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Rapid surface modification of EPDM with oxygen and nitrogen plasmas: a comparative study

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This work presents the adhesion properties of plasma treated EPDM (ethylene propylene diene monomer) vulcanized rubber used in missile and rocket manufacturing. The EPDM rubber surface was treated in a RIE (reactive ion etching) plasma reactor using two different gas mixtures, oxygen/argon and nitrogen/argon. Contact angle measurements were used to obtain the dispersive and polar components of the surface tension of the treated samples, and FT-IR was used to characterize the surface. Both plasma treatments promote an enhancement of the adhesive properties of the EPDM rubber. However, the improvement factor depends on the gas mixture used. For treatment with an oxygen/argon mixture, functional groups such as C-O, C=O, O-C=O, C-O-O and CO_3 are formed in the rubber surface. In the case of a nitrogen/argon mixture, the functional groups formed on the surface are C-N, C=N and C≡N, beyond the functional groups C-O, due to the rubber oxidation. Therefore, the higher polarity of nitrogen containing groups makes the treatment with the nitrogen/argon mixture more efficient.

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1. Introduction

Due to the low cost and good thermal and mechanical properties, EPDM rubber is widely used in different industrial segments, and is also becoming of great interest for the aerospace industry. Most of these applications require elevated adhesion of the EPDM rubber on the surface to which it is applied. In the particular case of missile and rocket applications, the EPDM rubber is used as thermal protection between the internal rocket or missile walls and the solid propellant, and this system must have excellent adhesion properties in order to obtain safe devices with high performance [1,2].

The disadvantage of most polymers and rubbers is their bad adhesion properties, which require a surface treatment while maintaining the bulk characteristics [1,2]. The conventional chemical methods for surface treatment are pollutants, and have low efficiencies. It is widely known that cold plasma treatment is an efficient and environmentally friendly process to modify the surface energy and functionality, and therefore to enhance the adhesion properties. However, the mechanism that leads to this adhesion improvement of the treated polymer surface still remains not fully understood. In general, the surfaces of polymers and rubbers treated by an argon plasma are exposed to the presence of oxygen containing groups such as carbonyl, carboxyl, and hydroxyl. These groups are formed due to the presence of the oxygen in the polymer structure and the reactions of long-lived polymer radicals with oxygen when the treated polymer surface is exposed to air. In a similar way, treatment with a nitrogen plasma introduces nitrogen-containing groups such as amides, imides, and nitriles, as well as oxygen containing groups due to the rubber surface oxidation [3].

In this work, we present a comparative plasma treatment study of the surface of EPDM rubber treated with O_2/Ar [4] and N_2/Ar [5] plasmas. The properties of the treated rubber surface were analyzed by Goniometry, Atomic Force Microscopy (AFM) and Fourier-Transform Infrared Spectroscopy (FT-IR).

2. Experimental setup

The EPDM rubber was prepared [4,5] in an open mixer of two coils, and vulcanized in accordance with the ASTM D-3182 e D-2084 standards [6]. The rubber surface treatment was performed in a specially constructed RIE reactor, excited by an adjustable r.f. power supply. The 13.56 MHz r.f. signal was applied to the smaller, 6 inches diameter, aluminum electrode, as described in detail elsewhere [7]. The samples (5 cm^2) were electrically isolated and supported by a glass plate, located between the two electrodes, 60 mm apart. In this way the samples were only bombarded by low energy particles. The plasma treatment parameters are summarized in the Table 1.

Table 1. Plasma treatment parameters.

Parameter	Range
Gas Mixtures	O_2/Ar and N_2/Ar
% Ar in the gas mixtures	0 – 100
Total gas flow rate (sccm)	3 – 60
RF power (W)	20 – 200
Treatment time (min)	1 - 20
Gas pressure (mTorr)	70 - 1000

The contact angle measurements were performed using a 500-00 Goniometer Drop Image Advanced-2004 from Ramé-hart at ambient temperature and pressure, before the plasma treatment, 1 hour and 24 hours after treatments. Measurements were made immediately after placing drops of de-ionised water or di-iodine methane on the sample surfaces. The contact angle values presented here are the average of seven measurements in different places on the sample surface, and the standard deviation was less than 5% of the measured values. However, the measurements of contact angle in samples of different rubber batches before the plasma treatment presented a dispersion of about 10%, which is related to the rubber preparation, vulcanization and manipulation processes.

Attenuated total reflectance (ATR) of the EPDM rubber surface measurements, before and after the plasma treatment, were performed on a Perkin-Elmer Spectrum One System, using a KRS-5 crystal.

AFM measurements were performed in an SPM-9500J3 from Shimadzu in dynamic mode, before and after treatment. The surface morphology, expressed in terms of the (rms) roughness, was calculated by software provided by Shimadzu.

3. Results and discussion

Fig. 1 shows the contact angle and the polar surface tension as a function of the gas mixture used in the plasma, for a total gas flow of 60 sccm, pressure of 150 mTorr, an r.f. power of 50 W and a treatment time of 10 min. The first point in the plot corresponds to the untreated sample. We can see that the pure oxygen plasma treatment causes a significant reduction of the contact angle value from 105° to 65°, while the addition of argon in the gas mixture basically does not alter the results. The dispersion of about 10% in the contact angle values can be related to the non-uniformity of the rubber surface during the fabrication process, as described above.

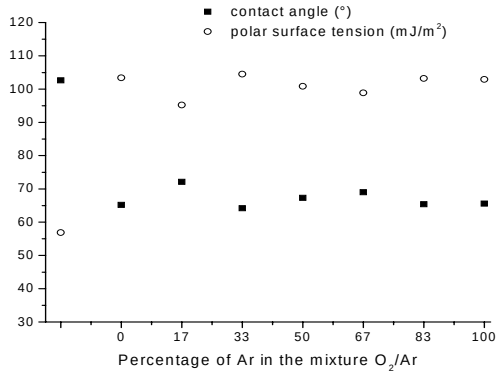

Fig. 1. Contact angle and polar surface tension versus O_2/Ar plasma treatment (the first point refers to the untreated sample).

Fig. 2 shows the contact angle and polar surface tension values, as a function of the argon nitrogen gas mixture used in the plasma, for a total gas flow of 60 sccm, pressure of 150 mTorr, an r.f. power of 50 W and a treatment time of 10 min. The first point for each parameter in the plot is the value for the untreated sample. The contact angle decreases with increasing argon concentration in the plasma, reaching a minimum value for about 17%. Then it increases with further argon content and has another minimum value for about 83% of Ar in the gas mixture. The plasma chemistry of the surface treatment is extremely complex, due to the large number of involved parameters and chemical species. Various studies of the gas phase in plasma surface treatment indicate the presence of maximum and minimum values for certain chemical elements. One particular study where this phenomena happens is the formation of ammonia and CHx radicals in the gas phase during the plasma nitrocarburizing process in variable $N_2/H_2/CH_4$ gas concentration mixtures [8,9]. These studies show that ammonia formation in the gas phase reaches a maximum for a nitrogen-rich gas mixture (about 75% N_2 - 22% H_2 - 3% CH_4), and decreases as the H_2 content increases, then giving rise to a new maximum in a hydrogen-rich gas mixture (about 22% N_2 - 75% H_2 - 3% CH_4). It is known that when the polymer is submitted to plasma, a large number of CHx radicals will be present in the gas phase, due to the action of the ionic, and electronic impact, and to UV radiation on the polymer surface [10]. The presence of CHx in our Ar/N_2 plasma could produce a similar gas mixture to that used in the nitrocarburizing process and then a possible formation of ammonia and NHx radical, which are very efficient in the creation of polar nitrogen containing groups on the polymer surface. If we consider ammonia formation in our plasma, it could be associated with the two contact angle minimum values obtained in Fig. 2, due to the formation of polar nitrogen-containing groups at the rubber surface. However, the real situation is that the contact angle varies between two values, and this association with the possible ammonia formation needs to be confirmed by a mass spectrometry study of the gas phase, or by XPS analysis of the treated rubber surface for instance.

Both the O_2/Ar and N_2/Ar treatments promote a reduction in the contact angle values, indicating the change in the rubber surface chemistry due to the grafting of oxygen and nitrogen containing groups.

The contact angle values, measured one hour and 24 hours after the samples being treated and stored in atmospheric conditions, are presented in the Table 2. Treatment with an O_2/Ar plasma creates saturated oxygen-containing groups that keep the surface energy stable for a 24 hour period. On the other hand, the surface treated with N_2/Ar creates unsaturated functional groups that are prone to oxidation, causing the ageing process to be more accentuated with a consequent decrease of the polar surface energy. Despite the ageing process due to the rubber surface oxidation, N_2/Ar plasma treatment is more efficient than O_2/Ar treatment. Due to the high polymer chain mobility at the surface, compared to the bulk, the surface can suffer different reorientations, depending upon the environment. The surface orientation can be accomplished by the diffusion of low molecular weight oxidized material into the bulk, and the migration of polar groups away from the surface [11]. For this reason, the rubber adhesion improvement obtained with a nitrogen plasma can be completely lost in a few days, when the sample is stored in the air.

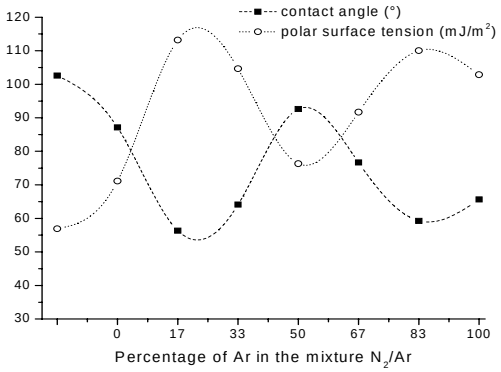

Fig. 2. Contact angle and polar surface tension versus N_2/Ar plasma treatment (the first point refers to the untreated sample).

Table 2. Effect of the aging and the gas used in the plasma treatment.

EPDM Samples	Contact angle (°)	Polar surface tension (mJ/m^2)
Untreated	102.6±1.0	56.9±1.8
O_2/Ar treated (1h aging)	63.0±0.7	104.0±1.3
O_2/Ar treated (24h aging)	65.4±0.8	103.2±1.1
N_2/Ar treated (1h aging)	24.8±0.5	138.9±0.3
N_2/Ar treated (24h aging)	54.1±1.3	115.5±1.4

Fig. 3 presents the FT-IR spectrum for the untreated and O_2/Ar and N_2/Ar plasma treated EPDM rubber samples. Samples treated in an oxygen containing plasma reduce the CH_2 and CH_3 band intensities around 2800 cm^{-1}, in favor of the new oxygen functional groups created at the rubber surface. In the same way, nitrogen plasma treatment presents a higher reduction of the CH_2 and CH_3, in favour of the nitrogen containing bands. In general, the depth of the surface modification obtained by our plasma conditions, studied by the angle resolved XPS technique, is typically a few hundred angstroms [11]. The concentration of nitrogen in this extremely thin modified layer is not high enough to be detected by the FT-IR technique, because the sample depth probe is about 1 μm. Chan et al [11] also did not detect the nitrogen containing groups using an FT-IR technique at the polymer surface, after treatment by a nitrogen plasma.

AFM analysis shows that plasma treatment reduces the surface roughness. The rms surface roughness values vary from 161 nm for an untreated EPDM surface to 139 nm and 76 nm after nitrogen and oxygen plasma treatment, respectively.

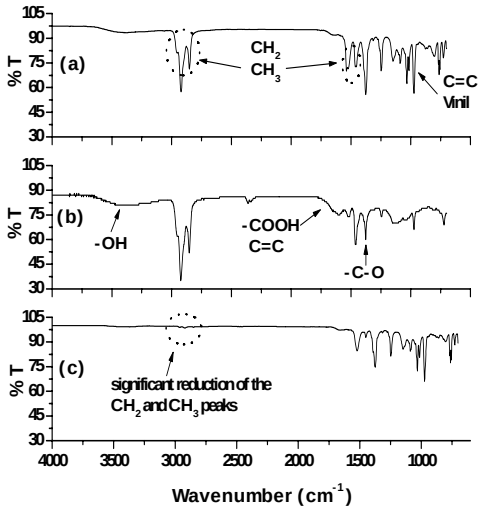

Fig. 3. FT-IR/ATR analyses of EPDM rubber (a) without treatment, (b) treated with an O_2/Ar plasma, (c) treated with a N_2/Ar plasma.

4. Conclusions

Low-temperature plasma is well suited for surface modifications of rubbers, to improve their adhesion properties.

EPDM rubber surface treatment by oxygen or by nitrogen plasma improves its adhesion properties. Further improvement in the adhesion properties can be obtained with the addition of different amounts of argon in the oxygen plasma. A plasma of pure argon gives the same adhesion properties as a pure oxygen plasma.

EPDM surfaces treated by a nitrogen plasma also present an improvement in the adhesion properties in two gas mixture concentrations, about 17% and 83% of Ar in N_2/Ar. The plasma chemistry of the surface treatment is

extremely complex, due to the large number of involved parameters and chemical species. To better understand the reasons for these two optimum conditions, a more detailed gas phase study using mass spectroscopy or surface XPS analysis of the treated rubber, for instance, is needed.

FT-IR analyses show the presence of oxygen containing groups at the rubber surface treated by oxygen and nitrogen plasmas. However, the nitrogen-containing groups were not detected. Similar behavior was obtained by Chan et al [11]. Nevertheless, the enhancement of the adhesion properties, for both oxygen and nitrogen plasma treatment, can be associated with the higher surface polarity due to these oxygen and nitrogen containing groups grafted into the rubber surface.

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