

PRELIMINARY RESULTS IN SYNCHROTRON X-RAY DIFFRACTION MEASUREMENTS OF RUBBER COMPOSITES STRUCTURE BEFORE AND AFTER EXPOSURE TO HYDROGEN

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Resume

In future years, fuel cells are expected to represent a promising technology as a source of heat and electricity in buildings and of electrical power for vehicles, since fossil fuels are exhausting and significantly degrade air quality. It is well known that, when exposed to a hydrogen environment, hydrogen embrittlement may affect materials such as iron and steel. But these are not the only materials that are used for hydrogen equipment. In particular, the rubber materials used for O-rings that seal high pressure hydrogen gas equipment show problems of internal fracture, called blister fracture, when the gas is rapidly decompressed. As many different kinds of fillers can be used, in this work we started to investigate the influence of the type of filler on the rubber composites structure, by means of X-ray diffraction measurements performed at the Elettra synchrotron radiation facility in Trieste. In this preliminary study, three kinds of samples were analyzed before and after exposure to hydrogen: Sulphur vulcanized EPDM, Peroxide vulcanized EPDM and Sulphur vulcanized NBR. While Peroxide vulcanized samples did not show significant differences in the diffraction pattern, changes could be detected in the crystalline form of Sulfure vulcanized rubber.

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1. Introduction

All over the world, the always increasing demand in energy is principally met by fossil fuels, which are exhausting and significantly degrade air quality. Starting with the Kyoto protocol, several countries have committed themselves to reducing emissions by a significant amount in the three more significant gases – carbon dioxide, methane, and nitrous oxide. In this scenario, fuel cells are expected to represent a promising technology as a source of heat and electricity in buildings, and of electrical power for vehicles. For example, hydrogen fuel cell cars outperform battery electric vehicles on both range and refueling time and are often

regarded as one possible future alternative to current battery electric vehicles. In fact, in order to actually take off, both fuel cells and electric cars will require a huge effort in establishing an adequate refueling/recharging infrastructure.

Besides the infrastructural requirements and the "public-acceptance" issue, several technological problems related to hydrogen production, distribution, storage and utilization remain to be addressed in order to achieve a major impact of hydrogen energy on our society. In particular, strength and fatigue of mechanical materials in a hydrogen environment represent two technological issues to be addressed.

Several materials may be used in hydrogen equipment and, while it is well known that in a hydrogen environment materials such as iron and steel suffer from a degradation in mechanical properties, called hydrogen embrittlement [1], it becomes of paramount importance to characterize also of the behaviour of other, organic, materials like, for example, the rubber used for O-rings.

The filler has an important role in the total performance of a rubber [2, 3]. The final properties of the rubber will depend on the filler characteristics and in particular on particle size, surface area and shape. In fact, stress transfer will be better achieved if the mineral particles are smaller. Moreover, if the filler particles are needle-like, fibrous or platy in shape, they will better intercept the stress propagation through the matrix. Increasing the surface area - decreasing the particle size - will improve tensile strength, abrasion resistance, tear resistance and will lower the rubber resilience. Another important factor is the particle surface activity, which is related to the compatibility of the filler with a specific elastomer and the ability of the elastomer to adhere to the filler.

The resistance to a specified elongating defines the rubber modulus, which is usually given at 300% elongation, four times the original rubber sample length. For an uncompounded elastomer, elongation derives from the disentangling of randomly oriented polymer chains and from weak chain-chain breaking. For instance, vulcanized, unfilled, elastomers more strongly resist elongation because the sulfur crosslinks must be stretched and broken to allow chain extension and separation. The addition of a filler provides additional resistance to elongation. Carbon black (CB) and Silica, each one having its own advantages, have been long utilized as the main reinforcing fillers for rubber.

Fracture growth and crack development in rubber have been studied in literature [4-7]. In particular, the rubber materials used for

O-rings that seal high pressure hydrogen gas equipment present problems of internal fracture, called blister fracture, when the gas is rapidly decompressed [8-10]. Since many different kinds of fillers can be used, we started to investigate the influence of type of filler on the rubber composite structure by means of diffraction measurements performed using the high power X-rays obtainable from a synchrotron light source.

2. Materials and method

The samples were extracted from different kinds of rubber: EPDM (Ethylene Propylene Rubber), vulcanized with Sulfur or Peroxide and NBR (Acrylonitrile Butadiene Rubber). A total number of 18 different rubber samples, filled with different kinds of CB and Silica, were investigated. The fillers investigated vary in mean number diameter and specific surface. Their composition is described in detail in Table 1.

The samples were cut in pieces of rectangular shape, approx. 10x20 mm, from rubber sheets 0.7 mm thick.

The samples were tested a first time before being put in a H₂ environment. Measurements were performed at the XRD1 beamline of the Elettra synchrotron facility in Trieste. Parameters of X-Ray diffraction measurements were as follows:

- distance $d = 60$ mm;
- wavelength $\lambda = 1.0$;
- area $A = 0.3 \times 0.3 \text{ mm}^2$.

Successively, the samples were simultaneously put in a hydrogen environment in a specially designed holder, as shown in Fig. 1, where the samples are depicted while placed on the bottom part of the pressurization chamber. Each sample in the chamber is identified in Fig. 2.

An average pressure of 4.7 bar was maintained for 124 hours. The exact pressure profile is shown in Fig. 3.

Table 1

Composition of the Sulfur Vulcanized EPDM samples (A, B, C, D, E, F, G, H, I, J, K), of the Peroxide Vulcanized EPDM samples (L, M) and of the Sulfur vulcanized NBR samples (N, O, P, Q, R)

SAMPLE	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
EPDM ESPRENE 505						100.0						100.0				100.0		
STEARIC ACID						1.0						0.5				1.0		
ZINC OXIDE						5.0						-				5.0		
SULFUR						1.5						-				1.5		
MBTS Accelerator						1.5						-				1.5		
TMTD Accelerator						0.7						-				0.5		
ZnEDC Accelerator						0.7						-				-		
DICMYL PEROXIDE						-						1.6				-		
CB SAF ASTM N110	-	25	50	-	-	-	-	-	-	-	-	-				-		
CB ISAF ASTM N220	-	-	-	25	-	-	-	-	-	-	-	-				-		
CB HAF ASTM N330	-	-	-	-	25	50	-	-	-	-	-	-	25	-	25	50	-	-
CB FEF ASTM N550	-	-	-	-	-	-	25	-	-	-	-	-	-			-		
CB SRF ASTM N774	-	-	-	-	-	-	-	25	50	-	-	-	-			-		
SILICA NIPSIL VN3	-	-	-	-	-	-	-	-	-	30	60	-	-	-	-	-	30	60

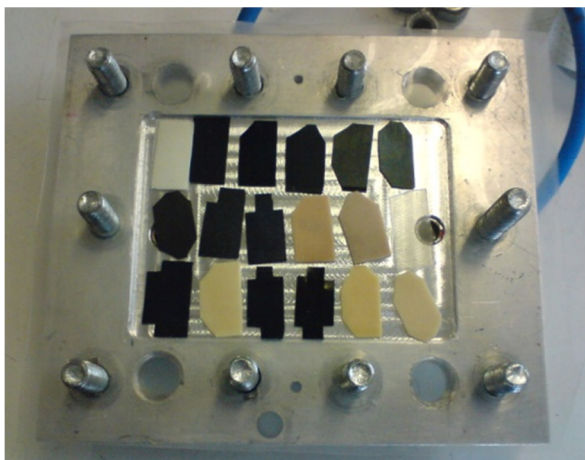


Fig. 1. The samples placed on the holder before exposure to the hydrogen environment (full colour version available online)

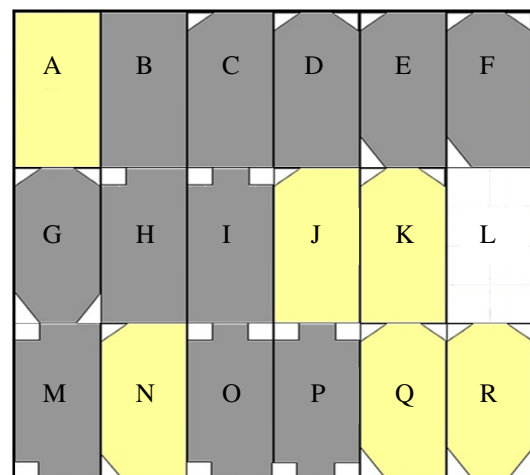


Fig. 2. Identification of the position of the samples (full colour version available online)

According to the different compositions, the samples exhibit a wide range of colours, from transparent to different shades of white, grey and black. X-Ray diffraction measurements were again performed on the samples, immediately after removal from the pressurized chamber. Parameters used for this second run at the XRD1 beamline were the same as those used for the test before exposure to hydrogen.

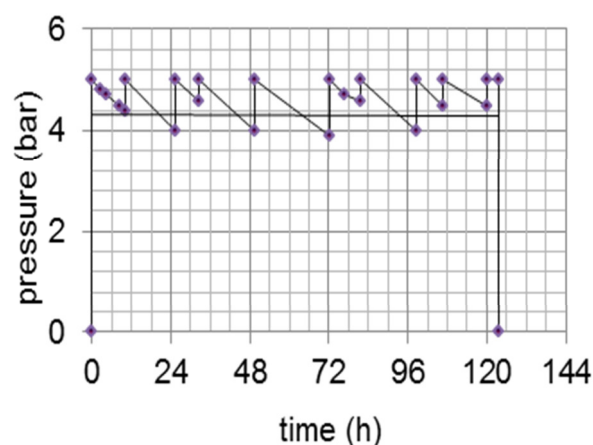


Fig. 3. Hydrogen pressure profile

3. Results

Fig. 4, 5, 6, 7 and 8 compare the synchrotron X-Ray diffraction patterns obtained before and after exposure to the pressure Hydrogen environment for each one of the samples. In the figures, x axis is 2θ value in radians and y axis is intensity in arbitrary unit (maximum peak normalized to 100).

The patterns of the fillers (CB and Silica) in their pristine form were obtained at the Powder Diffraction Beamline MCX of Elettra and are reported in Fig. 9.

The patterns of the accelerators (MBTS, TMTD, ZnEDC) were obtained by the International Centre for Diffraction Data database and do not show a crystalline form.

From the analyses of the figures, some indications can be drawn. It can be seen that the patterns of CB and Silica do not exhibit a crystalline structure. All the Sulfur Vulcanized EPDM samples and all the Sulfur vulcanized NBR samples exhibit a crystalline structure, that is slightly changed by exposure to a hydrogen environment. These changes are not detectable in the patterns of Peroxide Vulcanized EPDM samples, that do not show a crystalline structure.

4. Conclusions

In this preliminary work, we started to investigate the structural changes that may affect rubber exposed to a hydrogen environment, with special reference to the influence of the type of filler.

The problem was addressed by means of X-ray diffraction measurements performed at the Elettra synchrotron radiation facility in Trieste on different kinds of rubbers. Sulphur vulcanized EPDM, Peroxide vulcanized EPDM and Sulphur vulcanized NBR were analyzed. The diffraction patterns of 18 different samples were measured before and after exposure to a hydrogen environment.

In this preliminary set of experiments, changes could be detected in the crystalline form of Sulfure vulcanized EPDM and NBR rubber. The patterns from these samples show the diffraction from ZnO, which is added for vulcanization. These changes are not clearly understood yet, and are maybe linked to effects related to particle surface activity, particularly at the boundary of rubber and ZnO, which has some sulfur and stearic acid on the surface. Further investigation is planned in order to achieve a better understanding of the role of fillers on rubber performance in a hydrogen environment.

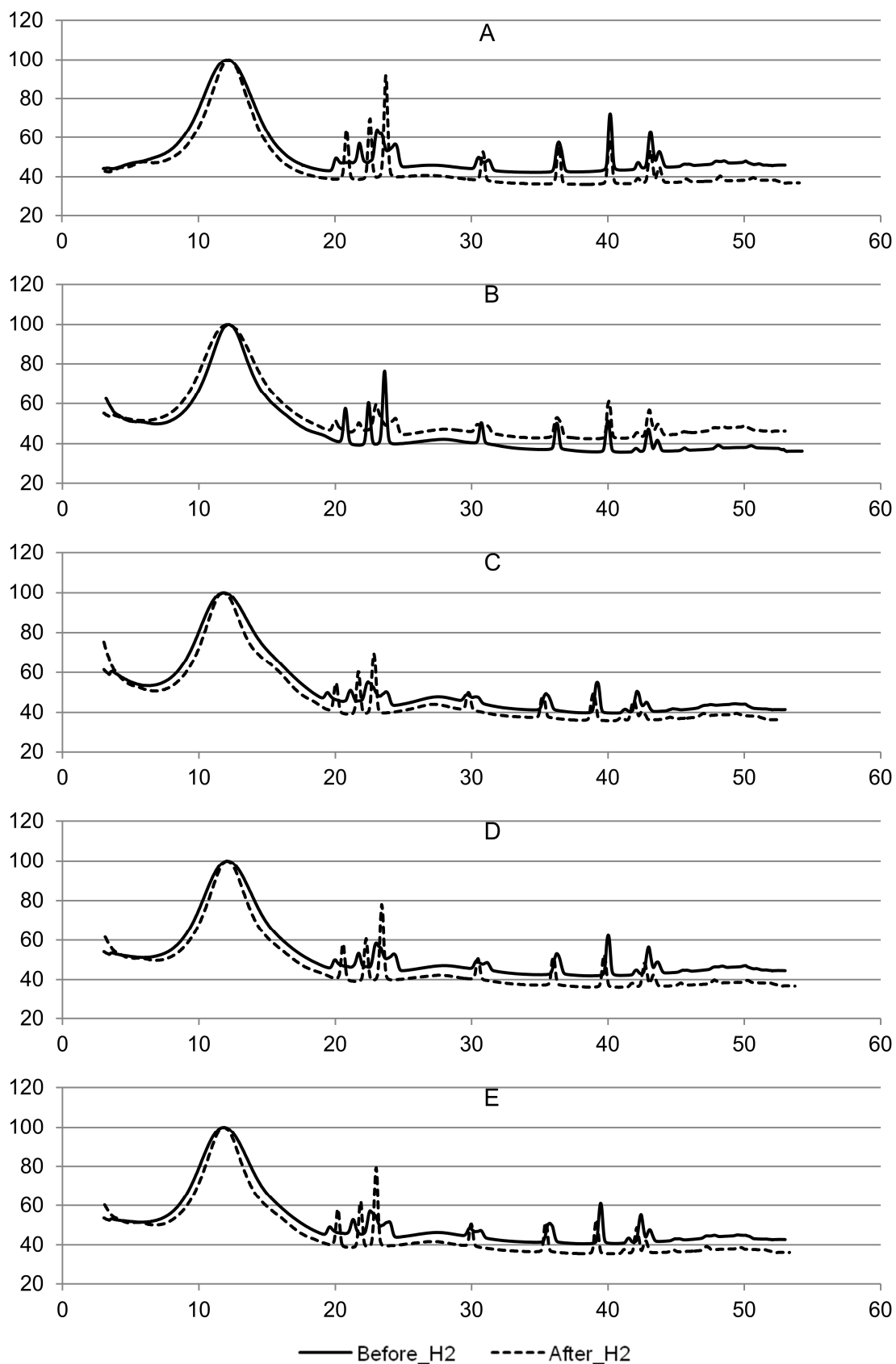


Fig. 4. Synchrotron X-Ray diffraction patterns before and after exposure to hydrogen of the Sulfur Vulcanized EPDM samples A, B, C, D, E.

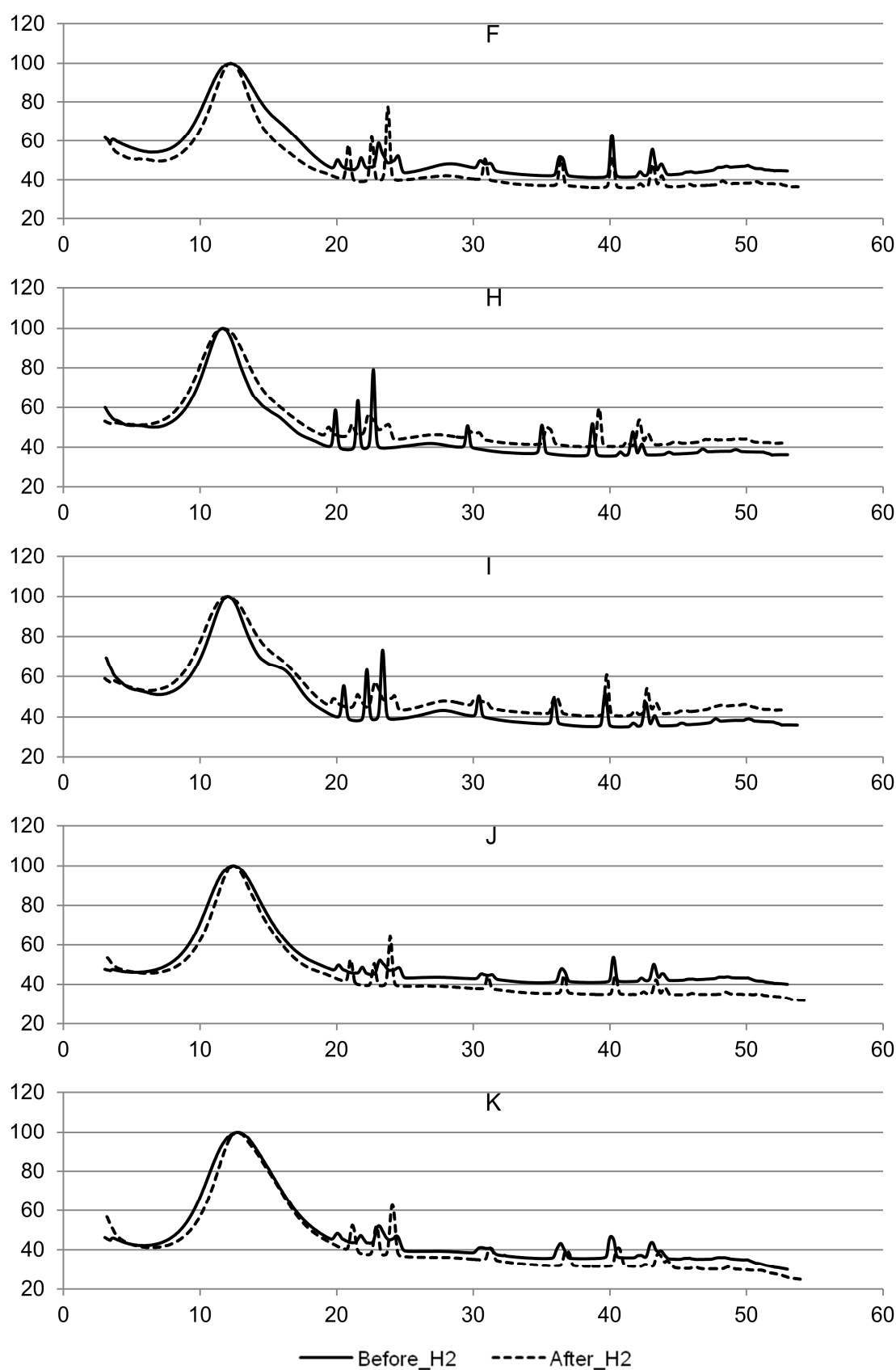


Fig. 5. Synchrotron X-Ray diffraction patterns before and after exposure to hydrogen of the Sulfur Vulcanized EPDM samples F, G, H, I, J, K.

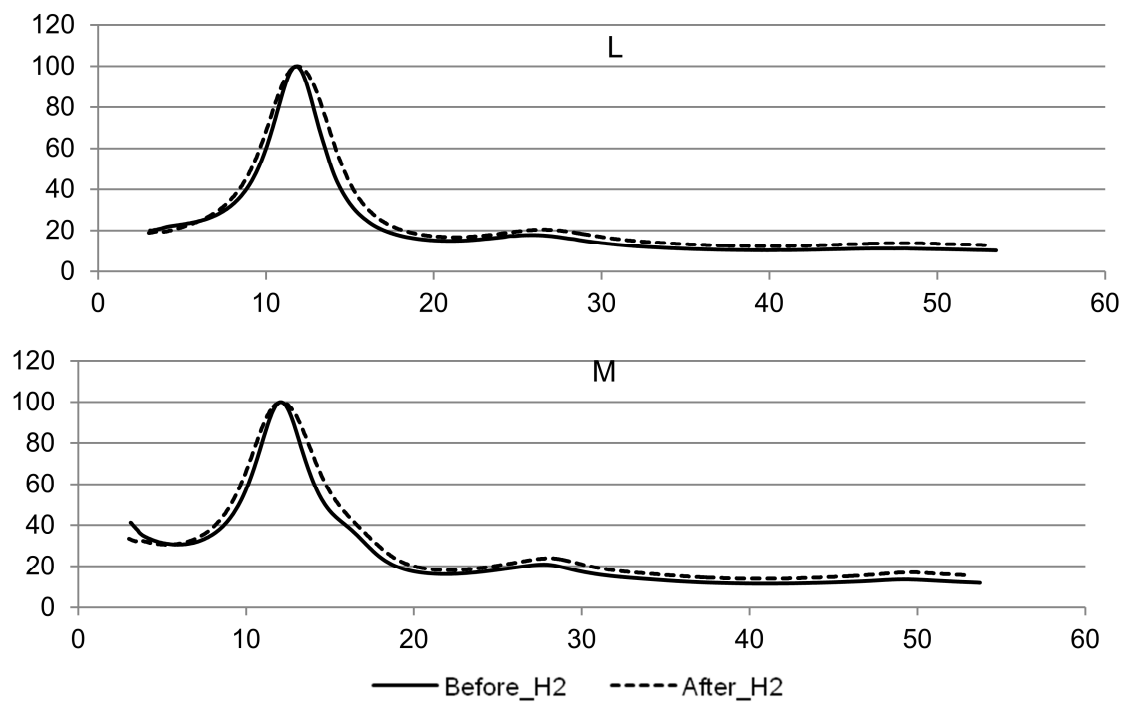


Fig. 6. Synchrotron X-Ray diffraction patterns before and after exposure to hydrogen of the Peroxide Vulcanized EPDM samples (L, M).

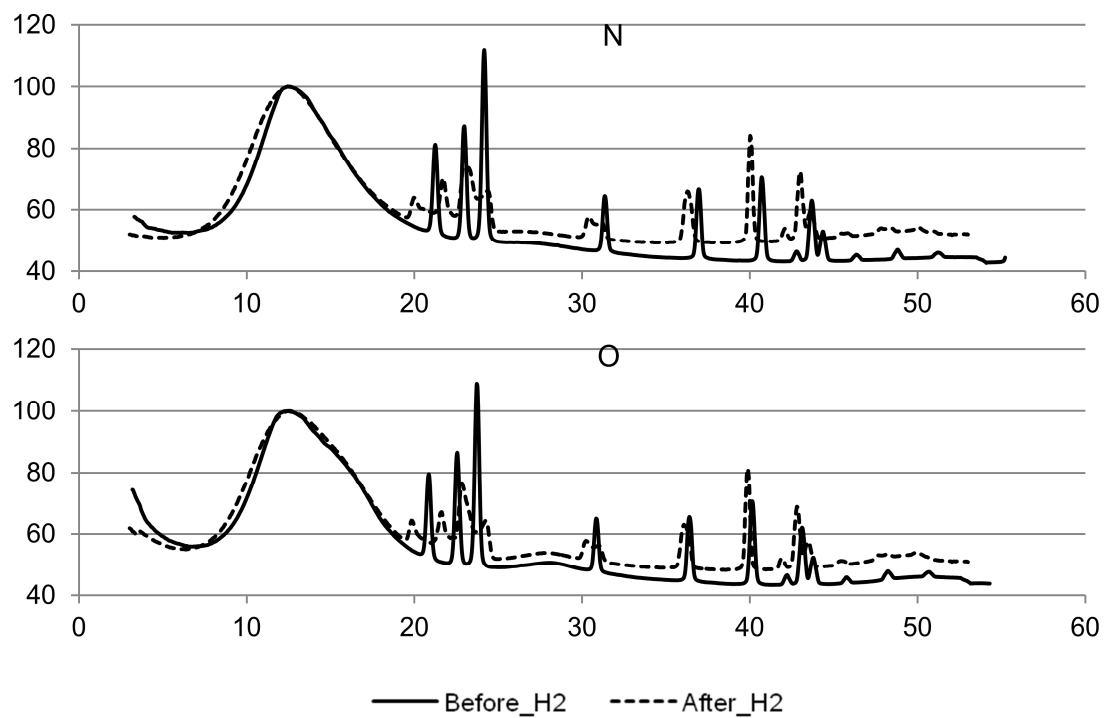


Fig. 7. Synchrotron X-Ray diffraction patterns before and after exposure to hydrogen of the Sulfur vulcanized NBR samples N, O

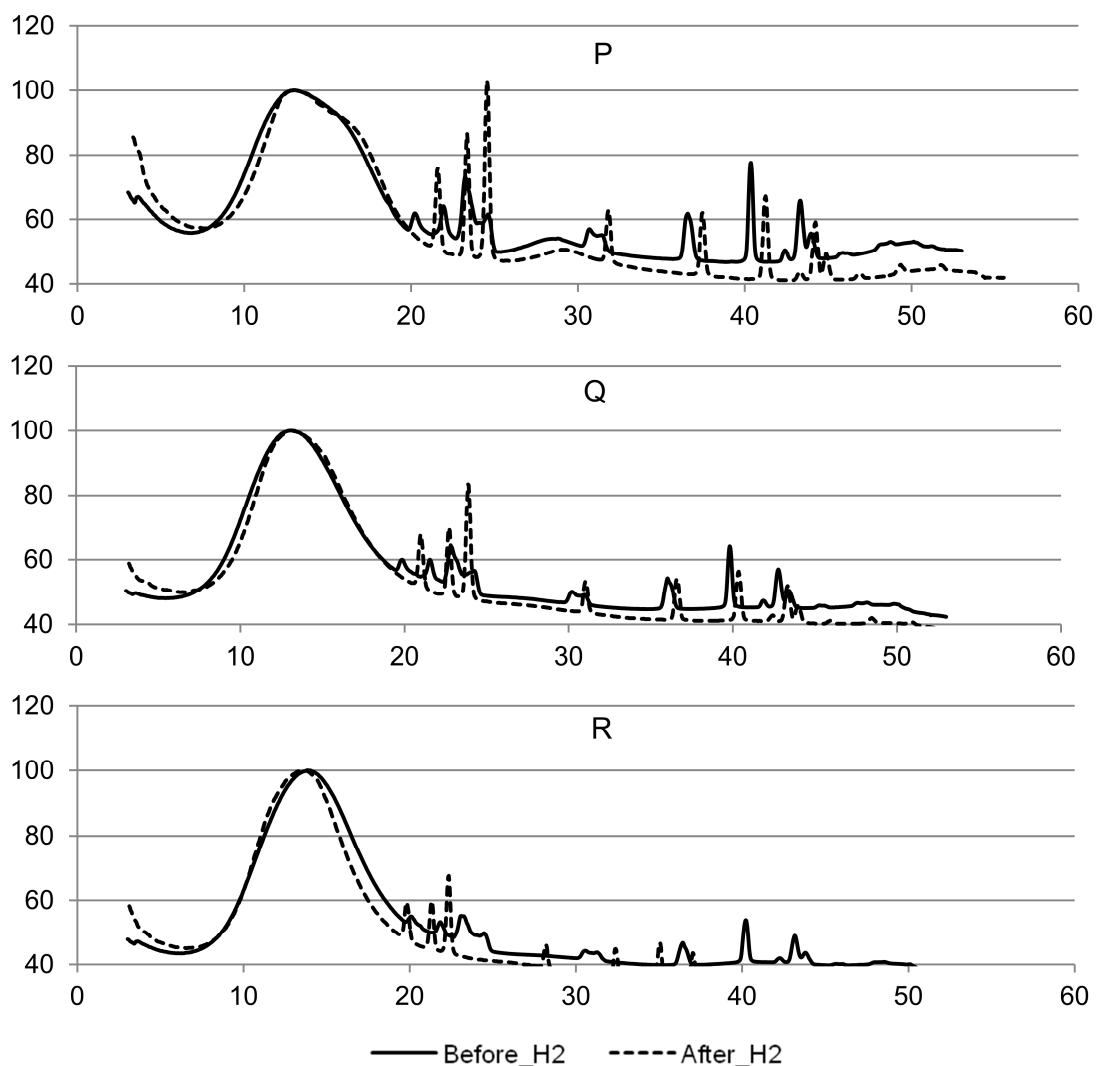


Fig. 8. Synchrotron X-Ray diffraction patterns before and after exposure to hydrogen of the Sulfur vulcanized NBR samples P, Q, R

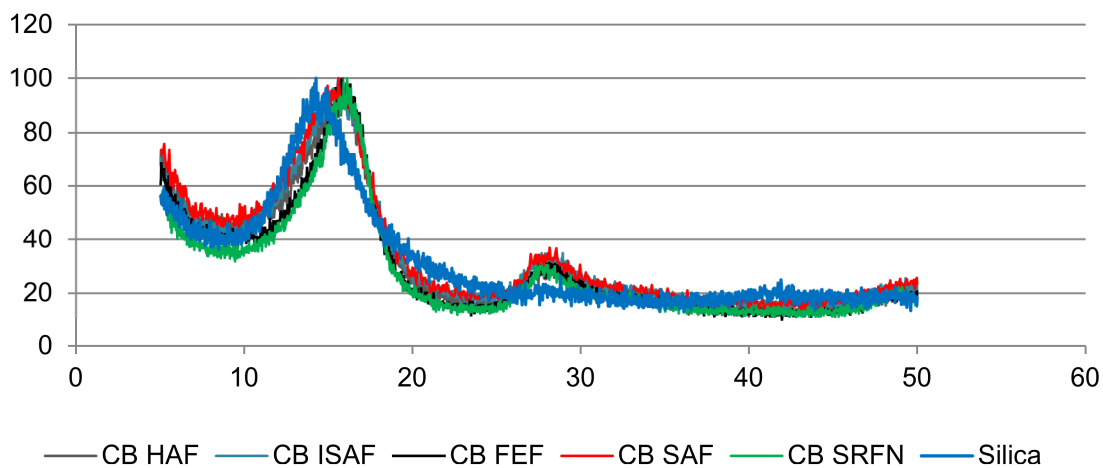


Fig. 9. Synchrotron X-Ray diffraction patterns of the fillers (no exposure to hydrogen) (full colour version available online)

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