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# INITIAL ATTEMPTS TO ENHANCING RUBBER SEALS QUALITY AND RELIABILITY

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#### ABSTRACT

Seal design engineers and end users are continually seeking improved sealing systems and materials. Thermoplastic polyurethanes (TPU) were developed for sealing applications because they provide superior strength and tribological performances combined with easy melt processability at very short cycle time [1]. It was expected that TPU can substitute cured rubber materials [2] but it was found that TPU performance is hardly depending on the molding process conditions as well as having comparatively much higher compression set [3, 4]. This is the reason why the traditional rubber materials still have a huge importance for seals technology. This paper describes the potential of thermal analysis methods to deliver improvements in seals quality and reliability made from NBR, H-NBR and FPM materials.

Keywords: rubber, seals, quality, thermal analysis, DSC, TGA, DMA.

#### **1. INTRODUCTION**

With the improvement in the world economy and domestic developments, quality is pushed to the forefront across a broad range of industries as they are becoming increasingly aware of the costs of poor quality. Appealing to reach optimized quality is an intensified weapon that will not only enhance poor quality but will also turn high quality into a strong competitive weapon making the fields that craved for this enhancement to be vigorously and extraordinarily successful. Available in different shapes and sizes from small millimeters to large meter diameters, seals work statically or dynamically to separate two pressurized rooms without leakage. A seal part is often a cent price product which is responsible for the whole functionality of complex and safety components. The acrylonitrile butadiene rubber (NBR), hydrogenated nitrile rubber (H-NBR) and fluoroelastomer (FPM) provide a very good oil resistance and can cover a wide service temperature range but conventional produced seals from those materials are often inhomogeneous and with inconsistent quality [5]. The production of elastomeric seal molded parts having homogeneous as well as optimal performance characteristics on a superior level of quality help ensure environmental compliance and safe, reliable operation in the different industries as well as preventing potential failure modes. Unfortunately, the present quality assurance methods such as hardness, compression set and tensile tests are less sensitive to small deviations and especially fail to detect quality differences between single parts manufactured in multi cavity mold. Therefore, the aim is finding an advanced and best non-destructive method to measuring quality of rubber seal parts effectively and rapidly. The question is how can this new competitive reality be reached? How can the quality model be thought of and applied? Actually the solution to this is more complicated than it seems to be as more questions should be considered. What is the management of choosing the right strategy and model for the research? How can good information be obtained to reach the final objective of a premium quality seals. In seeking answers for those basic questions, throughout this paper it is expected to shed light on the investigation of rubber materials used in the production of seals. In order to establish this first step, a holistic approach of possible influencing parameters on the final quality of vulcanized rubber part was done by measuring the rubber compounds before curing and also vulcanized compression molded rubber plates. These samples were analyzed by means of thermal analysis methods such as Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA), quasi-static Tensile Testing and relaxation experiment. Characteristics obtained through thermal analysis methods are the primary factors that will determine a way to develop solutions with respect to manufacturing and supplying superior seals which will have a strong carved foothold in the market.

# 2. EXPERIMENTAL

# 2.1. Materials

The following commercial grade materials were investigated:

Acrylonitrile butadiene rubber (NBR), black;

- Uncured NBR (rolled and unrolled).
- 2 mm thick plates, 70 Shore.

Fluoroelastomer (FPM), black;

- Uncured FPM (rolled and unrolled).
- 2 mm thick plates, 70 Shore (annealed and non-annealed).

For the tests, the uncured materials were kept in the refrigerator at about  $12^{\circ}C$  and the plates were kept in dry environments until testing at room temperature (*RT*).

## 2.2. Methods of characterization

## Differential Scanning Calorimetry (DSC)

Cured and uncured samples of FPM and NBR were measured using DSC. The DSC analysis were done in a DSC 821e from Mettler Toledo. The crucible type is ME 27331 (Al 40  $\mu$ l) and made of aluminum because it has a relatively high coefficient of thermal conductivity. About 10 mg with a tolerance of 0.1 mg of the sample were weighted and measured under nitrogen as a purge gas 60 ml/min, at a heating rate of 20 K/min. The following table highlights the used measurement methodologies.

Material	Methods [°C]	Isotherms [minutes]
NBR/FPM uncured	30_230_30_230 30_150_120_230	2_2_2_2 2_10_2_2 *
NBR/FPM plates	-80_23080_230 30_230_30_230	2_2_2_2 2_2_2_2

Table 1 Testing methodologies of DSC- \*Method for pre-curing simulation.

#### Thermogravimetric Analysis (TGA)

TGA plots of the same samples of NBR and FPM were recorded using TGA/SDTA851 from Mettler Toledo. TGA measurements for the samples (20 mg - 30 mg)

begins at room temperature with a constant heating rate of 20 K/min. Samples are heated in a nitrogen atmosphere till 600°C then nitrogen is replaced by oxygen up to 800°C. The flow of the purge gas is constant for both  $N_2$  and  $O_2$  at 100 ml/min.

#### Dynamic Mechanical Analysis (DMA)

DMA measurements of samples from the cured plates were carried out using a DMA device of the type GABO QUALIMETER EPLEXOR<sup>®</sup> 150. The cooling gas is liquid nitrogen. Temperature-sweeps were carried out on 2 mm thin dumbbell tensile 5A DIN EN ISO 527 specimens with about 4 mm punched from the 2 mm plates. For NBR samples a temperature range of  $-80^{\circ}$ C to  $+120^{\circ}$ C at a rate of 2 K/min and a frequency of 1 Hz was used while for FPM samples a temperature range of  $-50^{\circ}$ C to  $+170^{\circ}$ C at the same rate and frequency.

#### Tensile Strength Analysis (TS)

Tensile testing was done with dumbbell 5A DIN EN ISO 527 shaped specimens from the cured NBR and FPM plates to analyze stress/strain properties. The stress is calculated as engineering stress while the considered strain is the nominal one. Testing was done with a Zwick/Roell Z005, at room temperature and a crosshead speed of 10 mm/min.

## 3. RESULTS AND DISCUSSION

#### 3.1. Uncured NBR/FPM rubber samples

The rubber elastomers were banded on a two roll mill at defined machine settings in order to improve filler dispersion and enhance homogeneity. The NBR samples were rolled at a temperature of 50°C while FPM at 70°C. A temperature sensor is usually present at the rollers to make sure of applying the correct temperature for the process as higher temperatures than necessary might induce pre-curing which might affect the final product quality. Samples of NBR/FPM before and after rolling were measured directly after being out of the refrigerator (uncured) and after being left in RT for 1 month (aged).

DSC measurements were first performed on the raw elastomers, before processing, to evaluate the reactivity and the aging behavior. In order to establish this, samples were measured by two different methods starting from RT up to  $230^{\circ}$ C with an isotherm of 2 minutes and from RT also up to  $230^{\circ}$ C but with the exception that the samples were dynamically pre-cured by provoking curing at  $150^{\circ}$ C for 10 minutes while investigating the effect of constant temperature on the behavior of the curing with respect to time, followed by cooling down to  $120^{\circ}$ C then heating up to  $230^{\circ}$ C.

Starting with the not rolled/uncured samples, it was observed that complete vulcanization was achieved at the first heating using the method of  $30^{\circ}$ C -  $230^{\circ}$ C at 20 K/min with an enthalpy ( $\Delta$ H) of -28.9 J/g for NBR and -12.4 J/g for FPM while for the pre-cured samples at 150°C, full vulcanization was not achieved (only obvious in second heating) as the temperature range was insufficient yielding an enthalpy of -20.4 J/g for NBR and -9.4 J/g for FPM. It was also observed that there is no difference in the  $\Delta$ H values between the aged samples in RT and the uncured direct ones (Tables 2, 3). In addition, it is noticed that the not rolled and after rolling samples had the same  $\Delta$ H values as seen in (Fig.1, Table 2) for NBR and (Fig.2, Table 3) for FPM. NBR and FPM curves and thermal analysis data from (Figs. 1, 2) and (Tables 2, 3); makes it noticeable that the exothermic curing reactions of FPM with a peak height (h<sub>p</sub>) range of 0.1 - 0.2 W/g are significantly lower than NBR lying in the range of

0.2 - 0.4 W/g. This is also confirmed from the enthalpy values mentioned before. This is expected due to the different nature of NBR and FPM chemical structure as well as the different compounding additives to both elastomers. Diverging from the same route, NBR curing temperature (T<sub>c</sub>) for the rolled and after rolling samples showed no difference (Table 2) while the T<sub>c</sub> values for FPM showed significant difference. To be more precise, the T<sub>c</sub> values of the FPM uncured samples measured directly and after aging had values of 204.5°C and 205.5°C, for the after rolling samples 201.8°C and 201.3°C, respectively. Comparing the values together, it can be noticed that there is a difference of about 3°C between the unrolled and rolled FPM samples. Thus, three conclusions from DSC measurements for the uncured NBR/FPM samples can be reached, reactivity can be determined from the  $\Delta$ H values, reactivity of FPM is less than the reactivity of NBR and we can indicate if an FPM sample is rolled or unrolled from T<sub>c</sub> values.

As previously mentioned, aging of the samples was done in RT for a month as it was expected that storage of the samples in RT will gradually decrease the reactivity by time. Unlikely to the expectations, no difference was noticed to estimate the aging of the samples which can lead us to the synopsis that seal parts manufacturers can store the material out of the refrigerator, specifically, for one month during winter time so far without affecting the current known degree of quality in the processed parts. It should also be noted that different storage conditions could yield out different results, e.g. storage in RT during summer time or even exposure to sunlight or other kinds of UV radiations.

DSC measurements for only rolled NBR and FPM samples with 2 methods from  $30^{\circ}$ C to  $230^{\circ}$ C and from  $-80^{\circ}$ C to  $230^{\circ}$ C are shown in (Fig. 3). The -80 to  $230^{\circ}$ C method was used for glass transition temperature (T<sub>g</sub>) determination (Table 4). The T<sub>g</sub> of NBR at first heating is found to be approximately  $-38^{\circ}$ C and for FPM  $-17^{\circ}$ C while the T<sub>g</sub> at second heating for NBR is about  $-32^{\circ}$ C and for FPM  $-16^{\circ}$ C. It can be seen that the T<sub>g</sub> value of nitrile rubber is lower than the fluoroelastomer, also, the second heating in both materials is higher than the first heating which means that the cross linking density is higher and the elastomer has less mobility leading to more hardness as the curing process was complete as seen from the second heating which is considered a second annealing process where any unfinished curing from the first heating is completed. Additionally, the glass transition temperature of butadiene-acrylonitrile rubber depends on the acrylonitrile unit content in the elastomer macromolecule [6-8].

There is no obvious influence of the used  $T_g$  determination method (-80°C to 230°C) on the thermal analysis data obtained. This can be proved by comparing the values of  $\Delta H$ ,  $T_c$ ,  $w_p$ ,  $h_p$  of the two different methods in (Table 5), which have nearly the same values.



Fig. 1 DSC curves of NBR (rolled and unrolled), uncured (direct) and after aging.

	Thermal analysis data						
Sample	Method [°C]	ΔH [J/g]	T₀ [°C]	T <sub>ce</sub> [°C]	w <sub>p</sub> [°C]	h <sub>p</sub> [W/g]	
NBR (not rolled), direct	30_230_30_230	-28.9	192.9	194.5	23.7	0.4	
NBR (not rolled), after 1 month	30_230_30_230	-30.4	192.3	193.8	23.7	0.4	
NBR (not rolled), direct	30_150_120_230	-20.4	192.3	194.8	25.2	0.3	
NBR (not rolled), after 1 month	30_150_120_230	-19.2	192.2	193.8	25.1	0.2	
NBR (after rolling), direct	30_230_30_230	-30.1	193.3	194.7	23.7	0.4	
NBR (after rolling), after 1 month	30_230_30_230	-30.4	192.9	194.5	23.8	0.4	
NBR (after rolling), direct	30_150_120_230	-18.4	193.5	194.3	24.6	0.2	
NBR (after rolling), after 1 month	30_150_120_230	-18.9	192.8	194.2	24.8	0.2	

 $\begin{array}{l} \underline{Table\ 2}\ DSC\ values\ corresponding\ to\ Fig.1\ first\ heating.\ \Delta H=\ Enthalpy;\ T_c=\ Curing\ temperature; \\ T_{ce}=\ Extrapolated\ curing\ temperature;\ w_p=\ Peak\ width\ h_p=\ Peak\ height. \end{array}$ 



Fig. 2 DSC curves of FPM (rolled and unrolled), uncured (direct) and after aging.

	Thermal analysis data							
Sample	Method [°C]	ΔH [J/g]	Tc [°C]	T <sub>ce</sub> [°C]	w <sub>p</sub> [°C]	h <sub>p</sub> [W/g]		
FPM (not rolled), direct	30_230_30_230	-12.4	204.5	206.2	25.1	0.2		
FPM (not rolled), after 1 month	30_230_30_230	-12.5	205.5	207.5	25.3	0.15		
FPM (not rolled), direct	30_150_120_230	-9.4	199.8	201.8	27.8	0.1		
FPM (not rolled), after 1 month	30_150_120_230	-9.3	198.2	200.4	27.1	0.1		
FPM (after rolling), direct	30_230_30_230	-12.6	201.8	203.7	23.9	0.2		
FPM (after rolling), after 1 month	30_230_30_230	-13.6	201.3	202.4	24.1	0.2		
FPM (after rolling), direct	30_150_120_230	-9.1	196.2	198.2	26.5	0.1		
FPM (after rolling), after 1 month	30_150_120_230	-9.7	194.9	196.7	25.9	0.1		

 $<sup>\</sup>label{eq:constraint} \begin{array}{l} \underline{Table\ 3}\ DSC\ values\ corresponding\ to\ Fig.2\ first\ heating.\ \Delta H=\ Enthalpy;\ T_c=\ Curing\ temperature; \\ T_{ce}=\ Extrapolated\ curing\ temperature;\ w_p=\ Peak\ width;\ h_p=\ Peak\ height. \end{array}$ 



Fig. 3 DSC comparative curves of NBR and FPM (rolled), measured with 2 different methods.

Sample	Method [°C]	Tg 1st heating [°C]	T <sub>g</sub> 2nd heating [°C]
NBR		-38.7	-32.5
-80_23080_ FPM	<u>80 220 80 220</u>	-38.4	-32.2
	-80_23080_230	-17.8	-16.5
		-17.6	-16,3

Table 4 Glass transition temperature values from DSC corresponding to Fig. 3 first and second heating.

Sample	Thermal analysis data							
[After rolling and directly measured for reproducibility/comparative analysis]	Method [°C]	Т <sub>g</sub> [°С]	ΔН [J/g]	T₀ [°C]	Tœ [°C]	w <sub>p</sub> [°C]	h <sub>р</sub> [W/g]	
NDD		-	-30.1	193.3	194.7	23.7	0.4	
NDK 30 230 30 230	-	-29.2	192.9	194.6	23.4	0.4		
EDM	FPM	-	-13.5	201.6	204.8	24.1	0.2	
I'T IVI		-	-12.6	202.4	203.8	22.7	0.2	
NDD		-38.7	-29.7	192.3	193.9	23.8	0.4	
NDK	NBR -80_23080_230	-38.4	-28.8	193.6	195.3	23.9	0.4	
		-17.8	-13.5	202.2	204.1	24.4	0.2	
FPM		-17.6	-13.2	201.6	202.9	23.5	0.2	

<u>Table 5:</u> DSC values corresponding to Fig.3 first heating.  $\Delta H$ = Enthalpy; T<sub>c</sub>= Curing temperature; T<sub>c</sub>= Extrapolated curing temperature; w<sub>p</sub>= Peak width; h<sub>p</sub>= Peak height.

Thermogravimetric Analysis (TGA) and Simultaneous Differential Thermal Analysis (SDTA) studies have been made at a heating rate of 20 K/min for the uncured NBR/FPM samples with the curves shown in (Fig. 5), and the results summarized in (Table 6), respectively. TGA/SDTA analysis was made to determine the mass degradation behavior of the elastomers as a function of temperature. In all samples, the overall mass loss can be divided into six stages with respect to temperature and two stages with respect to atmosphere.

The weight loss under N<sub>2</sub> starts around 300°C and ends at 550°C while for O<sub>2</sub> it starts at 600°C and ends at 750°C. The first significant mass loss that occurs is at a temperature of 200°C and 250°C having values of approximately 1 %, 3 % for NBR and 0.4 %, 1 % for FPM, respectively. This might be attributed to low temperature volatile components that are usually present in the compounding receipt [9]. It can also be due to the evaporation or decomposition of extender oil and other organic non-polymeric additives present in the rubber compound. The extender oil is usually a mixture of hydrocarbons that serves to soften the rubber and improve work-ability [10].

In proceeding stages, the mass loss is mainly due to complex rubber decomposition influenced by the different additives that decompose at higher temperatures. The main reaction in (Figs. 4, 5) is the oxidative degradation accompanied by the biggest mass loss for NBR and FPM. The SDTA-curve shows around 200°C the curing of NBR which is in agreement with the DSC results; nevertheless the curing of FPM is not as obvious as with NBR. The TGA curves show that the mass loss values for NBR are higher than the mass loss values of FPM evaluated at same temperatures (Table 6.). At 750°C, NBR has a mass loss of about 96 % and FPM 87 % which means that the filler/ash content of NBR is 4 % while for FPM, 13 %. Thus, FPM has significantly higher inorganic content (about 2.5 times that of NBR) and this can be directly related to the higher rolling temperature used as the processing is harder due to the higher content of fillers. It should also be noted that after the completion of the TGA measurements, the residual of NBR showed a white color while FPM a grey one, which is another confirmation on the different used additives. In addition, the curves of FPM reveals the existence of a one-step degradation mechanism that can be seen from the exothermic peak of SDTA in the range of 600°C to 800°C; however, for NBR, a two-step degradation mechanism was observed. Both observations might be attributed to the different inorganic metallic oxides that start to decompose at higher temperatures and are incorporated in those two commercial used materials in seals production.

The assessment of Thermogravimetric Analysis reveals the different degradation behavior of NBR and FPM. Another realization is the more stability of FPM. The higher onset temperatures of degradation of FPM also indicates indirectly a good reference of the good thermal stability of the material. Thus, TGA curves can be used as 'finger-prints' in the identification of single elastomers and their various fillers or additives. From (Figs. 4, 5), it was noted that the difference between NBR measured directly or after aging in RT (this time for 2 months) has no difference; which was also proved before by using DSC measurements. The same applies to FPM.

Throughout the research work, measurements for reproducibility of the results were done in order to make sure of the obtained data. In this paper reproducibility proof is emphasized in (Fig.3)



Fig. 4 TGA and SDTA curves of NBR (rolled and unrolled), uncured (direct) and after aging.



Fig. 5 TGA and SDTA curves of FPM (rolled and unrolled), uncured (direct) and after aging.

Relative mass loss [%]						
100°C	150°C	200°C	250°C	550°C	750°C	
0.005	0.080	0.9	2.8	53.8	95.6	
0.003	0.100	1.0	2.9	53.7	95.7	
0.003	0.100	1.0	2.9	53.9	95.7	
0.020	0.100	0.9	2.7	53.7	95.6	
0.008	0.050	0.4	1.0	69.0	87.2	
0.040	0.007	0.4	1.0	67.0	87.3	
0.007	0.050	0.4	1.0	69.0	87.4	
0.004	0.040	0.4	1.0	69.0	87.4	
	100°C 0.005 0.003 0.003 0.020 0.008 0.040 0.007 0.004	Rel           100°C         150°C           0.005         0.080           0.003         0.100           0.003         0.100           0.020         0.100           0.008         0.050           0.040         0.007           0.004         0.040	Relative mass           100°C         150°C         200°C           0.005         0.080         0.9           0.003         0.100         1.0           0.003         0.100         1.0           0.003         0.100         0.9           0.003         0.100         0.9           0.003         0.100         0.9           0.004         0.007         0.4           0.004         0.040         0.4           0.004         0.040         0.4	Relative mass [%]           100°C         150°C         200°C         250°C           0.005         0.080         0.9         2.8           0.003         0.100         1.0         2.9           0.003         0.100         1.0         2.9           0.003         0.100         0.9         2.7           0.008         0.050         0.4         1.0           0.004         0.007         0.4         1.0           0.004         0.040         0.4         1.0	Relative mass Isss [%]           100°C         150°C         200°C         250°C         550°C           0.005         0.080         0.9         2.8         53.8           0.003         0.100         1.0         2.9         53.7           0.003         0.100         1.0         2.9         53.9           0.003         0.100         0.9         2.7         53.7           0.008         0.050         0.4         1.0         69.0           0.040         0.007         0.4         1.0         69.0           0.004         0.040         0.4         1.0         69.0	

Table 6. TGA mass loss values corresponding to Figs. 4 and 5.

#### 3.2. Cured 2 mm NBR/FPM plates

Dumbbell shaped 5A DIN EN ISO 527 specimens with width 4 mm and thickness of 2 mm were cut from the NBR and FPM plates to investigate using tensile tests and thermal analysis methods. For NBR plates a temperature of 165°C with pressure 100 bar for a time of 10 minutes was used to press the 2 mm plates of 70 Shore while for FPM a temperature of 170°C and a pressure of 220 bar for 5 minutes was applied respectively.

For FPM, annealing was performed after pressing at a temperature of 200°C for 24 hours to make sure that full cure of the plates is achieved as well as removing the volatiles constituents that are not completely removed during the pressing process (Fig. 6) [11].

$$MgO + HF \longrightarrow MgF_2 + H_2O$$

Fig.6 Reaction of magnesium oxide with hydrogen fluoride to give magnesium fluoride and water [11]

Tensile Testing results in (Fig. 7) on samples from the 2 mm thick, 70 Shore cured plate shows that the highest tensile strength was observed in the case of NBR. Comparing the FPM samples, it is observed that after passing the proportional limit of constant strain, the non-annealed FPM is weaker than the annealed one and having the lowest tensile strength value. At a nominal strain of 122 %; the NBR stress value is 14.5 MPa, 4.5 MPa for FPM non- annealed and 5.5 MPa for the annealed one (Fig. 7). This can be directly related to what is mentioned earlier about the annealing process and how it improves the hardness and the tensile strength while decreasing the elongation [11]. The FPM samples were strained to 30 % followed by a relaxation experiment up to 700 seconds.

The annealed FPM will reach after 100 seconds the highest stress of 1.8 MPa and after 594 seconds it comes down to 1.5 MPa while for the non-annealed FPM, the initial stress state is at 1.5 MPa and ends at 1.2 MPa within the same time interval. A 20 % relaxation for both samples of FPM was yielded but at different levels of stress as the non-annealed FPM is less stiff.



Fig. 7 Tensile curves of NBR plates and FPM plates (annealed and non-annealed).

From the DSC curves of the examined cured samples shown in (Fig. 8) it follows that under the conditions of measurements, for NBR as well as FPM annealed and non-annealed, there is no cross-linking effect recorded in the heating curves. Thus, one can assume that the curing was fully reached during the pressing of the plates. The nitrile rubber under investigation becomes glassy at a temperature of  $-35.8^{\circ}$ C during first heating and -33.7 during second heating, while the FPM, either annealed or non-annealed infests itself at a lower T<sub>g</sub> (Table 6). This supports the results from comparison between uncured NBR and FPM discussed earlier.



Fig. 8 DSC curves of NBR plates and FPM plates (annealed and non-annealed).

Sample	Method [°C]	T <sub>g</sub> 1st heating [°C]	T <sub>g</sub> 2nd heating [°C]
NBR 2 mm plate		-35.8	-33.7
FPM not annealed 2 mm plate	-80_23080_230	-16.6	-15.2
FPM annealed 2 mm plate		-16.7	-16.2

Table 7 Glass transition temperature values from DSC corresponding to Fig. 8 first and second heating.

The response of material to oscillatory deformation was measured using Dynamic Mechanical Analysis (DMA) to yield storage modulus (E'), loss modulus (E'') and tan  $\delta$  (E''/E') as a function of temperature. The TGA/SDTA as well as the DMA measurement results for NBR, FPM (annealed and non-annealed) separately are shown in (Fig. 9). The data of TGA curves represented in (Table 8) support tensile test measurements as the non-annealed FPM at early stages of applying temperature show more loss of mass; at 100°C, 150°C, 200°C, 250°C, 550°C, 750°C the mass loss is 0.001 %, 0.04 %, 0.1%, 0.3 %, 68.8 %, 87.0 % for the non-annealed FPM and 0 %, 0.02 %, 0.05 %, 0.1 %, 68.5 %, 87.0 % for the annealed FPM. This phenomenon is definitely because of the volatiles present in the non-annealed FPM that start decomposing with the early application of temperature. As higher temperature values are applied, the volatiles constituents in the non-annealed FPM sample are totally degraded yielding at 750°C the same mass loss for both the annealed and non-annealed Fluoroelastomer.

A comparative analysis of DMA plates results are shown in (Fig. 10). It is observed that at room temperature the three materials have the same value of  $E^*$  indicating that they have same hardness at RT, which is as well a confirmation of the already-known hardness of the plates (70 Shore). However, at other temperatures other than room temperature, the materials have different  $E^*$  values as shown in (Table 9) which indicates that the final product might have a different behavior than expected at various temperatures.

It is also observed that NBR is stable at a temperature range of 20°C to 120°C while FPM is more stable at higher temperatures, to be more precise, in the range between 80°C and 200°C. Thus, this supports in theory how FPM is used for special applications where extremely high resistance to high temperatures, ozone, oxygen or mineral oils is needed [11]. In addition, FPM curves (annealed and non-annealed) shows similarity to the results obtained from preceding tensile testing as well as thermogravimetry illustrating the weakness of FPM not-annealed. It should also be mentioned that FPM samples have more damping near RT and therefore more relaxation (tan  $\delta$ ) than NBR; 0.16 for NBR, 0.32 for non-annealed FPM and 0.36 for annealed FPM. This also supports the relaxation experiment from tensile testing where FPM non-annealed showed relaxation at a lower stress level.





Fig. 9 TGA/SDTA and DMA curves of NBR plates and FPM plates (annealed and non-annealed).

Formula	Relative mass loss [%]							
Sample	100°C	150°C	200°C	250°C	550°C	750°C		
NBR [70Sh A] 2 mm plate	0.04	0.2	0.7	2.1	53.2	95.4		
FPM [70Sh A] not annealed 2 mm plate	0.001	0.04	0.1	0.3	68.8	87.0		
FPM [70Sh A] annealed 2 mm plate	~ 0	0.02	0.05	0.1	68.5	87.0		

Table 8 TGA mass loss values corresponding to Fig. 9 TGA/SDTA curves.



Fig.10 DMA comparative curves of NBR and FPM (annealed and non-annealed) plates.

Sample		E* [MPa]					
		40°C	60°C	80°C			
NBR [70Sh A] 2 mm plate	10.8	9.4	8.5	8.3			
FPM [70Sh A] not annealed 2 mm plate	11.2	8.2	6.5	5.5			
FPM [70Sh A] annealed 2 mm plate	12.3	8.7	6.8	6.3			

Table 9 E\* values at different temperatures corresponding to Fig. 10.

## CONCLUSION

In order to achieve improved performance and quality one must gain a better understanding of the polymer structure and its related properties that can give more in-depth information on how to proceed with reaching the final objective. Application of several analytical thermal methods as well as simple mechanical tests were performed as an essential step to effectively evaluating key performance of elastomers used in seals production. The analytical techniques provided comparable results which were in most cases in good agreement. This definitely makes thermal analysis methods a good route to providing satisfactory results.

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