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RESEARCH

Investigations into the Degradation of PTFE Surface Properties by Accelerated Aging Tests

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A B S T R A C T

This paper describes an accelerate aging procedure used for investigating the surface alteration of PTFE gaskets commercialized by two alternative producers. These gaskets are installed in modern process plants where tires moulds are cleaned inside a multistage ultrasonic process. The surface of gaskets degrades inexplicably under ordinary operative conditions after a relatively short period. Even if these gaskets are exposed to a combination of ultrasonic waves, temperature, humidity and acid attack, the PTFE properties of resistance nominally exclude the possibility of severe erosion phenomena as highlighted during the real utilization. A possible explanation could be represented by the presence of unexpected chemical compounds emerging from the disaggregation of highly reacting elements from the tire composition. In particular, it is believed that the unpredicted combination of fluorides and chlorides could explain the violent chemical attack highlighted on steel tanks and on their gaskets. But no evidence exists. Thus, the experimental characterization of PTFE properties has to follow an appropriate accelerated aging, aiming at actuating the specific mechanics of wearing as in industrial use.

1. INTRODUCTION

Preliminary researches and investigations highlighted as commercial PTFE gaskets, when installed in specific ultrasonic cleaning plants, show degradation phenomena not compatible with the conditions of use [1].

It is the case of plants utilized for cleaning tires moulds by immersion in the washing tanks. The cleaning effect is obtained by the sum of several factors: ultrasound, chemicals, temperature and liquid agitation. This technology, known as Mould Ultrasonic Cleaning Systems (UMCS), is of military origin, developed for the cleaning of gun mounts [2]. These UMCS plants represent the largest ultrasonic cleaning systems currently existing, even larger than military ones, whose tanks are longer, but more narrow (Fig. 1).

Designed by RSM Keymical Srl in San Marino, the construction was entrusted to Himile Gaomi, China. The costs of plant varies from 320,000 to 450,000€ depending on the configuration.

Currently, there are 45 plants, installed in Germany, England, Italy, Brazil, Mexico, Turkey, Romania, Russia, China and Indonesia. They are used by Pirelli, Bridgestone, Continental, Toyo, Good Year, Michelin and others, and constantly monitored for design improvements [3].

Fig. 1. An Ultrasonic Mould Cleaning Systems plant .

The presence of a Chinese manufacturer which uses to procure components and parts on the Chinese market, left to imagine the possibility that the PTFE gaskets were qualitatively inferior to those specified in the project design (referring to an Italian PTFE producer), although nominally equal. Starting from this preconception, the first comparative analysis was performed, by means of microscope observations (optical and scanning) and infrared spectroscopy, which actually showed a not negligible behavioural difference between materials from two origins.

These differences were related to several aspects (composition, mechanical strength, etc.) showing a net superiority of the Italian PTFE (use as term of comparison), without, however, leading to an unambiguous indication of Chinese gaskets' unacceptability.

At the same time, it should be noted, that the earlier study covered only gaskets unused or ones whose conditions of use could not be determined with certainty.

Hence the need to launch a comparative study of PTFE gaskets being degraded in a controlled environment by acid and temperature.

This research describes the aggravated conditions of heat, humidity, acid attack used to speed up the normal aging processes of PTFE gaskets inside the UMCS plants. Even if this analysis has been realized before implementing a complete session of laboratory tests for the experimental characterization of materials, nevertheless, the effect of aging has been preliminary investigated by micrographs and absorption tests, as presented in the following sections with useful details.

2. MATERIAL

Polytetrafluoroethylene (PTFE), also known as Teflon [4], is a synthetic thermoplastic polymer showing remarkable properties.

According to the producers technical sheets, but also to several independent investigations, as in [5-9], PTFE has a high thermal stability between -200 °C and +260 °C, with high melting temperature (670 °C), unperishable over time.

It is also resistant to acids, alkalis, solvents and various chemicals inside a range 0:14 pH. Because of its extreme non-reactivity and high temperature rating, PTFE is often utilized in applications using acids, alkalis or other chemical reagents. Moreover, there are no experimental evidence of structural, material or tribological degradation in connection with the exposure to ultrasonic waves. Only under very uncommon circumstances PTFE degrades as reported in [10-11].

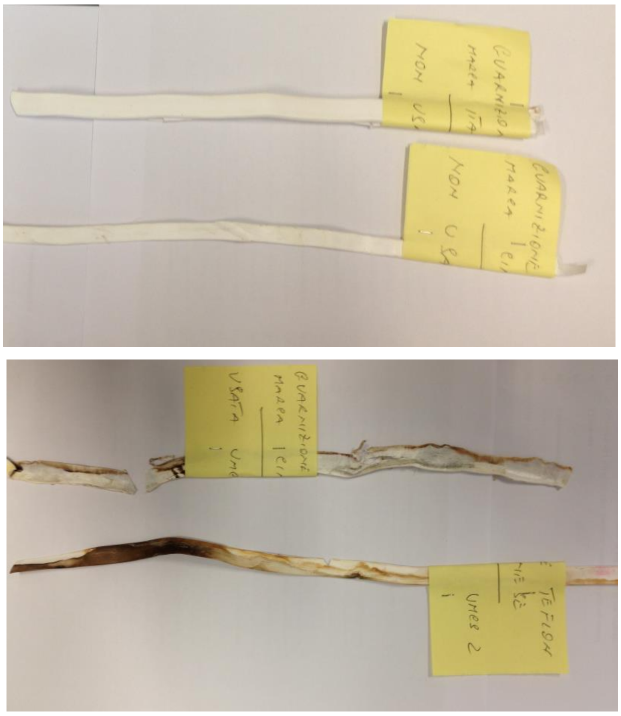


Fig. 2. PTFE gaskets before *(top)* and after *(down)* their use inside the UMCS [1,3].

In a few words, PTFE thermal and chemical stability makes this material a valid choice in a large number of industrial applications [12]. And, considering how far from these extreme conditions gaskets are in the case of UMCS, no relevant degradation in PTFE is expected. But evidences from maintenances suggested a different reality with deteriorate gaskets (Fig. 2).

Their progressive degradation under the persistency of UMCS operative conditions [3], including a correct recognition of mechanisms of wearing (e.g. fatigue, fretting, corrosion…), represents a relevant field of investigation, not distant respects to other recent analysis [13-17].

3. PROCESS

The *Ultrasonic Mould Cleaning System* (UMCS), as said, uses ultrasonic waves, in combination with temperature and chemical attack, to remove rubber scraps and other physical residuals from interstices of the moulds. The UMCS consists in a four-stage process where moulds are shifted between four metal basins and plunge into, alternatively, acid and basic baths. Several parts of the plants, including flange gaskets, are exposed to the same deteriorating environment. The "worst" situation is represented by the most aggressive acid bath in the process line, realized by a <1 pH solution of acid chloride, where 26-28 kHz of ultrasonic waves and a temperature between 70 and 80 °C is simultaneously applied [18]. Referring to the acid solution, in the previous investigation [1], an acid bath obtained by sulphamic and citric acids were initially supposed. It is noteworthy that the exact composition of solvents is subject to a strict industrial confidentiality.

But, recent chemical controls provided an interesting evidence [19]. In particular, they highlighted the presence of traces of fluorides, chlorides and other uncommon elements.

The solvents' producer categorically excludes the possibility that these elements were present inside the chemical solutions at the start, based on sulfamic and dodecylbenzenesulfonic acids. Therefore, it is presumed that they are a consequence of disaggregation of chemical elements inside the tire compound, passing into the mould and, finally, in the cleaning solution.

Figure 3 compares the surfaces of moulds before and after the ultrasonic cleaning. Usually, these residues, dissolved in liquid in form of organic or inorganic (e.g. metal) elements, are filtered away or settled on the bottom of the container as mud. But, sometimes, they are dissociated by water remaining in different chemical forms.

In general, the materials of modern pneumatic tires are synthetic rubber, natural rubber, fabric and wire, along with carbon black and other chemical compounds [20].

Fig. 3. Comparing tires mould surfaces before (up) and after (down) the Ultrasonic Cleaning.

In brief, a tire merges up to 300 different chemical elements, both organic and inorganic, natural and synthetic, and several of them could be easily disassociated in acids (Table 1).

Table 1: Tire compound composition [20].

Ingredients	Car	Lorry	OTR
Rubber/Elastomers	47 %	45 %	47 %
Carbon Black	21.5 %	22 %	22 %
Metal	16.5 %	25 %	12 %
Textile	5.5 %	--	12 %
Zinc Oxide	1 %	2 %	2 %
Sulphur	1 %	1 %	1 %
Addictives	7.5 %	5 %	6 %
Total Carbon-based materials	74 %	67 %	76 %

The only chemicals known to affect the carbon-fluorine bonds in the PTFE are certain alkali metals and the most reactive fluorinating agents [21,10-11], but not all potential chemical reagents have been combined in experiments.

Thus, even without the possibility to identify, at the moment, a specific single element or a combination of compounds, it is highly probably that these unanticipated chemical elements represent the main reason for the sudden degradation of PTFE in UMCS. In particular, it is believed that just the unexpected combination of fluorides and chlorides, together with the anomalous accumulation of deposits on the tank bottom, can explain the violent chemical attack highlighted on steel tanks and on their gaskets.

4. METHODS

Since the general uncertainty of the chemical composition, but also in order to propose several alternative “aggravated conditions” to speed up the normal aging processes of items, in line with an Accelerated Life Testing approach, different combinations for chloride and fluoride acids have been considered. For each of these combinations PTFE specimens by two different manufacturers, one Italian (IT) and a Chinese (CH) have been investigated.

Table 2. Aging conditions with indication of chloride (HCl) and fluoride (HF) concentrations.

#	H_2O	HCl	HF	°C	T
1	50 %	40 %	10 %	80°	1500 hr
2	90 %	10 %	0 %	80°	1500 hr
3	80 %	20 %	0 %	80°	1500 hr
4	87.5 %	10 %	2.5 %	80°	1500 hr
5	77.5 %	20 %	2.5 %	80°	1500 hr
6	70 %	30 %	2.5 %	80°	1500 hr
7	85 %	10 %	5 %	80°	1500 hr
8	75 %	20 %	5 %	80°	1500 hr
9	65 %	30 %	5 %	80°	1500 hr
10	70 %	30 %	0 %	80°+40°	1500+300 hr

Entering in further details, PTFE was provided in form of commercial Teflon tapes. Tapes were cut into segments from 200 mm to create individual samples. The other dimensions were dependent upon the specific tape marketed.

These samples were placed in containers and immersed in 10 different acid baths. In each container 2 samples were included, one Italian and one from China. Table 2 summarizes the aging conditions.

Each acid bath was characterized by a specific combination of hydrochloric *(HCl)* and hydro-fluoric acids (*HF*), provided by a concentration of, respectively, 0.1 % and 1 %.

The containers were placed in a T-controlled oven and maintained at a temperature of *80 °C* for a period of time equal to *1.500 hr* (2 months). A particular container (# 10), which is intended to represent the most common condition of use, was previously held at room temperature for additional 300hr without relevant effects.

At the end of the aging treatment, the specimens were extracted from oven, cleaned under running water, dried, weighed and placed in the oven (12 hr, 40 °C) to allow a complete drying.

5. ABSORPTION

During the experience emerged as Teflon, contrary to what was expected, released liquid after being subject to prolonged immersion. This release appeared progressive and long-lasting in time (even several days). This liquid absorption effect can be measured by the *coefficient of absorption*, which is given by the ratio between the difference of water-soaked weight of the material and the dried state. This parameter is quite common due to its significance in the commodity evaluation of many materials.

In the specific case, the absorption coefficient was evaluated by comparing the weights before and after drying. Figure 4 shows the weight increase related to the absorption of liquid by the PTFE specimens to vary the overall concentration of acids (*HCl + HF*). All the specimens increased their own weight by water absorption, also significantly: no specimen improved its weight less than 40 %.

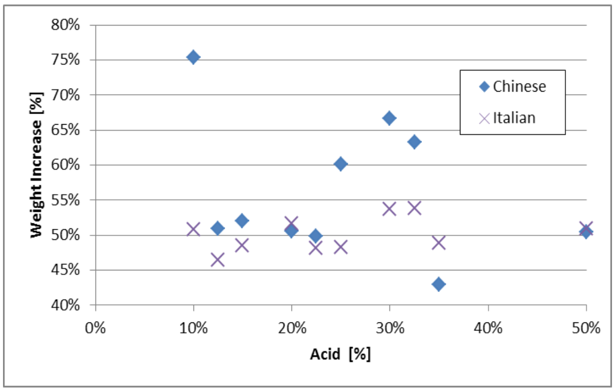


Fig. 4. Weight increase in the case of different aging conditions.

This effect neither appears particularly linked to the concentration of the acids, nor to the prevalence of one acid respects to the other. At the same time, the differences in behavior between the Italian and Chinese Teflon gaskets are evident. While the increase in weight for the Italian specimens remains basically stable between samples, within a band of variability around 10 %, Chinese ones show a greater deviation (>20 %). This variance is to be added to a larger increase in terms of absolute values (up to 66 %).

For a correct evaluation of this information, it should be noted that the absorption of liquid (or imbibition) is not a chemical process, but a physical one, and can be of capillary origin, osmotic or molecular. Capillary absorption occurs when the liquid penetrates by capillary action into existing holes, replacing the gas contained within them; osmotic imbibition occurs when the material is composed of capillaries delimited by semi-permeable barriers, whether empty or filled with solutions with a different concentration of the incoming one; molecular imbibition, properly referred to as swelling, when the material directly by binding molecules interact weakly (London forces, hydrogen bonding) with those of the solution.

Furthermore, it is also noteworthy that a higher imbibition is not in itself synonymous with lower functional capacity for the gasket. Indeed, a tendency to swell, thereby increasing the contact pressure in the flanges, could bring them to seal any interstices with greater efficiency. However, the result of absorption exhibited here leaves out indirect aspects.

Several studies and all commercial datasheet lead to consider the Teflon as an absolute strength material compared to its atmospheric agents thanks to a water absorption of 0 % (tests in accordance with ISO 175:2010 [21]).

The measure of absorption denies this indication leaving two explanations, especially factual in the case of Chinese Teflon: a. the quality of *this* PTFE is inadequate for the specific UMCS use; b. the presence of unexpected chemical elements in the cleaning solutions degrades gaskets anyway, making PTFE inappropriate *in any case*. Both options are against the general considerations according to which the PTFE would remain inert to all chemical reactants.

At the same time, these results clearly anticipate how the Chinese PTFE could be more sensitive to possible corrosive problems in consideration of the fact that a greater amount of acid would be absorbed inside the material by imbibition and penetrate to greater depths. In addition, it confirms a superior inherent variability in the characteristics of the material that represents a critical situation where, as in this case, it is foreseen a very next use at the most extreme conditions.

6. MICROGRAPHS

Before and after aging, the specimens were observed by two different optical microscopes and magnifications in order to optimize the images. In particular, the micrographs were repeated on different specimen surfaces (front and lateral), at different magnifications (50x, 100x, 200x, 400x). The most significant micrographs are shown in comparative format in Tab. 3 and 4. They also report additional images, in high magnification, on a Chinese sample, aged by #6 aging conditions, where defects (as inclusions) are evident (Fig. 5).

The comparison of images suggests a greater tendency of the Chinese PTFE to degrade, at least on a superficial level, than the Italian one. It also confirms the results of previous studies which indicated a lower quality in the case of Chinese Teflon (e.g. greater inhomogeneity, defects, ...). Geometrical faults on surface and partially altered zones are also evident.

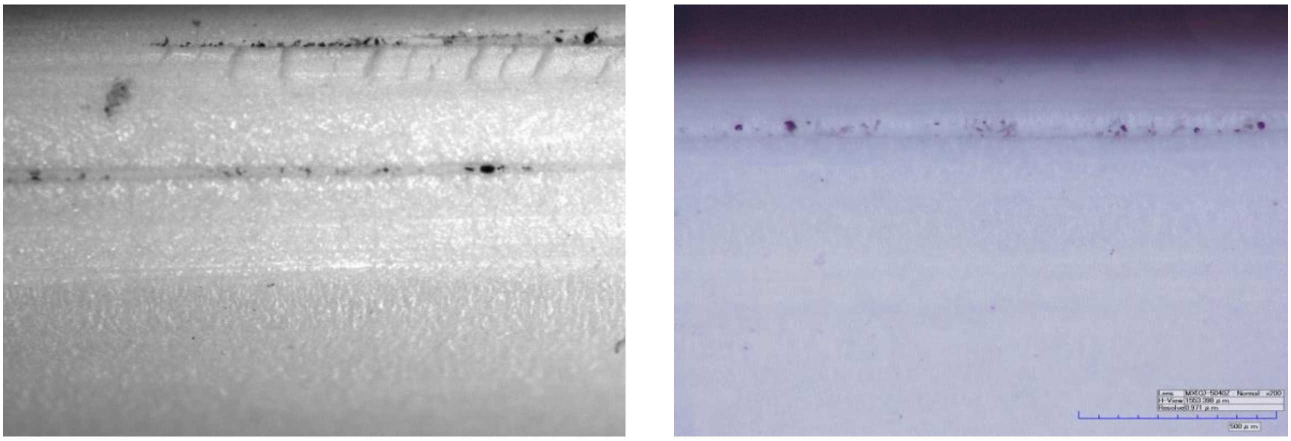


Fig. 5. Optical micrographs (200x and 400x) for Chinese aged sample showing defects and inclusions.

Table 3. Optical micrographs of *Italian* (up) and *Chinese* (down) samples before aging.

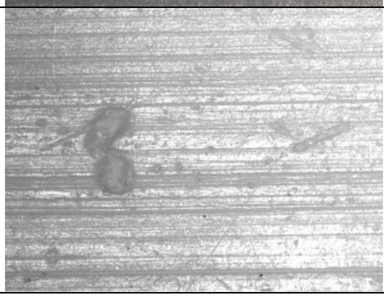
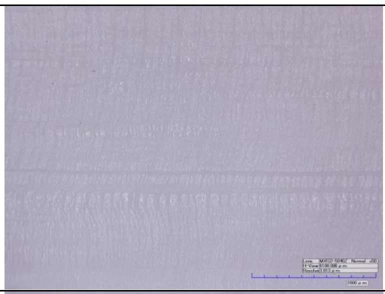
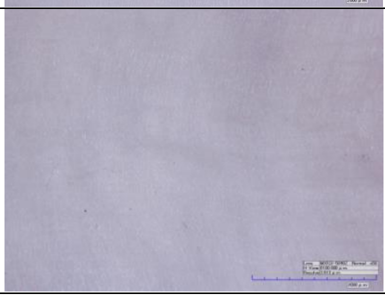
	50x	100x	400x
ITALIAN			
CHINESE			

Table 4. Optical micrographs of *Italian* (up) and *Chinese* (down) samples after aging.

	50x	100x	400x
ITALIAN			
CHINESE			

7. CONCLUSION

This paper permitted to continue the surprising investigation regarding the degradation of PTFE exposed, for a long period, to a combination of temperature, acid attack and ultrasonic waves. It also provided additional suggestions for the preliminary identification of potential mechanics of wearing. The interest for this argument is related to the evidence that commercialized gaskets in PTFE (or *Teflon*), installed in process plants for cleaning tires moulds by a ultrasonic process (UMCS), showed wearing effects against all results from previous similar investigations. According to a very large number of consolidated experimental studies, in fact, the PTFE is practically inert to all common chemical compounds. It would be only attacked by alkali metals in the elemental state, by chlorine-trifluoride and elemental fluorine. These elements are nominally absent inside the UMCS cleaning solutions. But, even in the case these elements were present (e.g. contaminants), it would be also quite complex to clear up their final effects on PTFE. The same investigations also demonstrated, sure enough, that these effects are conceivable only in the case of temperature and pressure higher away from the current plant operative conditions.

With the aim at moving fast toward a better comprehension of these unfamiliar phenomena, the surface degradation of samples after aging will be carefully analysed using FT-IR Analysis, Thermogravimetric Analysis (TGA) and, finally, Differential Scanning Calorimetry (DSC). All being well, these tests will fully detail the occurrences of wear degradation in PTFE during operation in terms of chemical attacks of unexpected elements. On the contrary, the explanation has to be searched in the influence of fast waves of pressure caused by the use of highly energetic ultrasonic waves. In this case, almost certainly a superposition of several effects (e.g. cavitation, tribocorrosion) has to be taken in count.

Acknowledgement

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 are produced and commercialized worldwide by Keymical Group.

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