Acid Aging Effects on Surfaces of PTFE Gaskets Investigated by Fourier Transform Infrared Spectroscopy

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A B S T R A C T

This paper investigates the effect of a prolonged acid and thermal attack, on the surface of PTFE by Fourier Transform Infrared Micro-Spectroscopy (μFT-IR). The materials are commercialized by two alternative producers in form of Teflon tapes. These tapes are installed in process plants where tires moulds are cleaned inside a multistage ultrasonic process. In these cases, Teflon tapes, having a role of gaskets, show inexplicably phenomena of degradation in relatively short operation periods. Even considering that these gaskets are exposed to the combined effect of ultrasonic waves, temperature, humidity and acid attack, the PTFE properties of resistance nominally exclude the possibility of these severe erosion phenomena. An interesting explanation can be related to the potential presence in the cleaning solution, mainly based on sulfamic acid, of highly reactive chemical compounds, as chlorides and fluorides, originated by the disaggregation of elements from the tire composition and/or additives used as processing aids and/or by catalytic effect generated by fluorine produced by PTFE degradation. In general, up to 300 different chemical elements, both organic and inorganic, natural and synthetic, are merged in a tire. Since this composition is practically unknown, especially regarding additives and "unusual elements", representing a secrecy of each tire manufactures, it is really complex to define the chemical composition of the cleaning solution with an appropriate precision. As a consequence, the gaskets have been treated with different mixtures of acids in the way to combine a larger range of possibilities. Thus, the μFT-IR experimental characterization of PTFE surface properties followed an appropriate accelerated aging, aiming at actuating the specific mechanics of wearing as in industrial use. The different acid treatments adopted for accelerating the aging of gaskets have highlighted the different behaviour of the PTFE matrix, but also differences between manufacturers.

1. INTRODUCTION

This investigation is part of a larger redesign and optimization activity aiming at improving the process safety and maintainability in the case of innovative production plants used for the surface treatment and cleaning of tires moulds. These plants, produced and commercialized by RSM Keymical Srl, are installed worldwide by large part of tire manufactures. The cleaning effect on tire moulds is obtained adding temperature, chemical reactions, liquid agitation and ultrasounds. This technology, known as Mould Ultrasonic Cleaning System (UMCS), is preferred in respect to other alternative solutions given a number of benefits in terms of efficiency, flexibility, cost, up to the possibility to clean complex geometries (e.g. spring-vents). In [1], a technology assessment regarding the existing systems for tire mould cleaning is reported, also detailing additional aspects as quality finishing, eco-sustainability, safety, etc.

In brief, the UMCS consists in a multiple stage process where an ultrasonic wave, in combination with temperature and acids, removes rubber scraps and other physical residuals from interstices of the moulds. Large details referring the UMCS technology and its plants are available in [2]. Nowadays, around 45 UMCS plants exist, all of them in operation since very few years. Anyway, minor several failures, as the loss of drops of cleaning solution from washing basins, highlighted unexpected seal deterioration. In particular, Teflon tapes used as gaskets in the acid basins exhibits degradation, especially on the surface, incompatible with conditions of use [3].

In fact, according to the traditional state-of-art, Teflon, correctly identified as polytetrafluoroethylene (PTFE), reveals a deep thermal and chemical stability that make this material a valid choice in a large number of practical applications [4,5]. In the conditions of usage characterizing the UMCS plants (as Temperature, pH), no relevant degradation in PTFE is expected [6,7]. Evidences from operation [8] suggested that one or more unexpected phenomena occurred in the way to represent a proper reason for further investigations.

It was initially verified if the properties of PTFE currently used in installations were exactly the same of the ones defined during plant design. In practice, a first comparative analysis was performed on nominal and real PTFE gaskets, by means of mechanical tests, micrographs, etc. [9], which showed a not negligible difference between the two materials.

This difference was related to several aspects (as chemical composition, mechanical strength, etc.) showing a net superiority of the nominal PTFE without, however, lead to an unambiguous indication of unacceptability for the used one.

Anyway, this previous research was focused on gaskets' initial properties, without considering their potential aging. Hereafter, the need to implement a comparative study of PTFE gaskets being degraded in a controlled environment by acid and temperature attack was also affirmed and results presented in [10- 12]. In particular, it [10] describes the aggravated conditions of heat, humidity, acid attack used to speed up the normal aging processes of PTFE gaskets inside the UMCS plants and before implementing the current complete session of laboratory tests for the experimental characterization of materials. Besides, [11] describe the effects of aging on PTFE chemical surfaces by Thermal Analysis permitting preliminary considerations regarding the use of PTFE in UMCS conditions and its aging mechanisms.

It also reports that, according to producers' technical sheets and independent investigations, PTFE presents a thermal stability up to +260 °C, unperishable over time. Furthermore, PTFE is resistant to acids, alkalis, solvents and various chemicals within a range 0-14 pH, while no specific information emerged about a structural, material or tribological degradation when exposed to ultrasonic waves. Referring to [13-15], it is stated that only under very uncommon circumstances PTFE degrades. In particular, the carbon-fluorine bonds in the PTFE can be effected by alkali metals (i.e. zinc oxide, present in 1-2 weight % in the rubber as vulcanization activator [16]), and fluorinating agents.

Specific chemical controls on the composition of the cleaning solutions after a reasonable operation time (around 1.500 hr) provided evidence regarding traces of fluorides [17]. Another drawback reported in the literature is that Teflon liberates fluorine in 70 % $HClO_4$ acid

at 20°C for 6 months or in nitric acid in a microwave oven, even if in analytical traces [18]. The chemical composition of these solutions before starting the washing process is strictly limited to sulfamic acid, which is the main constituent of the typical washing solution used as deoxidizer acid in ultrasound cleaning applications. Considering this, it can be presumed that fluorides manifest themselves as a consequence of the disaggregation of chemical compounds, which are present inside the tire compounds and/or as lubricants or additives used as processing aids [19]: these substances may reasonably be transferred into the mould and, at last, in the cleaning bath.

In [10] it is also fully detailed the aging conditions and the aging procedures used for preparing the PTFE samples before the current tests. In particular, it was intended to reproduce the worst process situation represented in the process line by the most aggressive acid bath, with an almost pH 1 solution composed by a mixture of sulfamic, hydrochloric and hydrofluoric acidss, and, simultaneously, a temperature between 70 and 80 °C.

2. MATERIAL AND METHODS

With the aim at passing over the uncertainty of the chemical composition, but also in order to propose several alternative conditions to speed up the aging processes, different combinations of sulfamic, hydrochloric and hydrofluoric acids have been considered. For each of these combinations PTFE specimens by two different manufacturers, one Italian (IT) and one Chinese (CH) have been investigated. The Italian specimens roughly represent the gaskets to be selected in a perfect accordance with all the design requirements. On the contrary, the Chinese ones are exactly the gaskets selected for the current UMCS plants, representative of failures.

The combination of acids used for accelerated experimental tests are summarized in Table 1, where acid solutions are labelled Sol. I and Sol. II. Specifically, Sol. I is a water solution of sulfamic acid (15 %wt) and hydrochloric acid (0.1 %wt) while Sol. II is a water solution of hydrofluoric acid (1 %wt). The containers with samples and acids were placed in a temperature controlled oven and maintained at 80 °C for

1.500 hr (2 months). At the end of the aging treatment, the specimens were extracted from oven, cleaned, dried and investigated by Fourier Transform Infrared Spectroscopy (FT-IR).

Table 1. Acid compositions (in accordance with accelerated aging procedure detailed in [10]).

#	H_2O	Sol. I	Sol. II
		%wt	
1	50	40	10
2	90	10	0
3	80	20	0
4	87.5	10	2.5
5	77.5	20	2.5
6	67.5	30	2.5
7	85	10	5
8	75	20	5
9	65	30	5
10	70	30	0

The FT-IR is an investigation technique which is used to obtain an infrared spectrum of absorption of a solid, liquid or gas. An FT-IR spectrometer simultaneously collects high spectral resolution data over a wide spectral range [20-22]. In particular, the two series of PTFE gaskets, have been subjected to IR analysis by mean of a μFT-IR spectrometer (Perkin Elmer Frontier, with Spotlight 200 microscope). These samples, treated with different mixtures of acid solutions, have been analysed to evaluate the different behaviours in response to the various acid treatments applied. With the aim at reducing the total number of experimental tests, only four specific combinations of acids (#1, #4, #6, #9) have been investigated. They have been selected to be between the most representative of aging phenomena in consideration of preliminary microscopic observations performed by a Hirox 3D Multifocal Microscope model HX 7700 (Fig. 1).

Fig. 1. Example of micrographs for a preliminary selection of the samples.

A comparison with new, untreated samples (#0) have been also implemented. The list of samples under investigation is reported in Table 2. The table also reports the weight percentage of acids used during the chemical attacks.

Table 2. List of analysed samples.

Sample	Treatment			Label
	#	***Sol. I***	***Sol. II***	
A	0	-	-	Chinese-New
B		-	-	Italian-New
C	1	40 %	10 %	Chinese-1
D		40 %	10 %	Italian-1
E	4	10 %	2.5 %	Chinese-4
F		10 %	2.5 %	Italian-4
G	6	30 %	2.5 %	Chinese-6
H		30 %	2.5 %	Italian-6
I	9	30 %	5 %	Chinese-9
J		30 %	5 %	Italian-9

Different FT-IR spectra, in μATR mode, have been acquired to check homogeneity of the surface. Cross-sections have been prepared using an X-Acto knife, avoiding excessive deformation of the section itself. These sections have been then used to verify the presence of a profile of degradation from the surface to the core of the material. The study was performed by means of line scans, that have been set from the top surface (zero point) to the bottom (where the adhesive is placed), in reflection mode, with an acquiring spot of 40x40 μm and a spatial resolution of 20 μm (granting 50 % overlapping); spectral resolution has been set to 2 cm^{-1} and, in order to lower signal-to-noise ratio, 64 scans for each point have been acquired. Once the map has been completed, it has been possible to notice if and where even little differences of composition have been.

3. RESULTS

3.1 Samples without treatments (#0)

New samples (#A, #B), unused and untreated, have been analysed, in order to have reference spectra for further comparison. Thanks to spectral libraries at disposal, samples from both manufacturers have been correctly identified as PTFE, Teflon (Fig. 2). These spectra show two sharp, intense and characteristic absorption bands at 1152 and 1205 cm^{-1}, which can be attributed to symmetric and asymmetric stretching vibrations of CF_2 bonds [23-25]

(Table 3). The two spectra are stackable at 97.5 %, showing only little differences due to a less regular baseline of the Italian new sample (#B).

Table 3. List of FT-IR signals identified.

| IR bands (cm^{-1})	Assignment
3600-3200 (3215)	O-H stretching
2924	CH_2 asymmetrical stretching
2854	CH_2 symmetrical stretching
1745-1730	-CF=CF- internal double bonds
1640	-CRR'=CH_2 terminal stretching
1445-1430	CH_2 scissoring
1205	CF_2 symmetric stretching
1152	CF_2 asymmetric stretching
1086	
1050	C-O hydroxyl stretching
1035	
1009	=CH_2 out-of-plane bending (terminal methylene)
982	
880	=CHR out-of-plane bending (terminal partially substituted methylene)
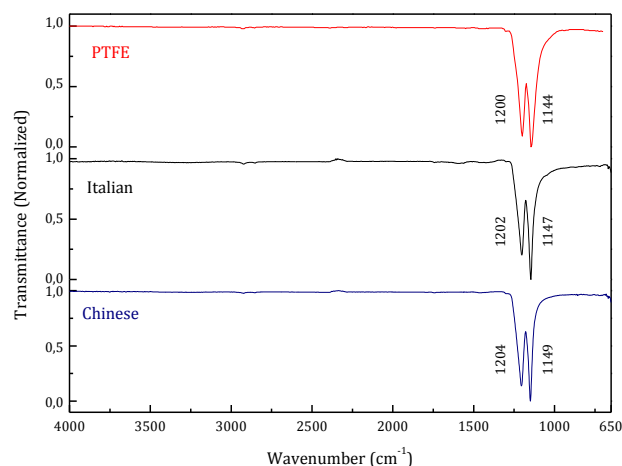
Fig. 2. normalized FT-IR spectra of new samples surfaces compared to standard PTFE (Teflon) spectrum.

In order to evaluate the presence of gradients along the thickness of treated samples, a line scan of the new samples, for comparison, have been acquired for both manufacturers. These sort of investigation have been already used with success for other types of polymers [26, 27]. The results of the line scans of new samples are shown in Fig. 3. In ordinate, distance of the line scan is reported. In abscissa, infrared spectrum with wavelength comprised from 4000 to 650 cm^{-1}, is reported. Colour variation denotes absorption intensity for each wavelength. The false colour map shows how the registered spectrum changes along the line scan. In both spectrographs, the only signals presents are the ones that were attributed to PTFE.
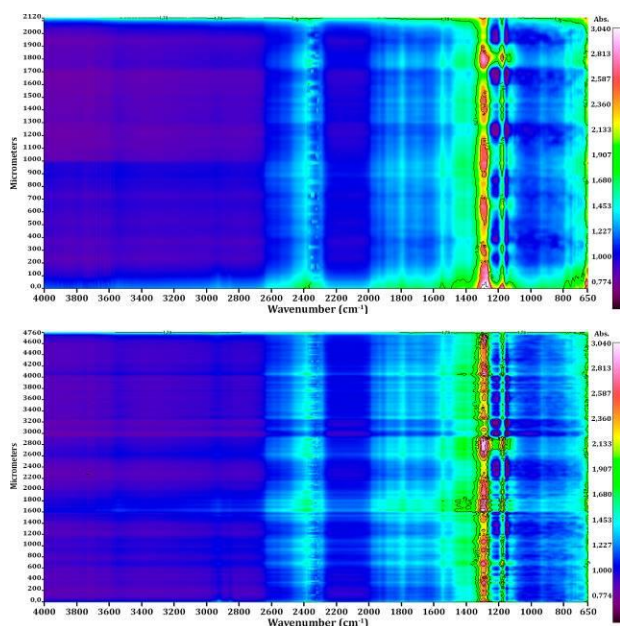
Fig. 3. results of the line scans of the Chinese (#A, up) and Italian (#B, down) new samples.

The slight signal present along both profiles at ≈2400 cm^{-1} is due to atmospheric carbon dioxide and should not be considered. As expected, new samples don't show any sign of degradation.

3.2 Samples with treatment #1

Samples #C and #D, subjected to acid treatment denominated #1 (see Table 2), show a partial superficial hydroxylation, highlighted by the presence of a broad band between 3200 and 3600 cm^{-1}, with a weak maximum at 3215 cm^{-1} (ascribable to O-H stretching), and two more defined absorption bands at ≈1730 cm^{-1} (internal double bonds, -CF=CF-) and ≈1440 cm^{-1} (methylene CH$_2$ scissoring) [13,24,28]. Other less intense bands were found at 1051 and 1038 cm^{-1} (doublet, C-OH hydroxyl stretching) [29], 1008 and 880 cm^{-1} [28] (Table 3). The comparison between new samples and #1 treated samples spectra are shown in Fig. 4.
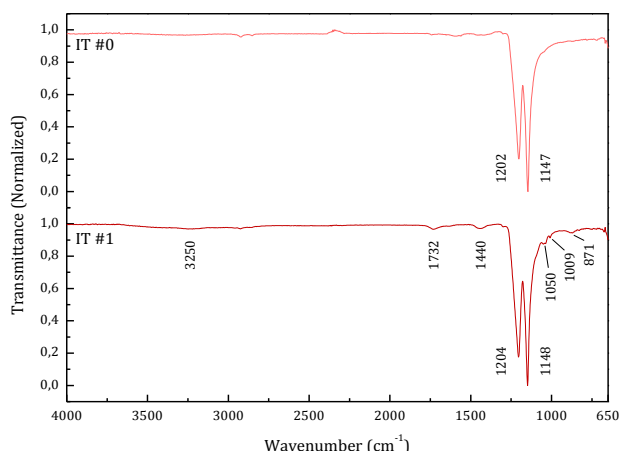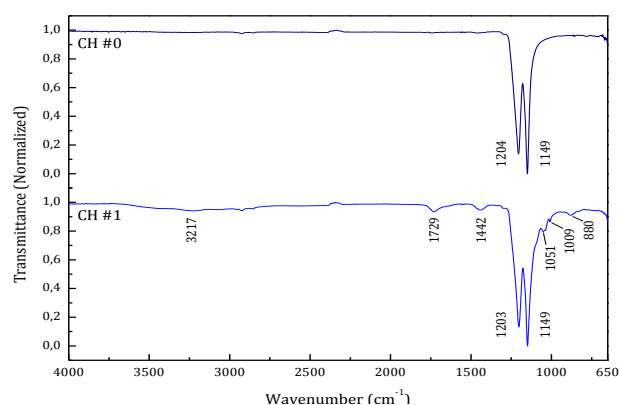

Fig. 4. Comparison between FT-IR spectra of the new (#0) and #1 treated samples. Chinese (#A vs. #C), up; Italian (#B vs. #D), down.

The comparison between spectra shown in Fig. 4 reveals that Chinese sample (#C) seems to have been affected most by the acid treatment in respect to the sample (#D). This effect can be also seen comparing directly the spectra of both the #1 treated samples, as shown in Fig. 5, after having normalized them using the 1150 cm^{-1} signal.

Fig. 5. Comparison between Chinese (#C) and Italian (#D) samples, after treatment #1.

In order to evaluate the presence and intensity of a degradation gradient from the surface to the core of the gasket, a line scan on the sample sections has been acquired. The false-colour image shown in Fig. 6, represents the result of the line scans. Observing the Chinese sample (up image), it can be noticed that the broad signal in the 3600-3200 cm^{-1} region (O-H hydroxyl stretching) results more intense from the upper surface up to 350-400 μm inwards, while it is less intense on the opposite surface. A similar trend is noticeable for the internal double bonds signal (-CF=CF-, 1732 cm^{-1}), while the one at 1442 cm^{-1} (CH$_2$ scissoring) shows a substantial symmetry between the two surfaces, with a significant presence of the signal even at the material core, in the central areas of the cross section.
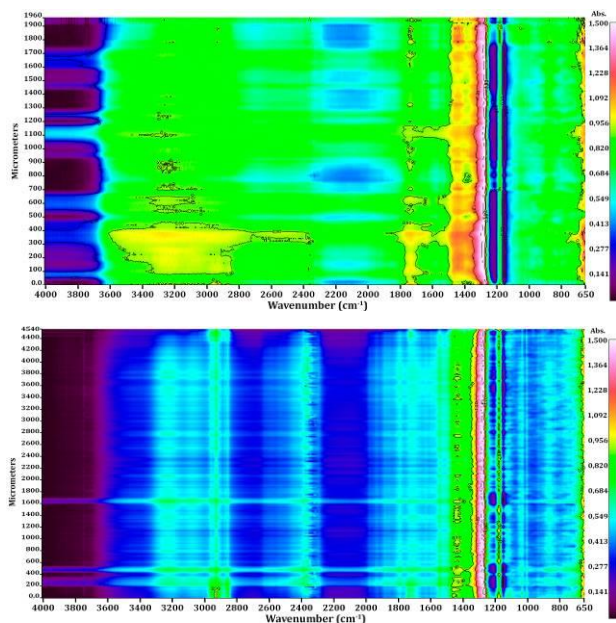
Fig. 6. Results of the line scans of samples with #1 treatment: Chinese (#C), up; Italian (#D), down.

The Italian sample (down image) shows a minor damage due to the acid treatment, with few signs at the upper surface (at the bottom of the image) and up to 400 μm inwards. There are also weak signs of degradation in the inner part of the gasket.

Comparing the degradation effects, the penetration of the chemical attack seems to be the same for both samples, while the intensity of the degradation appears to be stronger for the Chinese sample.

3.3 Samples with treatment #4

Chinese sample, (#F), subjected to treatment #4, shows a very inhomogeneous surface, with clear but various signs of degradation, as it can be seen in Fig. 7 (up): in all of the spectra reported, hydroxyl (≈3215 and ≈1047 cm^{-1}), internal double bonds (≈1730 cm^{-1}) and methylene (≈1430 and ≈880 cm^{-1}) signals are present. Moreover, another signal that could possibly be assigned to stretching vibration of terminal methylene groups (-CRR'=CH$_2$), appears at 1620-1640 cm^{-1} [28,30]. In the third spectrum reported (#4_c, green line) a marked decrease of the intensity of the CF$_2$ stretching absorption band can be observed at 1205 cm^{-1}. Simultaneously, a more pronounced increase of both the hydroxyl and the internal double bond absorption bands is clearly noticeable. Finally, the appearance of quite intense absorption

bands at 2854 and 2924 cm^{-1} (C-H symmetric and asymmetric stretching, [31,32]), as well as a fairly visible shoulder at 1460 cm^{-1} (CH$_2$ scissoring) [33,34]. The sum of these factors denotes a major presence of internal double bonds, methylene and hydroxyl groups, and this could reasonably mean that both defluorination and hydroxylation occurred.

Italian sample (#F) shows a rather more homogeneous superficial composition, as it can be seen by the overlay of different spectra acquired in various surface areas (Fig. 7). Moreover, it seems that Italian sample exhibits greater resistance to this particular chemical attack when compared to Chinese one.
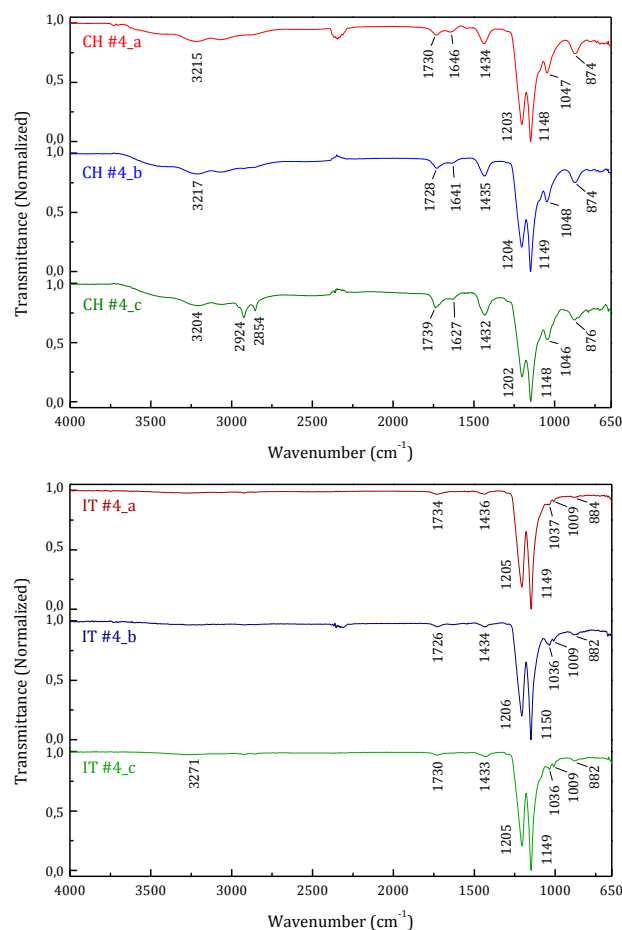

Fig. 7. Compositional variability of samples surfaces after treatment #4: Chinese (#G), up; Italian (#H), down.

The line scans of the two samples (Fig. 8) reflect what already pointed out by the superficial analysis. Chinese sample line scan (on the top), shows a marked superficial degradation on both surfaces, with a faint degradation profile. The Italian sample line scan (on the bottom) shows a

291

negligible presence of damage on the surfaces, but also signals related to hydroxyls and internal double bonds in the central areas of the cross-section.
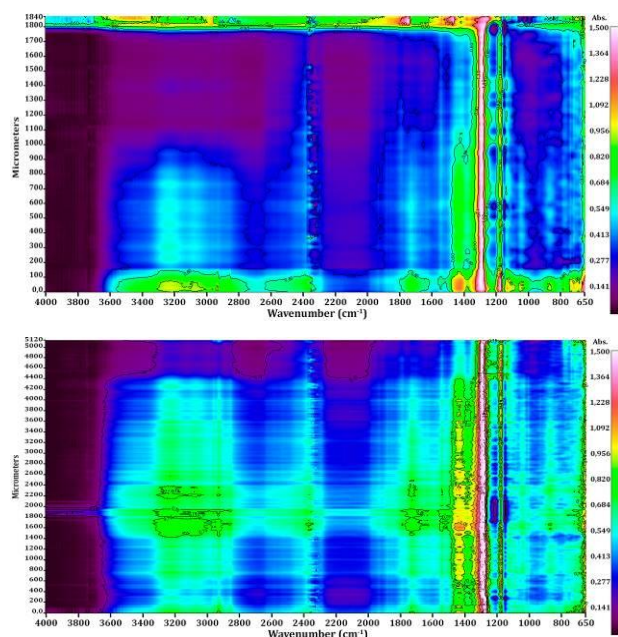

Fig. 8. Results of the line scans of samples, with #4 treatment: Chinese (#E), up; Italian (#F), down.

3.4 Samples with treatment #6

Chinese (#G) sample subjected to treatment #6 shows a pronounced superficial degradation, and a limited compositional variability (Fig. 9, up). Italian sample exhibits less deterioration and an almost absent variation in composition (Fig. 9, down).

The greater compositional variability of the surface shown by Chinese sample subjected to treatment #6 is also reflected in the core of the material. This behaviour is deducible from the mosaic image shown in Fig. 10, where it's clearly visible the presence of reddish stains along the section. To better understand the nature of these stains, two line scans for this sample have been acquired: the first one passing through the red stain, indicated with a red line; the second one in an area free of these stains, indicated with a blue line.

The differences in aspect visible in Fig. 11 correspond to compositional differences as it can be seen from the comparison of the FT-IR line scans reported in Fig. 12: the upper is referred to the line scan passing through the reddish stain (in red on the cross-section visible

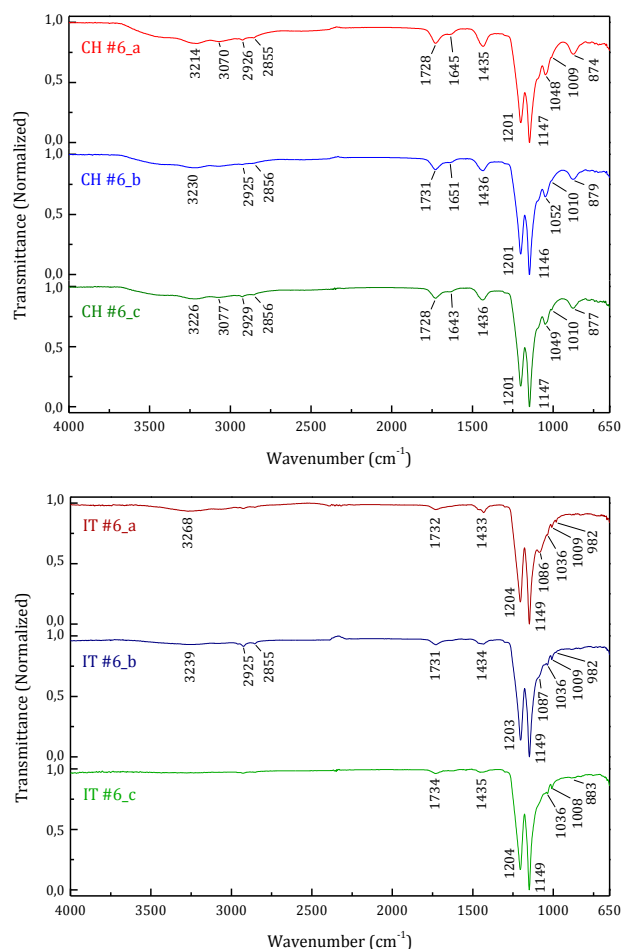image), the one at the bottom to the line scan passing afar from the red stain.

Fig. 9. Compositional variability of samples surfaces after treatment #6: Chinese (#G), up; Italian (#H), down.
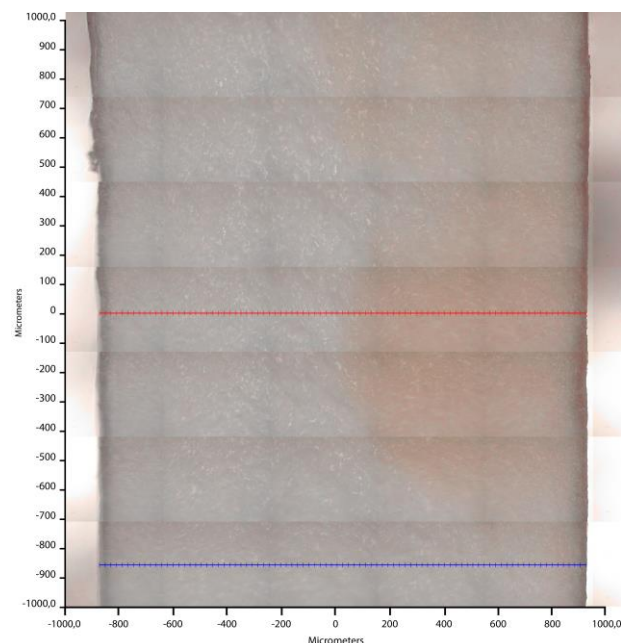

Fig. 10. Cross-section of Chinese sample (#G) subjected to treatment #6.
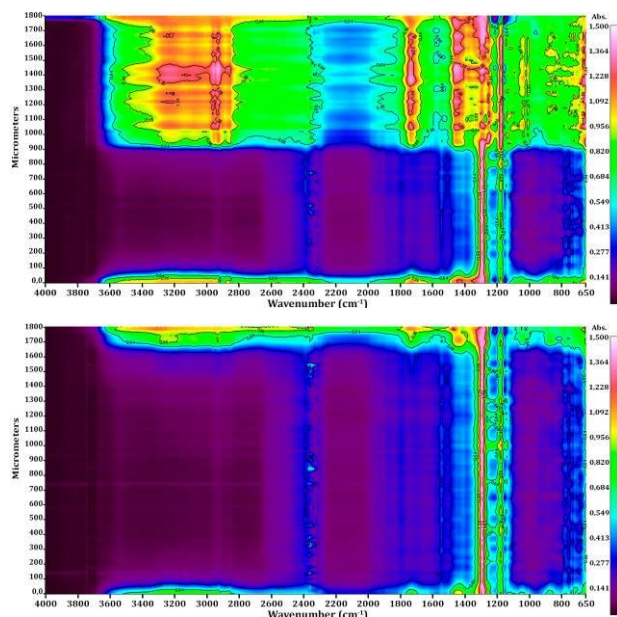
Fig. 11. Comparison between two line scans of Chinese sample (#G) subjected to treatment #6.

It can be seen how the change in colour in the visible image (Fig. 10) is directly related to a strong degradation of the PTFE matrix. However, signs of hydroxylation could be found also in the line scan referred to the blue line (Fig. 11, right), even if only at the two surfaces, especially at the bottom surface (the top of the line scan image, the surface at right in the visible image).
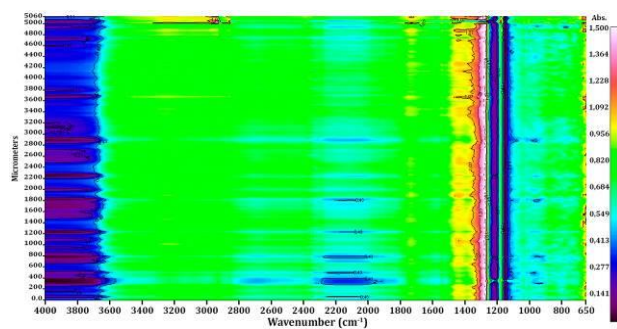

Fig. 12. Result of the line scan of the Italian (#H) sample, treatment #6.

Italian sample shows a diffuse, but not so intense degree of degradation along the whole cross-section (Fig. 12). On the bottom surface (the upper part of the image), stronger hydroxylation can be noticed, possibly due to the presence of decomposition products from the adhesive layer.

3.5 Sample with treatment #9

Both Chinese and Italian samples subjected to treatment #9 exhibit quite good superficial resistance and a limited compositional variability. Chinese sample seems to be slightly more degraded, and this seems to be confirmed by the presence of red-coloured fissures on the surface (Fig. 13).
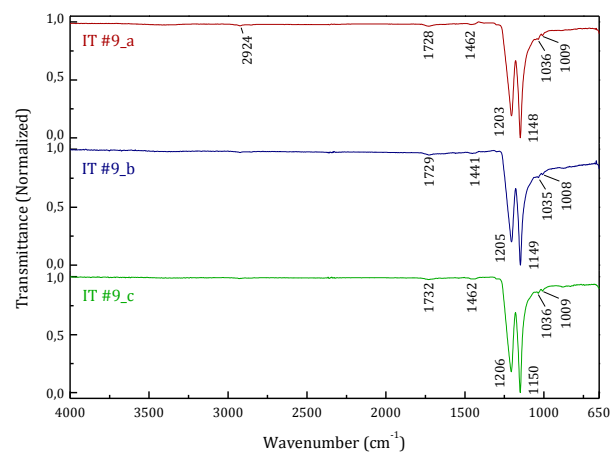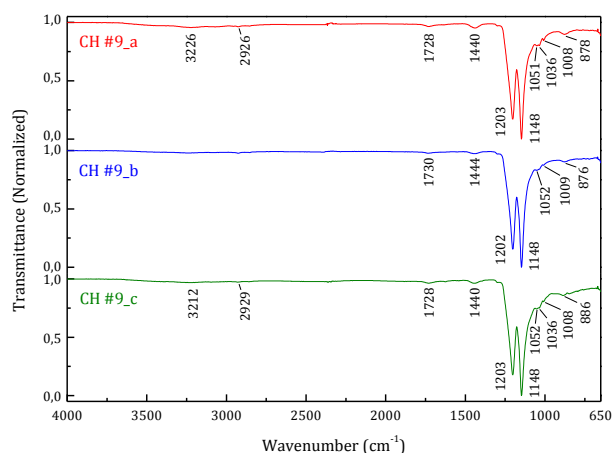

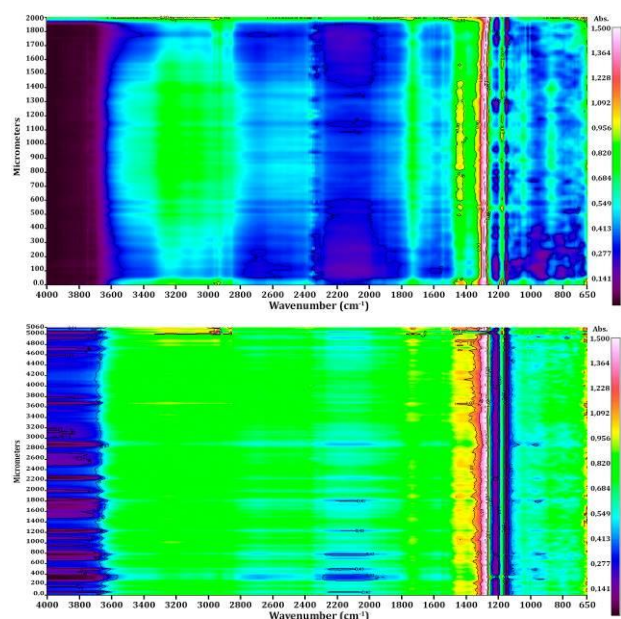**Fig. 13.** Compositional variability of samples surfaces after treatment #9: Chinese (#I), up; Italian (#J), down.

Fig. 14. Line scans of samples after treatment #9: Chinese (#I), up; Italian (#J), down.

Tab. 4. Summary of analysis results of the samples.

Acid Treatment	Manufacturer	DI$_\%$ (Surface)	E$_r$%	In-depth Degradation	Surface damages
#1	Chinese	4,4	59	Medium	No
	Italian	5,6	14	Negligible	No
#4	Chinese	16,3	35	Weak	No
	Italian	3,7	31	Weak	No
#6	Chinese	19,2	34	Strong in some areas	Yes
	Italian	6,7	30	Negligible	No
#9	Chinese	3,2	27	Negligible	Yes
	Italian	2,9	26	Negligible	No

The line scans of both samples confirm the limited superficial compositional variation and the presence of weak related signals along the whole cross-sections (Fig. 14). These signals seem to be more uniform in the case of the Italian sample, while the Chinese one exhibit a less homogeneous degradation profile: presence of slight hydroxylation signs on both surfaces, then a rapid decrease from 50 to 400 μm in depth, and finally a further, gradual increase to the centre of the cross-section.

4. CONCLUSIONS

This paper investigates the degradation of PTFE exposed, for a long period, to a combination of acids and temperature. Two series of PTFE gaskets, produced by two different manufacturers (one from Italy and other from China) have been subjected to IR analysis by mean of a μFT-IR spectrometer. These gaskets have been treated with different mixes of acid solutions. These samples have been analysed to evaluate different behaviours in response of the various acid treatments at high temperature. Results have highlighted different behaviours for the PTFE matrix, but also differences between Teflon manufacturers. In particular, all samples subjected to treatment exhibits different degrees of hydroxylation and defluorination, put in evidence by the presence of characteristic signals of hydroxyl groups (≈3215 cm^{-1}), internal double bonds (1730 cm^{-1}) and diffuse methylene signals. This behaviour seems to confirm the results previously reported, where the degradation of PTFE was obtained by electron irradiation or plasma treatments rather than acid attacks, and often on thin films rather than thick commercial gaskets [11,12,20,21]. In The principal results have been summarized in Table 4, using the -CF$_2$- (≈1203 cm^{-1}) to -CF=CF- (≈1730 cm^{-1}) peaks area to calculate a "percentage degradation index" (DI$_\%$), in manner analogous of what reported in

standard method ASTM F2102-13 for the calculation of the "oxidation index" [35].

Furthermore, the calculation of deviations from the mean value could provide a numerical indication of the homogeneity of the superficial degradation. More in depth, having higher DI$_\%$ variations from the average value mean that there is a wider DI$_\%$ range and therefore a greater inhomogeneity of the surface. This approach suggests us the following conclusions:

- The highest degree of degradation is shown by samples subjected to treatment #6, which was not, theoretically, the most aggressive acid solution, being composed of 30 %wt Sol. I plus 2.5 %wt Sol. II. This indicates a possible synergy of the two acid solutions used, due to the fact that samples treated with the same amount of Sol. I in absence of Sol. II shown almost no sign of degradation and were not included in the present study.

- The less degraded samples seem to be those subjected to treatment #9. The corresponding acid solution consists of 30 %wt Sol. I plus 5%wt Sol. II. This suggests that the probable synergistic effect of hydrofluoric acid may be more complex than expected.

- In between, treatment #1 and #4 are placed, with different behaviours shown by the two different manufacturers: Chinese gasket subjected to treatment #4 has a DI$_\%$ four times higher than DI$_\%$ of the #1 treated sample; Italian gasket exhibits an opposite trend, having the #1 treated sample a slightly higher DI$_\%$ than the #4.

- Treatment #1 is the only one where Italian samples behave worse than Chinese ones, whereas in all other cases (especially #4 and #6) Chinese samples show far worst results.

- Regarding the superficial homogeneity, our experimental data suggest that in all cases

Chinese samples exhibit a less homogeneous surface after the treatment.

The possible synergistic effect of the two acid solutions used could be object of future studies, as well as a limit or stoichiometric concentration of both solutions in order to have a marked increase in the degradation effects of the PTFE matrix.

It also provided additional suggestions for the preliminary identification of potential mechanics of wearing.

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