for mixing compounds was used. The samples were vulcanized for 12 min by hot pressing at 150 °C to form about 2mm thick rubber sheets.

In the present work, all the samples were stored in a desiccator after surface treatment had been completed until they were analyzed. The samples were analyzed within 24 hours after the plasma treatment.

2.2. FTIR – ATR analysis

The literature indicates the strength and suitability of FTIR, coupled with appropriate experimental techniques, such as ATR, diffuse reflectance (DRIFT), photo-acoustic (PAS) for surface studies [19]. The selection of a specific technique for a particular surface analysis depends upon factors, such as sample nature and morphology, and required sensitivity. In ATR method, it is only necessary to maintain good contact between the sample and the ATR crystal to obtain good quality spectra when used for others rubber-like polymers [11,20]. Then, if the quality of the optical contact is ensured by the good elasticity of samples of EPDM the FTIR-ATR spectroscopy method can be an excellent choose to detect the presence, of oxygen-containing groups and its concentration variation on a rubber surface, after each plasma treatment [21].

The surface atomic composition of plasma-treated EPDM were analyzed using the FTIR with a SPECTRUM 2000 PERKIN-ELMER spectrometer, with ATR accessory on Ge crystal ($\alpha = 45^0$), resolution 4 cm^{-1}; gain 1; spectral range 4000 to 600 cm^{-1}; 40 scans. This technique was used to characterize all the samples of this work. The spectra were compared with a non-treated sample. The most important regions of the spectra for these analyses are show in (table 1).

TABLE 1. Regions of the spectra observed in this work.

Region (cm^{-1})	**Groups**
3500 – 3200	-OH
1608 – 1597	C=C and –COOH
1245 – 1144	-C-O

2.3. Plasma treatment

EPDM rubber samples were plasma-treated in a home-built RIE reactor where power applied at 13,54 MHz [18]. The experiments were performed varying the process pressure from 70 mTorr to 1000 mTorr, RF power input from 50W to 200W, and processing time from 1min to 10 min, as shown in (table 2). In order to investigate the influence of the plasma parameters on the superficial modifications, the samples were divided in three batches. In the fist batch of samples, the gas used in the processes was pure oxygen. These samples were treated at different values of processing time and rf power. In the second batch of samples, argon gas was added into the chamber and the influence of the rf power on the FTIR spectra was studied. Finally, in the third batch, the total gas flow (Ar + O_2) was decreased and the role of the pressure on this process was also studied.

TABLE 2. Conditions of the RIE plasma used in the treatments of EPDM/B samples

Sample Number	Gas Mixture	Total Gas Flow (sccm)	Partial Gas Flow (sccm)		Pressure (mTorr)	RF Power input (W)	Processing time (min)
			O_2	Ar			
1	O_2	60	---	---	150	50	**1**
2	O_2	60	---	---	150	50	**5**
3	O_2	60	---	---	150	50	**10**
4	O_2	60	---	---	150	**100**	10
5	O_2	60	---	---	150	**200**	10
6	O_2/Ar	60	40	20	150	**50**	10
7	O_2/Ar	60	40	20	150	**100**	10
8	O_2/Ar	60	40	20	150	**200**	10
9	O_2/Ar	3	2	1	**70**	50	10
10	O_2/Ar	3	2	1	**100**	50	10
11	O_2/Ar	3	2	1	**150**	50	10
12	O_2/Ar	3	2	1	**200**	50	10
13	O_2/Ar	3	2	1	**500**	50	10
14	O_2/Ar	3	2	1	**1000**	50	10

3 - RESULTS AND DISCUSSION

3.1. First batch of samples - treatments were performed using only oxygen as gas discharge. The effects of the processing time and rf power on the superficial modifications were studied. The experimental conditions of these tests are presented in Table II, and the FTIR spectra are presented in Figure 1 and 2.

Figure 1 shows the FTIR-ATR spectra of vulcanized EPDM/B surface before and after the RIE plasma treatment for different processing times from 1 min to 10 min, for 50W input rf power. There is an increase in the intensity of the three regions of the spectra when the processing time increases.

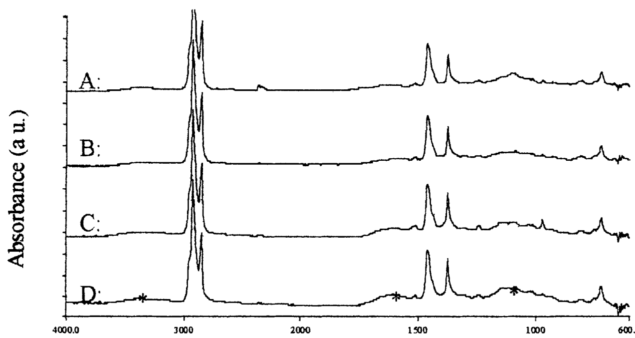

FIGURE 1. Overlaid FTIR-ATR spectra of EPDM/B before and after plasma treatment by RIE, for different processing times: (A) EPDM/B reference, (B) sample 1, (C) sample 2, (D) :

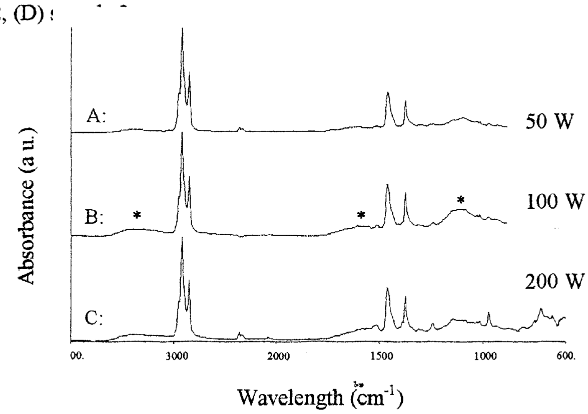

FIGURE 2. Overlaid FTIR-ATR spectra of EPDM/B before and after plasma treatment by RIE, for different RF power input: (A) EPDM/B reference, (B) sample 4, (C) sample 5.

3.2. Second batch of samples - argon gas is added to oxygen. Tests were performed during 10 minutes and the FTIR spectra of these samples were also obtained. Figure 3 shows that the best value of power, in which the intensity of the bands are maximized, is 50 W. Then, the addition of argon in the discharge promotes a reduction in the level of the rf power needed to optimizing the process. This phenomenon is probably related to the increase of the roughness of the rubber caused by ion argon bombardment during the sputtering process.

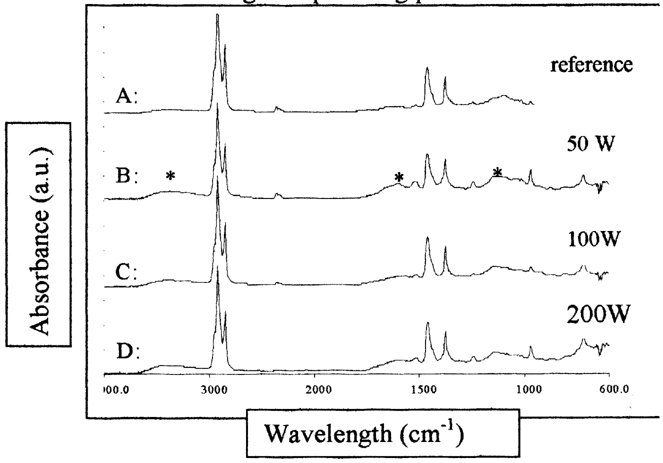

FIGURE 3. Overlaid FTIR-ATR spectra of EPDM/B before and after plasma treatment by RIE, for different RF power: (A) EPDM/B initial, (B) sample 6, (C) sample 7, (D) sample 8.

Figure 2 shows that there is an optimal value of rf power (100W) for which the intensity of the spectra is maximized. This phenomenon is probably caused by change in the reactivity of the plasma formed.

3.3. Third batch of samples - the influence of the gas pressure is studied. Figure 4 shows the FTIR-ATR spectra of vulcanized EPDM/B surface before and after the RIE plasma treatment. All the parameters were maintained constant, except the pressure, that was varied from 70 mTorr to 1000 mTorr. From these figure, it is possible to observe that the modifications in the spectra caused by the plasma treatment increase with the pressure, until 150 mTorr. After this pressure the intensity of the bands decreases. This phenomenon is probably related to the maximization of the plasma density which is governed by the balance between ionization rate and recombination.

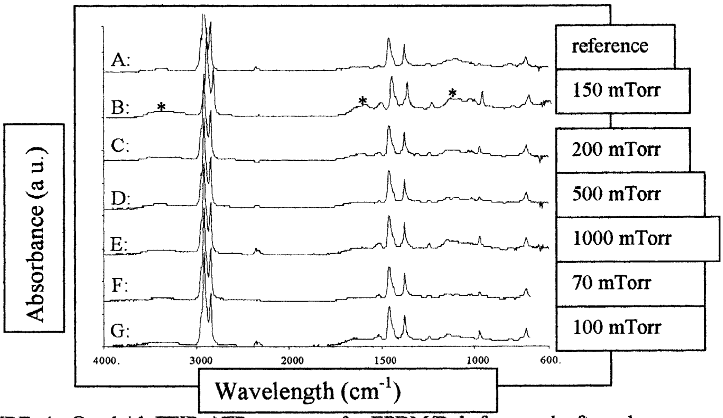

FIGURE 4. Overlaid FTIR-ATR spectra of EPDM/B before and after plasma treatment by RIE, for different gas pressure: (A) EPDM/B reference, (B) sample 11, (C) sample 12, (D) sample 13, (E) sample 14, (F) sample 9, (G) sample 10.

4 - CONCLUSION

The EPDM/B surface samples treated by rf plasma were analyzed by FTIR–ATR with a view to study the oxygen containing radical groups formation at their surfaces. It was observed the formation of OH, COOH and C-O chemical groups for all operational conditions of the discharge, but for special values of these conditions the intensity of bands (in the FTIR spectrum) related to these groups are increased. These effects were observed with respect to the variation of the gas composition (O_2/Ar), rf power, processing time and gas pressure.

The analysis of the IR spectra showed that rf plasmas produced into a RIE reactor can promote the formation of new radical groups on the rubber surface, which could be is advantageous to enhance its adhesion characteristics.

5 - ACKNOWLEDGMENTS

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6 - REFERENCES

(1) I. F. HUSEIN, Y. ZHOU, S.QIN, J.I. KLEIMAN and K. MARCHEV, Mat. Res. Soc. Symp. Proc. **438**, 511-516 (1997).

(2) Y. CHAOTING, S. GAO and Q. MU, J. Mat. Sci. **28**, 4883-4891 (1993).
(3) L. MASCIA and Z. ZANG, Appl. Surf. Sci. **93**, 1-7 (1996).
(4) R. Li, L.YE and Y-W. MAI, Composite – ***Part A*** **28**, 73-86 (1997).
(5) T. CHAU K.C. KAO, G. BLANK and F. MADRID, Biomaterials **17(13)**, 1273-1277 (1996).
(6) A. NIHLSTRAND, T.HJERTBERG and K.JOHANSSON, Polym. **38(7)**, 1557-1563 (1997).
(7) C. M. CHAN, T-M. KO and H.HIRAOCA, Surf. Sci. Reports **24**, 1-54 (1996).
(8) P. GRONING, M.COLLAUD-COEN, O.M. KUTTEL and L.SCHLAPBACH, Appl. Surf. Sci.**103**, 79-89 (1996).
(9) D. M. CHOI, C.K. PARK, K.CHO and C.E.PARK, Polym **38(25)**, 6243-6249 (1997).
(10) J.Y. LAI, Y.Y. LIN, Y.L. DENQ, S.S.SHYU, and J.K. CHEN, J. Adhesion Sci. Technol. **10(3)**, 231-242 (1996).
(11) A. V. KONDYURIN, J. Appl. Polym. Sci. **48**, 1417-1423 (1993).
(12) P. WANG, K.L.TAN,C.C. HO, M.C. KHEN and E.T. KANG, European Polymer Journal **36**, 1323-1331 (2000).
(13) S. HAN, Y. LEE, H. KIM, G-H.KIM and J-H. YOON, Surf. and Coating Technol. **93**, 261-264 (1997).
(14) L.S. PENN and H.WANG, Polymer for Advanced Technol. **5**, 809-817 (1994).
(15) M. M. PASTOR-BLAS, J.G. DILLARD, A.TORRÓ-PALAU and J.M. MARTINS-MARTINEZ, Surf. and Interface Analyses **26**, 385-399 (1998).
(16) S. SAITOH, M.YOSHIKAWA and K.NAITO, Thin Solid Films **316**, 165-168 (1998).
(17) K. GRUNDKE, H.J.JACOBASCH, F.SIMON and ST SCHNEIDER, J. Adhesion Sci. Technol. **9(3)**, 327-350 (1995).
(18) M. MASSI, R. D. MANSANO, H.S. MACIEL, C. OTANI, P. VERDONCK and L.N. NISHIOCA, Thin Solid Films **343**, 378-380 (1999).
(19) T. NGUYEN, Progress in Organic Coatings **13**, 1-34 (1985).
(20) M. W. URBAN, Progress in Organic Coatings **16**, 321-353 (1989).
(21) A. L. SMITH, Applied Infrared Spectroscopy (1979), John Wiley & Sons, New York.