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RESEARCH

Experimental Evaluation of the Surface Alteration of Gasket Samples under Operative Conditions

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A B S T R A C T

This paper investigates the surface alteration of gasket samples commercialized by two alternative producers. These gaskets, in polymeric materials, are installed in process plants used for cleaning tires molds by a pioneering ultrasonic process. They are exposed to a combination of ultrasonic waves, temperature, humidity and acid attack causing several erosion phenomena. Their surface degradation under ordinary operative conditions was investigated using mechanical and tribological tests. The experimental characterization was performed by optical microscopy, scanning electron microscopy, thermograms, differential scanning calorimetry curves and infrared spectra aiming at defining the specific mechanics of wearing. As a conclusion, it was possible to state that even if samples exhibit similar chemical structures, their thermal and mechanical properties as well as their geometric dimensions are different. Such differences in the materials might cause various unexpected wear behaviors when gaskets are employed in the same working conditions.

1. INTRODUCTION

A gasket is a mechanical seal which fills the space between two or more mating surfaces, generally to prevent leakage from or into the joined objects while under compression [1]. Gaskets allow functioning mating surfaces on machine parts where they can fill irregularities.
Gaskets account for a very small proportion of the overall cost of industrial systems yet they are often of decisive importance for the proper functioning of equipment. They permit to control and predict leak rates from valve stems, pumps, basins, flanges, etc.

Gaskets come in many different designs based on industrial usage, budget, chemical contact and physical parameters [2,3].

According to the specific use, gaskets can even assume a different denomination. This investigation specifically refers to *flange gaskets*. A flange gasket is a type of gasket made to fit between two sections of pipe that are flared to provide higher surface area. Flange gaskets come in a variety of sizes and shape.

Instead of pipes, these specific gaskets match the metal basins installed inside an innovative family of process plants used for surface treatments and cleanings of tires molds (Fig. 1). This process, also named as *Ultrasonic Mold Cleaning System,* uses ultrasonic waves in combination with temperature and chemical attack, to remove rubber scraps and other physical residuals from interstices of the molds.

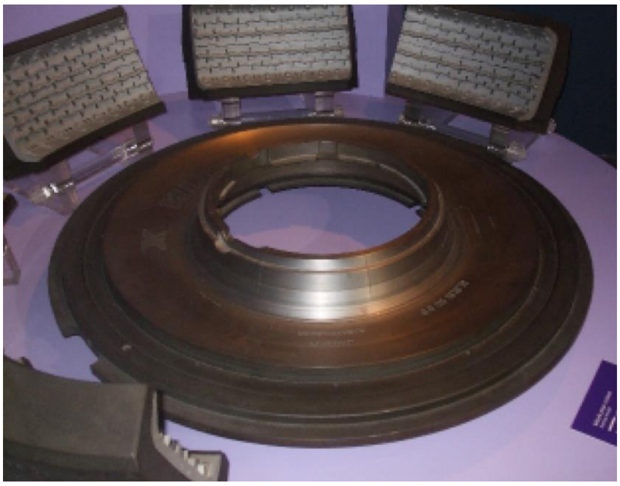

Fig. 1. Metal mold used in tires production and sections of tires (Courtesy Michelin).

The UMCS consists in a four-stage process where molds are shifted between four metal basins and plunge into, alternatively, acid and basic baths. The mold remains in each basin for a proper interval of time, exposed to a specific combination of ultrasonic wave's intensity, *room* temperature and chemical attack. While these environmental conditions permit to clean the molds, several parts of the plants (as metal sheets, welding's and, finally, flange gaskets) are exposed to the same deteriorating phenomena (Fig. 2). Their progressive degradation under the persistency of all these operative conditions, including a correct recognition of mechanisms of wearing (e.g. fatigue, fretting, corrosion…), represents a relevant field of investigation [4,5].

Fig. 2. Example of use of PTFE gaskets inside a plant for tyre moulds treatment (Courtesy Keymical)

Gaskets are normally made from a flat material, a sheet such as rubber, silicone, metal, neoprene, fiberglass, nitrile rubber, plastic polymers (such as polychlorotrifluoroethylene) or, as in this specific investigation, polytetrafluoroethylene (PTFE), better known as Teflon [6].

PTFE is a synthetic thermoplastic polymer showing a white solid aspect at the room temperature and physical/chemical proprieties (Table 1) appropriate to numerous applications.

Table 1. Main conventional proprieties for PTFE [7].

Property	**Value**
Density	2200 kg/m^3
Melting point	600 K
Thermal expansion	112–125 · 10^{-6} K^{-1}
Thermal diffusivity	0.124 mm^2/s
Young's modulus	0.5 GPa
Yield strength	23 MPa
Coefficient of friction	0.05–0.10

Its stability and insulation propriety, combined with high melting temperature, makes the material of valid choice as a high-performance substitute for the weaker and lower-melting-point polyethylene commonly used in low-cost applications. In industrial applications, owing to its low friction, PTFE is used where sliding action of parts is needed. And the extremely high bulk resistivity makes it an ideal material for fabricating long-life part in plants [8].

PTFE has a high resistance to both acids and bases. There is no known solvent for PTFE. The polymers in PTFE are uniformly sheathed with fluorine atoms, making PTFE inert to virtually all chemicals. Only under uncommon circumstances PTFE degrades (e.g. reacting with sodium or ionized oxygen). It also degrades under extreme electron bombardment [9,10]. In any case, these reactive situations are not normally encountered outside of special laboratory conditions.

Finally, PTFE is not affected by ultraviolet, visible or infrared light; while there are no experimental evidences of structural, material or tribological degradation in connection with the exposure to ultrasonic waves. Because of its extreme non-reactivity and high temperature rating, PTFE is often utilized as the liner in hose assemblies, expansion joints, and in pipe lines, particularly in applications using acids, alkalis or other chemicals. Then, no wearing phenomenon is awaited during the ordinary use of PTFE since its excellent resistance proprieties.

Considering the large use of PTFE in industry, several researches were focused on this material and the experimental validation of proprieties. Between the others, since its completeness and depth, it is convenient to highlight [11] where a temperature depending characterization of a PTFE material was carried out using various thermal analysis and thermophysical properties test techniques. For instance, the thermal expansion, density changes, thermal diffusivity and thermal conductivity were determined, together with the main viscoelastic properties (as storage and loss modulus). Measurements were carried out from −125 °C up to 150 °C and over. Other investigations were specifically related to surface proprieties and resistances, especially in connection with the use of PTFE as constituent in composite materials. For instance, the tribochemical characteristic of filled PTFE is presented in [12].

Coming back to similar applications, several papers also report technical solutions for improving the proprieties of PTFE in gaskets and, as consequence, their fields of application. For instance a new high compressive strength PTFE gasket material consisting of microfibres with additional filler materials is presented in [13] discussing the deformation and leakage behaviour of gaskets. Adding, advanced aspects in utilisation of gaskets were also investigated as in [14] where factors affecting high temperature relaxation behaviours of expanded PTFE gaskets where analysed.

The determination of the resistance of gaskets used in industrial applications to temperature, surface wear and chemical attack represent a relevant field of research and continue technical improvements. For instance, in order to manufacture gaskets for receptacles containing aggressive chemical substances, a patent permits a film of PTFE to adhere directly on a sheet of rubber avoiding additional glues [15]. Another patent describes a shielded gasket assembly for use in corrosive gas and liquid environments comprising a core gasket of a synthetic rubber and a shielding material of expanded PTFE [16].

Finally, several researches and patents propose improvements in materials, as in the case of a new copolymer, the elastomeric vulcanizate of which is suitable for use where extraordinary resistance to environmental attack by a temperature of 380° C. and corrosive fluids is required, comprising copolymerized units.

2. MATERIALS AND METHODS

This paper investigates the surface initial status and progressive alteration during use in the case of two types of gaskets, nominally equivalent, but commercialized by two alternative producers. These gaskets are realized by an expanded PTFE tape with an adhesive side, and can replace all types of asbestos gaskets and in rubber. *PTFE tape* represents an ideal solution of gasket in applications involving pumps, transmissions, compressors, or for the sealing of containers of gas or liquid (Fig. 3). Being soft and flexible, it can guarantee a perfect seal on uneven surfaces.

Fig. 3. Utilization of expanded PTFE tape as gasket.

According to its technical sheets, this expanded PTFE tape (known by the commercial name of *Adhefhon*) can withstand high pressures and has a high thermal stability, unperishable over time. It is resistant to acids, alkalis, solvents and various chemicals (within a range 0:14 pH). Finally, it has a large operating temperature, between -200 °C to + 260 °C.

Since these operative conditions, especially for the temperature, can be considered as extreme respect to the applications under investigation, no relevant degradation in PTFE is expected. But gaskets collected during maintenances suggested to perform an in-depth analysis.

As a consequence, N. 4 types of gasket samples were delivered in order to investigate if some differences exist between the various samples.
The delivered samples were named as:

- ✓ *Italian New*
- ✓ *Chinese New*

with the aim at highlighting the origin in the case of unused ("New") gaskets, and

- ✓ *UMCS 1*
- ✓ *UMCS 2*

with the aim at identifying the specific process plant *(Ultrasonic Mold Cleaning System)* where the sample has been used.

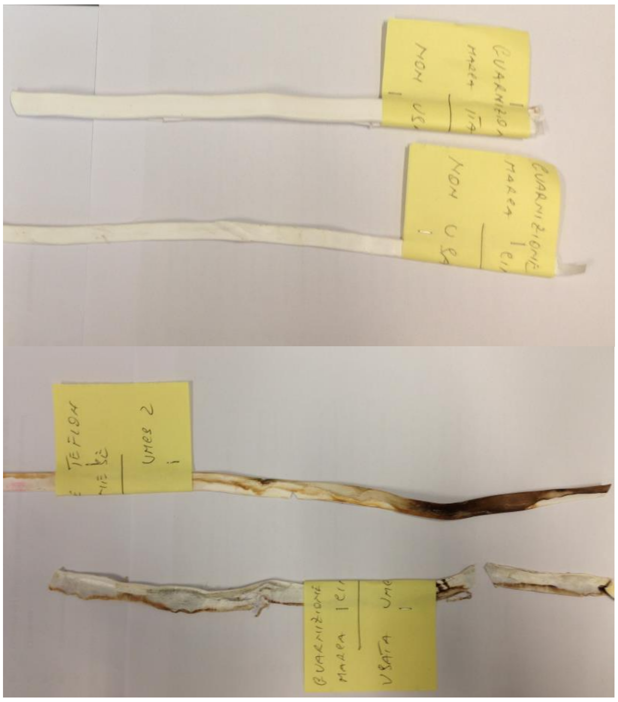

Fig. 4. PTFE tapes from both producers before *(top)* and after *(down)* their utilization inside the Ultrasonic Mold Cleaning Systems.

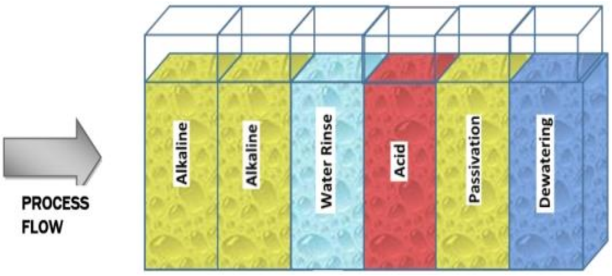

Fig. 5. Process stages and relative chemical baths in the Ultrasonic Mold Cleaning System [17].

Both *UMCS1* and *UMCS2* represent Chinese gaskets. No sample of used Italian gaskets is currently available for comparative tests. In depends to the policy adopted in the manufacturing of *UMCS*s that limited the adoption of Italian gaskets at the level of prototypes without including them as constructive parts in the final productive plants.

According to the evidence of precedent failures, the "worst" situation is represented by the acid bath in the process line (Fig. 5), realized by a <1 pH solution including sulphamic and citric acids, where 26-28 kHz of ultrasonic waves and a temperature between 70 and 80 °C are simultaneously applied [17].

Entering in details, *UMCS1* and *UMCS2* represent gaskets both installed inside an acid basin in two different plants. These plants are located in the same factory in a German and used in analogue conditions of production. In particular, plants are *24/24hr* active and gaskets were removed for maintenance after about 90 operative days (around 2.000 working hours).

Samples and their degradation have been experimentally investigated by:

- optical microscopy;
- scanning electron microscopy;
- thermograms;
- differential scanning calorimetry curves;
- infrared spectra.

In order to determine the wear mechanisms as a consequence of regular gasket functioning. And, considering the excellent proprieties of PTFE, a simultaneous incidence of multiple wear mechanisms is also plausible.

3. EXPERIMENTAL INVESTIGATION

All the samples consist of stripes of polymeric materials. Samples *Italian New* and *Chinese New* are mainly white (Figs. 6 and 7), whereas *UMCS1* and *UMCS2* exhibit a brownish/white color (Fig. 8).

Fig. 6. Images by optical microscopy: *Italian New* (up) and *Chinese New* (down).

These images on samples surface were obtained by optical microscope observations (optical microscope Model OLYMPUS SZX10, with an enlargement 1X). *Italian New* and *Chinese New* samples differ for dimensions and surface morphology. *Italian New* has a thickness of 4.5 ±0.5 mm and width of about 12.0 ±0.5 mm (Table 2.). Its surface does not show any evident defect. *Chinese New* sample exhibits a thickness of 2.5 ±0.5 mm and width of 9.0 ±0.5 mm with evidences of macroscopic surface alterations (Fig. 7).

Table 2. Geometrical differences between *Italian New* and *Chinese New* samples.

Property		*Italian New*	*Chinese New*
Width	mm	12.0 ±0.5	9.0 ±0.5
Thickness	mm	4.5 ±0.5	2.5 ±0.5
Section Area	mm^2	54	22.5

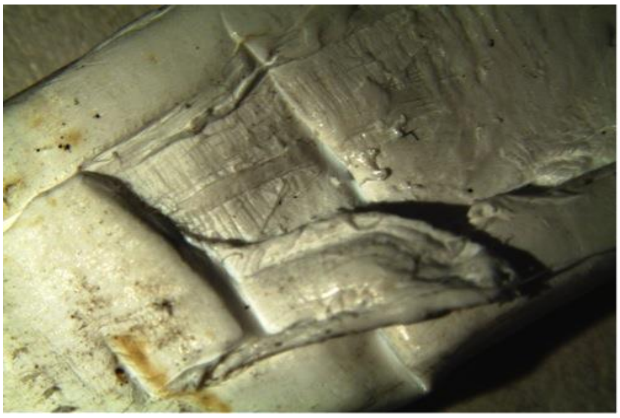

Fig. 7. An image by optical microscopy showing evidences of geometrical faults and partially altered surfaces in *Chinese New* sample (not existing in *Italian New* ones).

Fig. 8. Images by optical microscopy: *UMCS1* (up) and *UMCS2* (down).

Geometrical faults on surface and partially altered zones are even more evident in *UMCS1* and *UMCS2*. In these samples, representing gaskets at the end of their operational time, surface defects are easily detectable also by visual estimation, represented by large brown colored areas (Fig. 9).

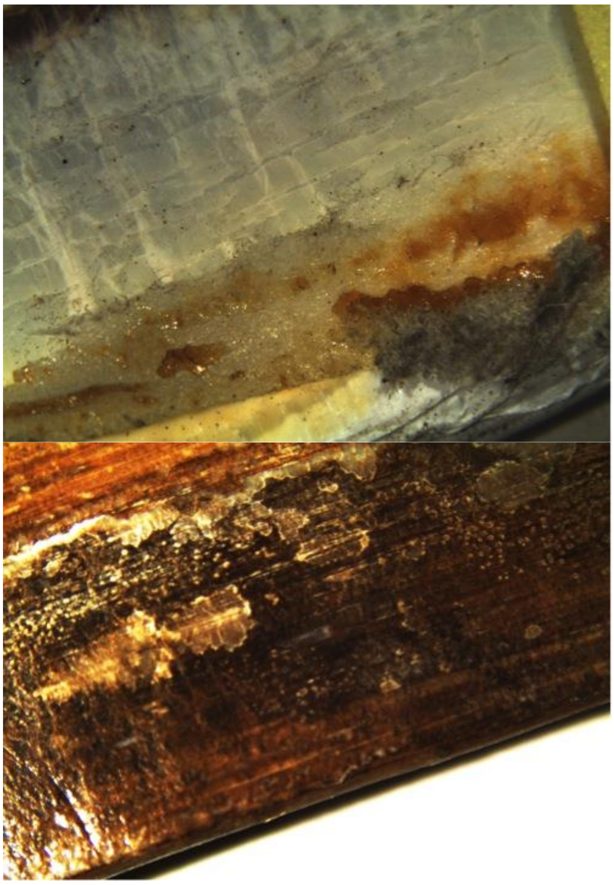

Fig. 9. Images by optical microscopy showing evidences of geometrical faults and partially altered surfaces in *UMCS1* (up) and *UMCS2* (down).

The surfaces of *Italian New* and *Chinese New* samples, obtained by cold fracture, were investigated by scanning electron microscopy *(SEM model FEI XL20)* after metallization. A smooth surface is found on *Italian New* (Fig. 10). On the contrary *Chinese New* shows a rough surface (Fig. 11). Even if, especially at this initial stage of investigation, there is no possibility to directly relate surface characteristics for materials (as smoothness) with functionalities of gaskets (as resistances), SEM images continue to confirm net dissimilarities between samples (as showed by optical images).

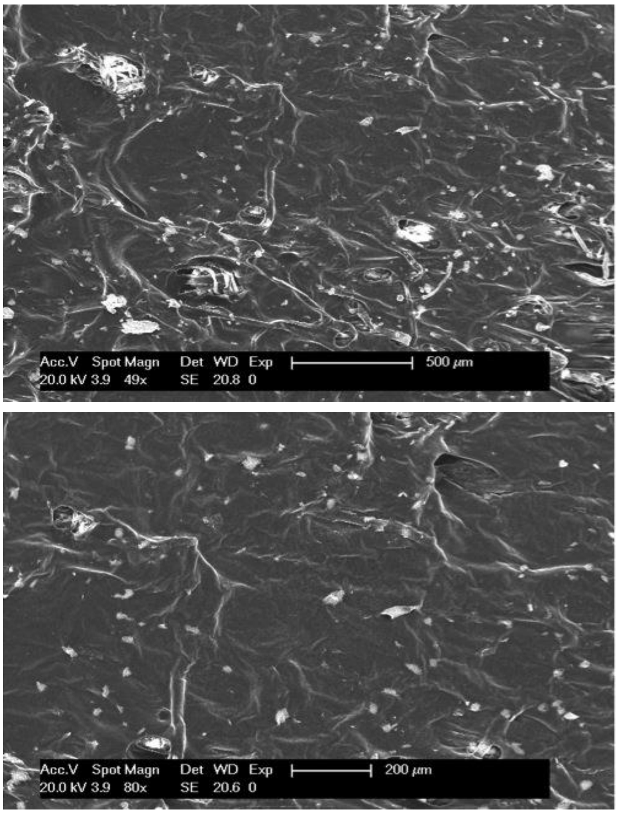

Fig. 10. Scanning electron microscopy for *Italian New.*

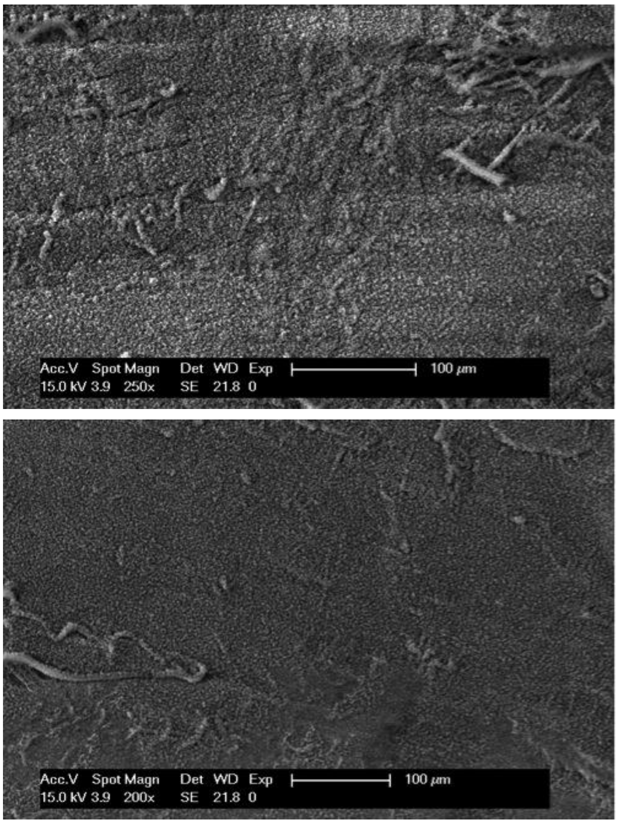

Fig. 11. Scanning electron microscopy for *Chinese New.*

All the samples were submitted to thermogravimetric analysis (*TA Analysis Q50* model). This technique measures the weight loss of the material as the sample is heated from room temperature up to 700 °C at scheduled heating rate (15 °C/min).

The thermograms for *Italian New* and *Chinese New* samples are reported in Fig. 12 (blue lines in the plot refer to the derivative of the signal and the maximum corresponds to the highest degradation rate during the scan). Although the different curves are similar, *Chinese New* starts decomposing at lower temperatures reaching the highest decomposition rate at a slightly lower temperature than *Italian New*.

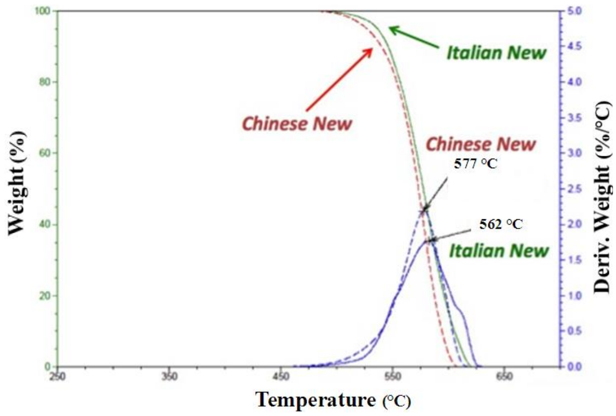

Fig. 12. Thermograms of *Italian New* (green line) and *Chinese New* (red line) samples.

The comparison between the thermograms of *UMCS1*, *UMCS2* and *Chinese New* is also reported in Fig. 13. It is evident how *UMCS1* and *UMCS2* start decomposing at lower temperatures compared to *Chinese New*, which is stable up to 475 °C. Both *UMCS1* and *UMCS2* start decomposing at about 150 °C and the weight loss of *UMCS2* is about 15 % at 500 °C. Moreover, a slight residue (<5 %) is present at the highest temperatures (>600 °C) in both *UMCS1* and *UMCS2*.

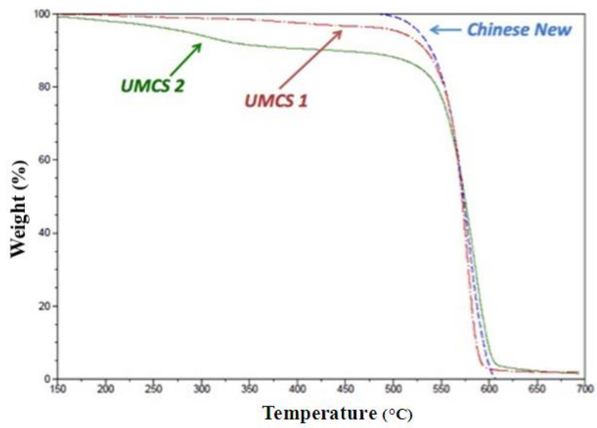

Fig. 13. Thermograms of *UMCS 1*, *UMCS 2* and *Chinese New.*

Samples were also characterized by Differential Scanning Calorimetry (*Q10 TA Instruments* model). This technique allows to determine the presence of exothermic and/or endothermic transformations in the material when it is heated at constant rate (15 °C/min) from temperature below 0 °C up to 130 °C.

The curves obtained for all four samples, *Chinese New, Italian New, UMCS1* and *UMCS2,* are collectively reported in Fig. 14. All the investigated materials show similar plots: outside analogous general trends, in all the thermograms the same endothermic peak (between 0 and 40 °C) is present, including a maximum at the same precise value of temperature (about 14 °C).

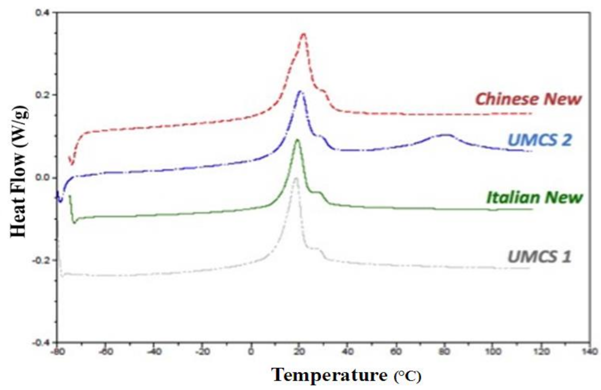

Fig. 14. Differential scanning calorimetry curves of *Italian New*, *Chinese New, UMCS 1* and *UMCS 2.*

This similarity between materials is not confirmed by Table 3 where the enthalpy of the transformation associated to endothermic peaks is reported. Evaluated enthalpy can change from 7.4 to 12.8 J/g according to the specific sample under investigation, even if related to the same thermic transformation. Furthermore, on sample *UMCS2* a second (weak) peak is present at higher temperatures (≈ 85 °C) showing an enthalpy of 3.5 J/g respect to a new and unexpected, thermic transformation.

Table 3. Enthalpy associated to the endothermic peak in the temperature range of 0-40 °C.

Sample	Enthalpy (J/g)
Italian New	12.8
Chinese New	10.9
UMCS 1	7.4
UMCS 2	9.8

After the determination of hardness (by means of Shore A test), *Italian New* and *Chinese New* samples were submitted to tensile tests at room temperature by applying a strain rate of 50 mm/min by means of a CEAST equipment. The values of hardness, fracture strength and strain at break are reported in Table 4.

Table 4. Mechanical characterizations for *Italian New* and *Chinese New.*

Property	*Italian New*	*Chinese New*
Hardness (A)	57 ± 2	49 ± 3
σ_r (MPa)	7.8 ± 0.4	2.3 ± 0.3
ε_r (%)	500 ± 50	400 ± 35

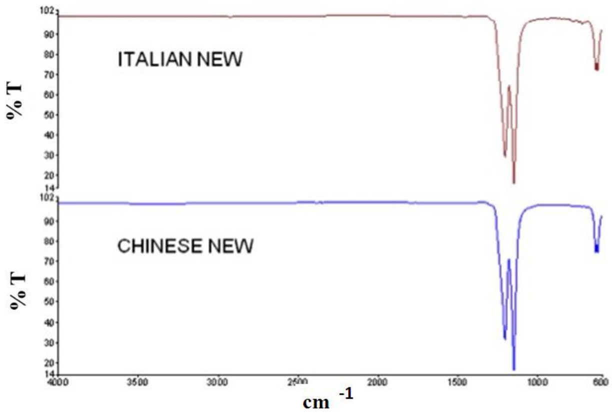

Fig. 15. Infra-red spectra of *Italian New* and *Chinese New.*

As final test the infra-red spectra *(Perkin Elmer Spectrum Two ATR)* of *Italian New* and *Chinese New* samples were performed in order to check their chemical structures (Fig. 15). Both materials show the two coupled absorbing bands in the same frequencies as well as a third band of lower intensity around 600 cm^{-1}. No differences are outlined by this technique in the *Italian New* and *Chinese New samples* supplied.

4. CONCLUSION

This experimental study permitted to investigate wear degradation of PTFE exposed, for a long period, to a combination of temperature, acid attack and ultrasonic waves. It also provided an initial suggestion for the identification of specific mechanics of wearing. The interest for this argument is related to the evidence that commercialized gaskets in PTFE (or *Teflon*), installed in process plants used for cleaning tires molds by a ultrasonic process (UMCS), showed wearing against all results from previous similar investigations. A comparison of mechanical and tribological proprieties between *used* and *unused* samples was realized, also including the case of two different gaskets' manufacturers. The surface degradation were analyzed using optical microscopy, scanning electron microscopy, thermograms, differential scanning calorimetry curves and infrared spectra.

As initial results, although samples from different producers (labelled in the article as *Italian New* and *Chinese New*) exhibit very similar chemical structures, their thermal and mechanical properties are largely different, as well as their geometric dimensions. These differences in materials and geometries might cause various behaviors when gaskets are employed in the same working conditions.

Other differences between samples also emerge comparing the thermal properties in the case of gaskets installed for long periods inside the production plants (namely *UMCS1* and *UMCS2*). Analysis highlights unexpected phenomena of wear degradation in PTFE material related to its utilization in operation. Since the difficulties to retrace the conditions of functionality of plants and their frequent changes during the processes, the present experimental information is not appropriate for definitive considerations.

The complex nature of wear is manifest and has to be investigated in isolated studies towards the definition of specific wear mechanisms or processes.

A full characterization of gaskets under controlled external conditions is requested. It will be realized by a comparative analysis of progressive degradation for both PTFE tapes during Accelerate Life Tests (ALTs). ALTs will be arranged repeating the same session of experimental investigations here reported on samples, degraded by a full immersion in a hot acid bath (80 °C, 0 pH).

A preliminary analysis of functionality suggests that PTFE are mainly exposed to the surface fatigue since the fast waves of pressure related to the use of ultrasonic waves, but it is also under a corrosive attack by acid on degraded surfaces (tribocorrosion). At the same time, additional wear phenomena (maybe cavitation) are doubtless presented, even if not yet fully recognized. In fact, a large overlapping of wear mechanisms, leading to a greater rate of wear than the sum of the individual mechanisms, is evident according to an unexpected fast wear of gaskets inside the industrial systems.

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 molds. These plants are produced and commercialized worldwide by Keymical Group.

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