

Acid Aging Effects on Surfaces of PTFE Gaskets Investigated by Thermal Analysis

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ABSTRACT

This paper investigates the effect of a prolonged acid attack on the surface of PTFE by Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). PTFE is very non-reactive, partly because of the strength of carbon-fluorine bonds and for its high crystallinity, and, as a consequence, it is often used in containers and pipework with reactive and corrosive chemicals. The PTFE under analysis is commercialized by two alternative producers in form of Teflon tapes. These tapes are adopted, as gaskets, in process plants where tires moulds are cleaned by acid solutions inside a multistage ultrasonic process. In this case, PTFE shows, in a relatively short operation time, inexplicably phenomena of surface degradation, which could be related, in general terms, to an acid attack. But, even considering the combined effect of ultrasonic waves, temperature, humidity and acid attack, the PTFE properties of resistance nominally exclude the risk of the extreme erosion phenomena as observed.

The present experimental research aim at investigating this contradiction. A possible explanation could be related to the presence in the cleaning solution of unexpected fluorides, able to produce fluorinating agents and, thus, degrade carbon-fluorine bonds. Considering more the 300 chemical elements a tire compound consists in, it is really complex to preserve the original chemical composition of the cleaning solution. In this research PTFE samples have been treated with different mixtures of acids with the aim at investigating the different aging effects. The thermal analysis has permitted the experimental characterization of PTFE surface properties after acid attack, providing evidence of the degradation phenomena. In particular, 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.

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1. INTRODUCTION

This experimental study is part of a larger investigation aiming at improving the process efficiency in the case of innovative production plants used for the surface treatment and cleaning of tires moulds. Mould cleaning and maintenance are of major concern for the tire industry. Cleaning process has to remove fouling and residues of rubber from sensitive surfaces of mould avoiding wear or damage effects (Fig. 1).

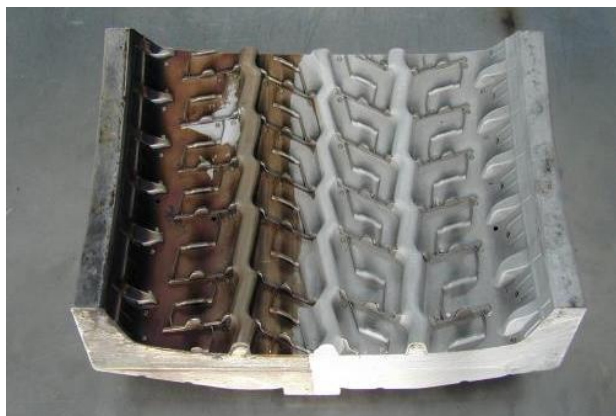


Fig. 1. Effects of the cleaning processes on moulds.

Several technologies are used, each one with specific advantages and limits in applications. A comparative assessment of tire mould cleaning solutions is presented in [1], detailing aspects as productivity, cost effectiveness, quality finishing, eco-sustainability, safety, etc.

It is also reported that the so called *Mould Ultrasonic Cleaning Systems* (UMCS) represents a preferable choice in terms of efficiency and flexibility especially in the presence of very complex and fragile geometries.

The UMCS technology consists in a cleaning process where ultrasonic waves, in combination with temperature and acids, remove rubber scraps and other physical residuals from interstices of the moulds. Tire moulds and their parts are immersed in a sequence of washing baths, where chemical compounds attack the residues, cleaning the mould surfaces.

Useful information referring this technology, including several technical details regarding the proper way to manage UMCS plants are available in [2]. In particular, the guideline emphasises the attention to be focused by final users toward a constant monitoring of the chemical solutions.

Even if this document represents the guideline for a specific UMCS, similarities emerge with other plant manufactures. It depends on the fact that a precise chemical composition for solutions seems to be a relevant aspect in cleaning efficiency. On the contrary, it results evident that a residue from treatments tends to accumulate as sediments on the bottom of the basin [3].

Other investigations suggest that specific elements from this leftover could be dissociated in the cleaning solution modifying its chemical compositions and properties. This aspect has been always considered by manufacturers in terms of loss in process efficiency or quality. And, for this reason, a periodical action of renovation for basins and solutions is regulated.

Nevertheless, recently, minor failures, as drops of solution from washing basins in relatively new plants, highlighted an unexpected deterioration of seals. In particular, Teflon tapes, used as gaskets in the most concentrated acid basins, exhibits degradation theoretically incompatible with normal conditions of use [3].

In fact, according to the material datasheets [4,5] or independent researchers [6-9], Teflon, better identified as Polytetrafluoroethylene (PTFE), reveals a deep thermal and chemical stability that make this material a valid choice in a large number of challenging applications, including UMCS. Referring to [10-12], it is stated that only under very uncommon circumstances PTFE degrades.

The existence of unexpected fluorides [13] in the washing solution, emerging from the breakdown of tire compound and/or used as lubricants or processing aids, just after few weeks of plant operations times, could be the major reason for this quick PTFE degradation. It is noteworthy that, inside a tire compound more than 300 chemical elements could be present [14]. On the contrary, a consolidate know-how [12] reported how 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 [15]) and fluorinating agents. With the aim of investigate this relatively unknown aspect, an intense research activity has been developed. A first comparative analysis was performed on PTFE gaskets before and after the

use in UMCS by means of mechanical tests and micrographs. It showed a not negligible difference between the two situations [16].

Table 1. Acid compositions (in accordance with accelerated aging procedure detailed in [17]).

#	H ₂ O	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

Then, a comparative study on the PTFE surface properties, after accelerated aging in controlled environment was also realized and detailed in [17-19]. In particular, it [17] describes the aggravated conditions of heat, acid attack (with an almost pH 1 solution composed by a mixture of sulfamic, hydrochloric and hydrofluoric acids, and, simultaneously, a temperature between 70 and 80 °C) used to speed up the normal aging processes of PTFE gaskets in the way to correctly represent their utilisation inside the UMCS plants. Besides, [18] describes the effects of aging on PTFE chemical surfaces by Fourier Transform Infrared Spectroscopy (FT-IR) permitting preliminary considerations regarding the use of PTFE in UMCS conditions and its aging mechanisms. The current research intends to merge further experimental results by useful thermal analysis. With the aim at allowing a quick comparison with the previous results, all conditions used in the former experiments (e.g. for accelerating the PTFE chemical surface degradation), are maintained and summarized in Table 1.

2. MATERIAL AND METHODS

In Table 1 are reported the different chemical compositions used to speed up the aging processes by acid attack. Different combinations for *Sol. I* (sulfamic acid 15%wt, hydrochloric acid 0.1%wt) and *Sol. II* (hydrofluoric acid 1%wt) have been evaluated with the aim to compare the effects of the two solutions in different ratios. For each of these combinations, PTFE specimens by

two different manufacturers, one Italian (*IT*) and one Chinese (*CH*), have been investigated. Specimens have been immersed in the solution and maintained in oven at 80 °C for 1.500 hr. This approach was intended to reproduce the worst process situation represented in the process line by the most aggressive acid bath, with almost pH 1 solution of sulfamic, hydrochloric and hydrofluoric acids and, simultaneously, a temperature between 70 and 80 °C.

With the aim at reducing the number of experiments, two specific combinations of acid attacks have been investigated (#6, #9). A comparison with new, untreated samples (#0) have been also implemented (Table 2). These samples have been selected representing respectively the most and least aggressive treatment as preliminary identified by the microscopic observations performed by a Hirox 3D Multifocal Microscope Model HX7700 (Fig. 2) and by the Fourier Transform Infrared Spectroscopy (FT-IR) investigation [18].

Table 2. List of samples analysed by TGA and DSC.

Sample	Treatment			Label
	#	SolI	SolII	
A	0	-	-	Chinese-New
B		-	-	Italian-New
G	6	30 %	2.5 %	Chinese-6
H		30 %	2.5 %	Italian-6
I	9	30 %	5 %	Chinese-9
J		30 %	5 %	Italian-9

At the end of the aging treatment, the specimens were extracted from oven, cleaned, dried and investigated by Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).

Changes in physical and chemical properties of the polymers have been measured by TGA as a function of increasing temperature (considering a constant heating rate) [20-22]. This technique has permitted to investigate physical and chemical phenomena, such as degradation temperatures and absorption of low molecular weight moieties. In particular, in the present work, TGA has allowed the characterization of materials through the analysis of characteristic decomposition patterns and the evaluation of degradation mechanisms and reaction kinetics. By TGA, it has been also possible to verify the presence (or absence) of organic/inorganic contents.

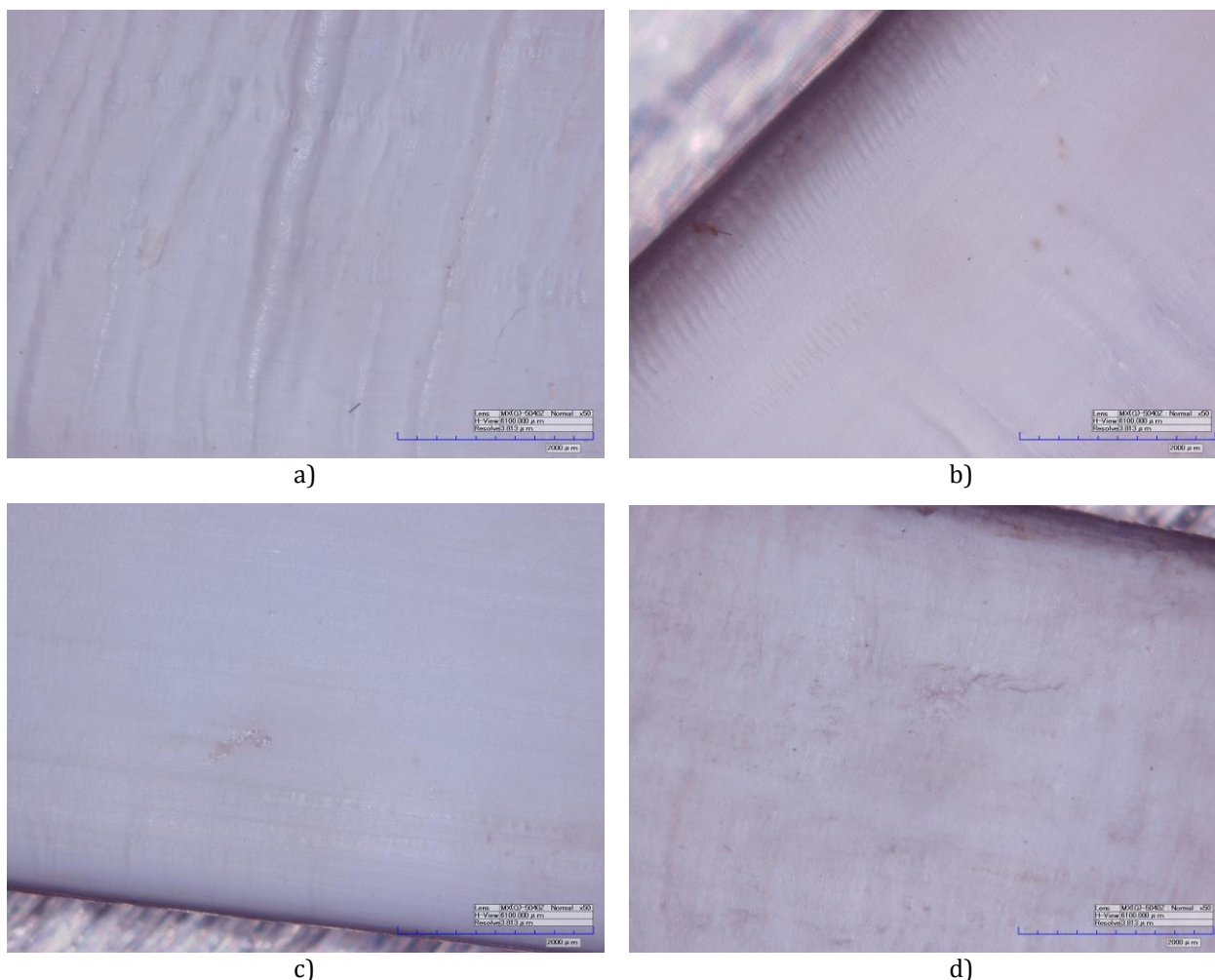


Fig. 2. Examples of micrographs used for a preliminary selection of treatments and samples under investigation: a) Italian #6; b) Italian #9; c) Chinese #6; d) Chinese #9.

This information has been useful for completing the chemical analysis and corroborating alternative hypothesis on the material structures.

By Differential Scanning Calorimetry (DSC), it is possible to analyse the difference in the amount of heat required to increase the temperature of samples and references (as a function of temperature). By observing this difference, it has been possible to measure the amount of heat absorbed during thermodynamic transitions, investigating subtle physical changes (phase changes, melting) [23-25].

The untreated and treated gaskets have been sampled both on the surface and in the core. TGA has been performed on 6-8 mg of material, using a TA Q600 instrument, set to a heating rate of 10 °C/min, from room temperature to 800 °C. Analyses have been realized in inert atmosphere (N₂, 100 mL/min) until 750 °C, and then the

atmosphere has been switched to air in order to oxidize any eventual organic residue [26].

The choice of the inert atmosphere has been made to avoid the introduction of thermo-oxidative phenomena during the analysis. DSC has also performed under nitrogen atmosphere, on 4-5 mg of polymeric material, using a TA Q2000 instrument, set to run two heating scans from -80 °C to 360 °C at a heating rate of 10 °C/min. Only experimental results from the second scan have been used for the purposes of this work [27].

3. RESULTS

3.1 Untreated samples (#0)

A sample purchased by the two manufacturers performs similarly, with just few TGA and DSC differences. Italian sample seems to undergo

thermal decomposition to a slightly higher temperature (Fig. 3a), according to the DTG (Derivative Thermogravimetric Analysis) curves obtained (expressed as maximum degradation rate temperatures). A DSC result also shows a very similar behaviour between the two materials (Fig. 3b). Both the samples exhibit two partly overlapped crystalline phase transitions, typical of PTFE at atmospheric pressure centred at 21/22 °C and 30 °C, in agreement with literature [28,29].

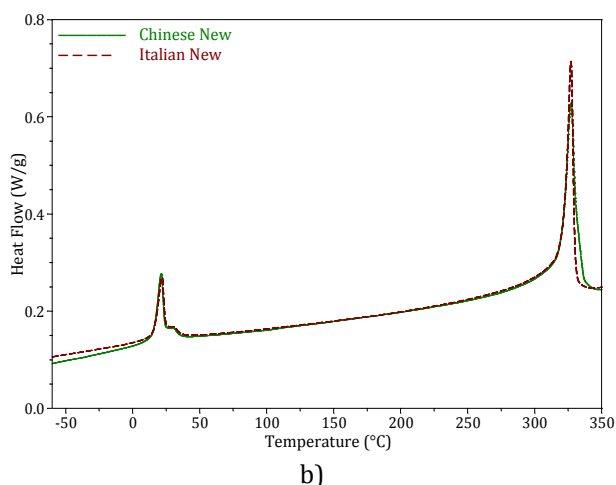
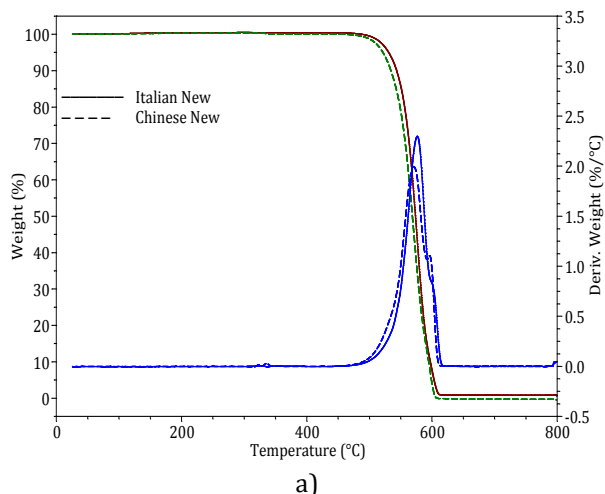


Fig. 3. TGA (a) and DSC (b) thermograms of Chinese and Italian untreated samples (#0) (exo-down).

In Table 3, onset temperature and total enthalpy change are reported considering the two thermal transitions as a single event. The second thermal event observed in both manufacturer's samples, centred at 327 °C, is the main melting of PTFE according with literature [30]. The difference in the onset melting temperature could be considered negligible.

Chinese sample shows a fairly higher enthalpy value for both events (phase transitions and

melting), that could be associated with a slightly higher degree of crystallinity. In fact, crystallization and melting enthalpy in PTFE are supposed to be directly proportional [31].

Table 3. Thermal analyses results of new samples.

		Manufacturer	Chinese A (#0)	Italian B (#0)	
TGA	Decomposition T	°C, peak	571	576	
		°C, onset	543	551	
	Weight Loss	%wt	100.0	99.5	
	Residue @ 750 °C	%wt	0.00	0.87	
DSC	Phase transition	Onset T	°C	15	16
		1 st peak T	°C	21	22
		2 nd peak T	°C	30	30
		ΔH	J/g	8.4	7.9
	Melting	Onset T	°C	319	321
		Peak T	°C	327	327
		ΔH	J/g	34.2	32.2

Results obtained by thermal analyses of the new untreated gaskets are reported in Table 3.

3.2 Treated samples (#6, #9)

Samples subjected to acid treatment #6 and #9 were analysed both at the surface and in the core of the gaskets. TGA thermograms (Fig. 4 and Table 4) show four different weight losses, with the first three that could be probably attributed to compositional changes due to the acid treatments. The last one is, instead, due to the complete pyrolytic decomposition of the PTFE chain, via depolymerisation at monomers. In Table 4, TGA analysis results are summarized. The first three weight losses show different trends depending on the acid treatment applied.

Amongst samples subjected to treatment #6 (#G and #H), the surface samples behave in a very similar manner, both in weight losses temperatures and entities. The Italian core and surface samples show the same weight loss temperatures, but their entities are generally slightly lower (Figs. 4a and 4b). The principal observation regards the core of the Chinese sample subjected to treatment #6, which undergo one single weight loss, in the same manner to what happens to the related Chinese new untreated sample. This fact is consistent with the μFT-IR analysis previously executed, which have highlighted the simultaneous presence of highly degraded surface as well as nearly unmodified areas in the core of Chinese sample subjected to treatment #6.

Samples subjected to treatment #9 (#I and #J) show a similar trend. The core samples exhibit lower weight loss entities which occur at slightly lower temperatures when compared to the surface samples. Comparing Chinese and Italian samples, the weight loss temperatures of Chinese core sample are higher than the Italian one, while the entities do not seem to have a particular trend (Figs. 4c and 4d).

The last and more abundant weight loss, attributable to the depolymerisation of PTFE at its monomer, varies in entity from 81.9 to 100 %wt according to the previously three weight losses. Residue at 750 °C also varies between 0 and 4,78 %wt.

Samples treated with acid attack #6 do not exhibit a precise trend (Figs. 4a and 4b). Chinese core sample behave similarly to the related untreated sample, and exhibits lower residue than the surface sample. The Italian core and

surface samples show instead similar behaviour. Temperatures of this main weight loss are quite consistent between core and surface but differs of 7 to 15 °C between Chinese (lower T) and Italian (higher T). In any case, both onset and peak temperature measured are generally higher than those of new samples.

Samples subjected to treatment #9 show coherent values for Chinese and Italian samples, both in entities and temperatures (peak and onset) of the weight loss, which are all very similar between the two manufacturers (Figs. 4c and 4d). Even in this case, all the degradation temperatures measured are higher than those of untreated samples.

The simultaneous higher residue and lower entity of the last weight loss (related to the PTFE decomposition) exhibited by the samples subjected at #9 treatment, seems to indicate that the aforementioned acid attack resulted in a more aggressive aging rather than #6 treatment.

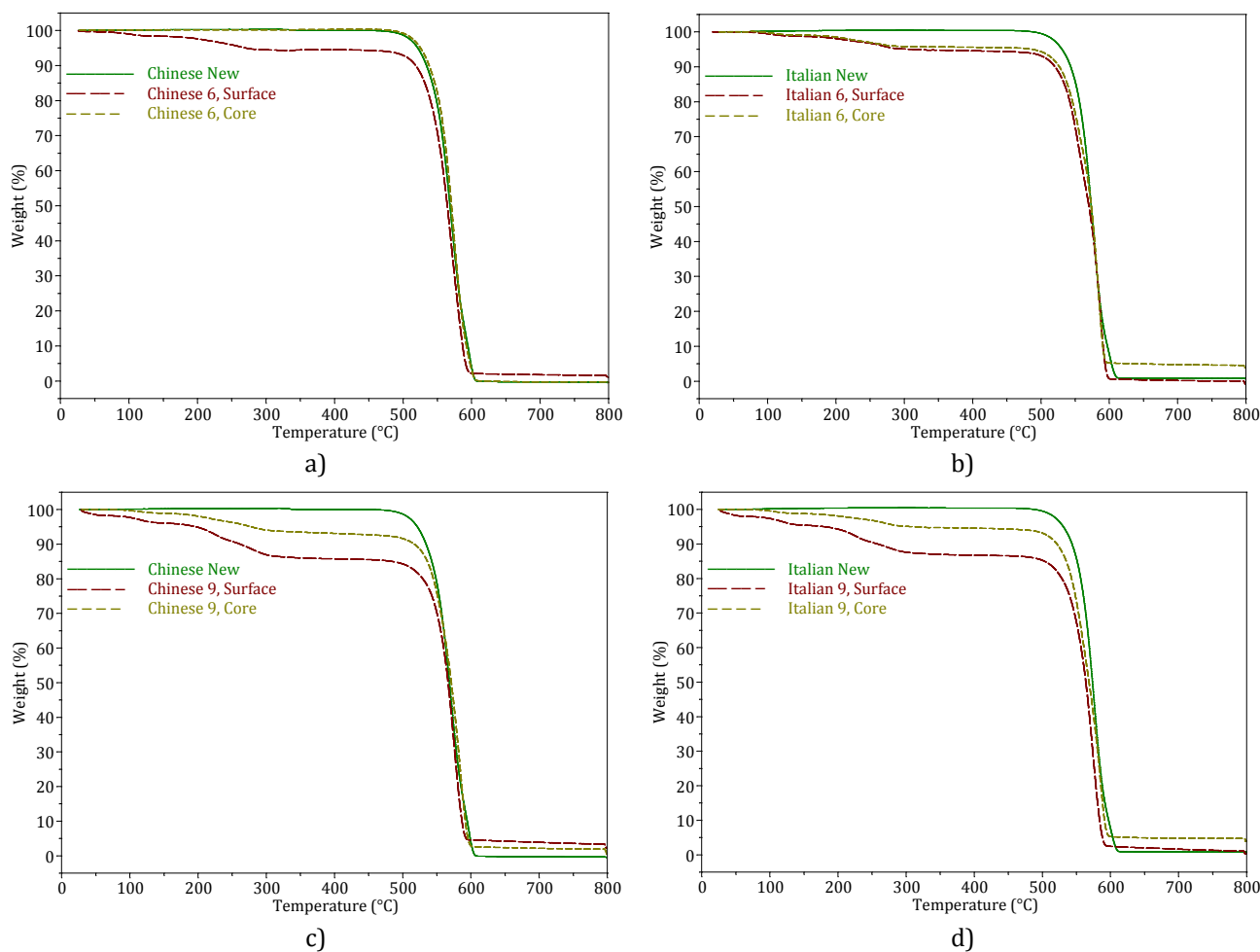


Fig. 4. TGA thermograms of Chinese samples (left) and Italian samples (right), subject to treatment #6 (upper) and #9 (lower). New untreated, Surface and Core thermal traces are reported.

Tab. 4. Summary of TGA and DTG results for both treated and new samples.

Sample	Position Sampled	1		2		3		4			Residue (%)
		Weight Loss (%)	T (°C)	Weight Loss (%)	T (°C)	Weight Loss (%)	T (°C)	Weight Loss (%)	T (°C)	Onset T (°C)	
A Chinese #0	Core	-	-	-	-	-	-	100.0	571	543	0.00
B Italian #0	Core	-	-	-	-	-	-	99.2	576	551	0.87
G Chinese #6	Surface	1.66	100	1.61	212	2.24	261	92.6	571	541	1.69
	Core	-	-	-	-	-	-	100.0	575	548	0.00
H Italian #6	Surface	1.24	105	1.64	213	2.74	269	93.9	586	556	0.01
	Core	0.97	109	1.92	219	1.45	264	90.5	583	557	4.64
I Chinese #9	Surface	3.90	117	4.96	225	5.44	278	81.9	575	550	3.57
	Core	1.04	112	2.35	215	3.90	275	90.2	584	552	2.02
J Italian #9	Surface	4.55	118	4.98	226	3.77	273	85.2	574	548	1.34
	Core	1.25	102	1.69	210	2.56	271	89.7	585	550	4.78

Tab. 5. DSC results of new untreated and treated samples.

Sample	Position	1 (phase transitions)			2 (melting)		
		T peak (°C)	T onset (°C)	ΔH (J/g)	T peak (°C)	T onset (°C)	ΔH (J/g)
A Chinese #0	Core	21	15	8.4	327	319	34.2
B Italian #0	Core	22	16	7.9	327	321	32.2
G Chinese #6	Surface	21	15	6.4	326	319	25.6
	Core	22	16	6.9	328	319	31.4
H Italian #6	Surface	22	16	7.1	327	321	29.8
	Core	21	15	7.1	326	321	31.0
I Chinese #9	Surface	21	16	7.0	327	319	28.1
	Core	21	15	8.0	327	317	33.0
J Italian #9	Surface	22	16	7.6	327	321	28.0
	Core	22	16	7.5	327	321	29.3

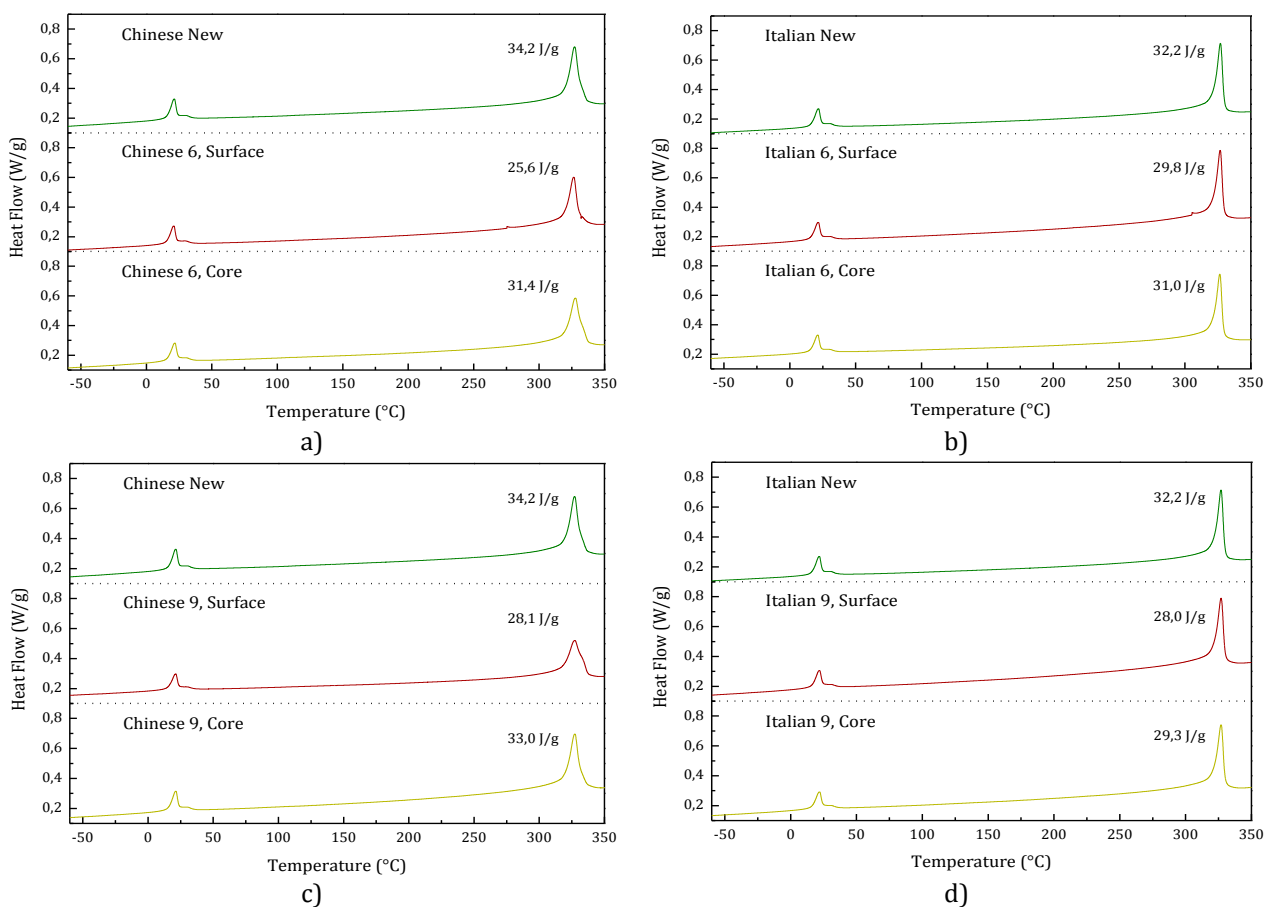


Fig. 1. DSC thermograms of Chinese (left) and Italian (right) samples subject to treatment #6 (upper) and #9 (lower). New Untreated, Surface and Core thermal traces are reported (exo-down).

DSC analyses of treated samples show the same pattern recorded by new samples, with the presence of crystalline phase transitions peaks located at the same temperatures (both peak and onset), with significant variations in the enthalpies (ΔH) of both the 1st and 2nd thermal events (Table 5 and Fig. 5). A decrease in these melting enthalpy values is related to a reduced crystallinity of the PTFE, which in turn could be the result of the presence of defects in the polymer chain due to degradation. The results reported in Table 5 show a relative pronounced variation in the phase transitions enthalpy of Chinese samples centred at around 21-22 °C, highlighting also a higher decrease in both surface samples enthalpy (treatment #6 and #9) with respect to the corresponding core samples. Instead, Italian surface samples exhibit ΔH similar to their corresponding core samples. Furthermore, treated samples show slightly lower values of ΔH when compared with the corresponding new samples.

Finally, the lower ΔH associated to the first phase transition has been measured for both Chinese and Italian samples subjected to treatment #6.

The measured melting enthalpies are much more variable in entity amongst the samples, but the trends are quite similar to those observed for the previously discussed phase transitions (Fig. 5). Melting enthalpies variation of the treated samples, with respect to the correspondent new untreated samples, are slightly higher for Chinese samples (1-7 J/g, Fig. 5, left) rather than for Italian ones (2-4 J/g, Fig. 5, right). However, a little difference could be pointed out in the behaviours exhibited by the samples of the two manufacturers in relation to the treatment: a Chinese sample seems to be more susceptible to treatment #6 (i.e. lower enthalpies), while Italian samples show slight lower ΔH values after treatment #9.

Finally, as general trend, all samples exhibit melting ΔH of the surfaces lower than that of the cores.

4. CONCLUSIONS

This paper investigates the surface and core degradation of PTFE (Teflon) gaskets exposed to

different acid attacks. In particular, different combinations for *Sol.I* (sulfamic acid 15%wt, hydrochloric acid 0.1%wt) and *Sol.II* (hydrofluoric acid 1%wt) have been considered as accelerating aging factors with the aim to compare the effects of the two solutions in different ratios. Experimental measures have been performed by Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). Two series of PTFE gaskets, produced by two different manufacturers (one from Italy and other from China) have been treated and compared with new untreated samples. The samples have been analysed to evaluate different behaviours in response of the various acid treatments. Experimental TGA and DSC data have highlighted different behaviours for the PTFE matrix (core and surface), but also differences between Teflon manufacturers. These results denote a rather clear evidence of progressive degradation of PTFE by chemical attack. Specifically, thermogravimetric analysis (TGA) data seems to indicate a slightly higher amount of degradation in samples subjected to aging treatment labelled as #9, especially in the case of the Italian samples. DSC analysis shows that the treatment #6 is responsible of a generally higher decrease in phase transitions enthalpies, as well as of the melting enthalpies, particularly in the case of Chinese samples. In fact, the lower enthalpies exhibited by treated samples are sign of a more marked reduction of their crystallinity degree. This fact could be a consequence of a greater presence of defects in the polymer chains, possibly induced or enhanced by the chemical attack. These results are generally in accordance with those previously obtained by μ FT-IR analysis on samples treated in the same manner [18]. However, regarding the superficial and internal homogeneity, our experimental data suggest that in all cases Chinese samples exhibit a slightly inhomogeneous degradation after the treatments.

Acknowledgement

This research is part of a larger investigation aiming at improving the design in the case of innovative production plants used for cleaning tires moulds. These plants are produced and commercialized worldwide by Keymical Group.

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