Thermal Behavior and Mechanical Performances of KAFLON 72B and 79P Samples Subjected to Annealing at 305°C

Final Report after 240 hours annealing
12/05/12

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AIM AND SCOPE

This work is addressed at evaluating the thermal and mechanical performances of two samples marked KAFLON 72B and KAFLON 79P, provided by FLUORTECNO and subjected to annealing at the temperature of 305 °C for different time periods.

METHODS

As indicated by FLUORTECNO, all measurements were executed using the same annealing and mechanical testing procedure described in the Report of 20/09/05 and titled "*Comportamento termo-meccanico del campione KAFLON 72B invecchiato ad alta e bassa temperature*".

Specimens with predetermined size (22X5.6X3 mm) were prepared using a punch. The samples were aged at 305°C for various time periods.

All the mechanical measurements were carried out using a dynamic-mechanical analyzer DMTA V (Rheometric Scientific) and employing the Three Point Bending geometry. Strain sweep tests were performed at the frequency of 1 Hz and the strain amplitude was set in the region between 10^{-3} and 0,3 %. The modulus values were determined in the linear region at the strain amplitude of 0.01%.

Thermogravimetric analysis was performed using a Mettler-Toledo thermo-balance mod. LF1100 under nitrogen flow.

Differential Scanning Calorimetry (DSC) measurements were performed using a Mettler-Toledo calorimeter mod. 812 between room temperature and 320°C under nitrogen flow using the thermal cycle detailed below:

- First heating from 25 to 320°C at heating rate of 20°C/min;
- First cooling from 320 to 25°C at cooling rate of 10°C/min;
- Second heating from 25 to 320°C at heating rate of 10°C/min;
- Second cooling from 320 to 25°C at cooling rate of 20°C/min.

RESULTS AND DISCUSSION

DSC analysis of samples KAFLON 72B and KAFLON 79P

Figures 1 and 2 report the DSC thermograms of KAFLON 72B and KAFLON 79P, respectively.

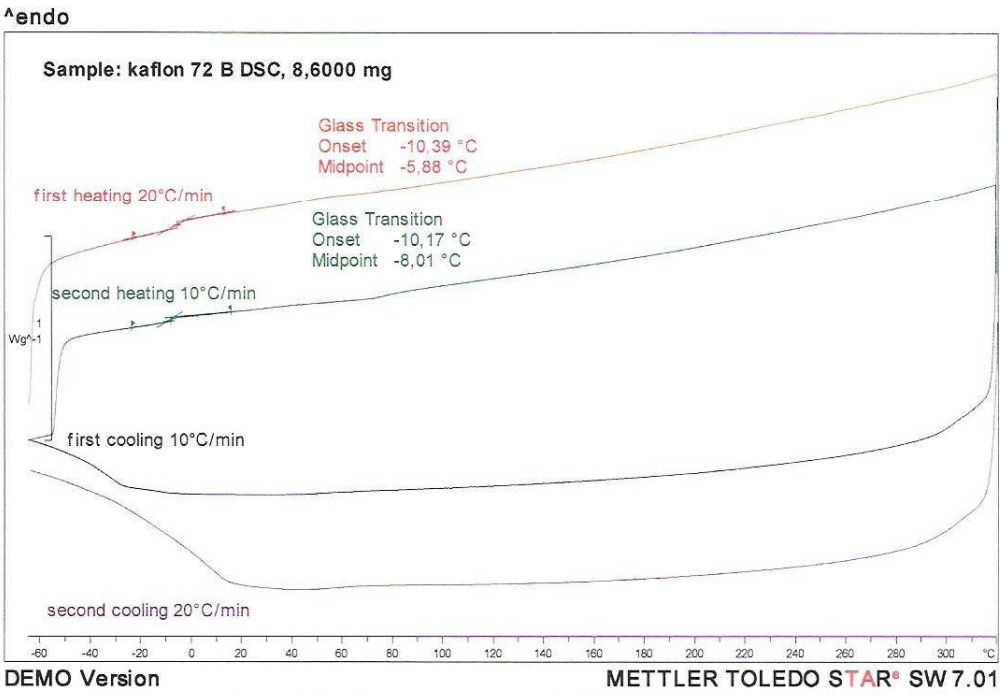

Figure 1. DSC thermogram of KAFLON 72B sample.

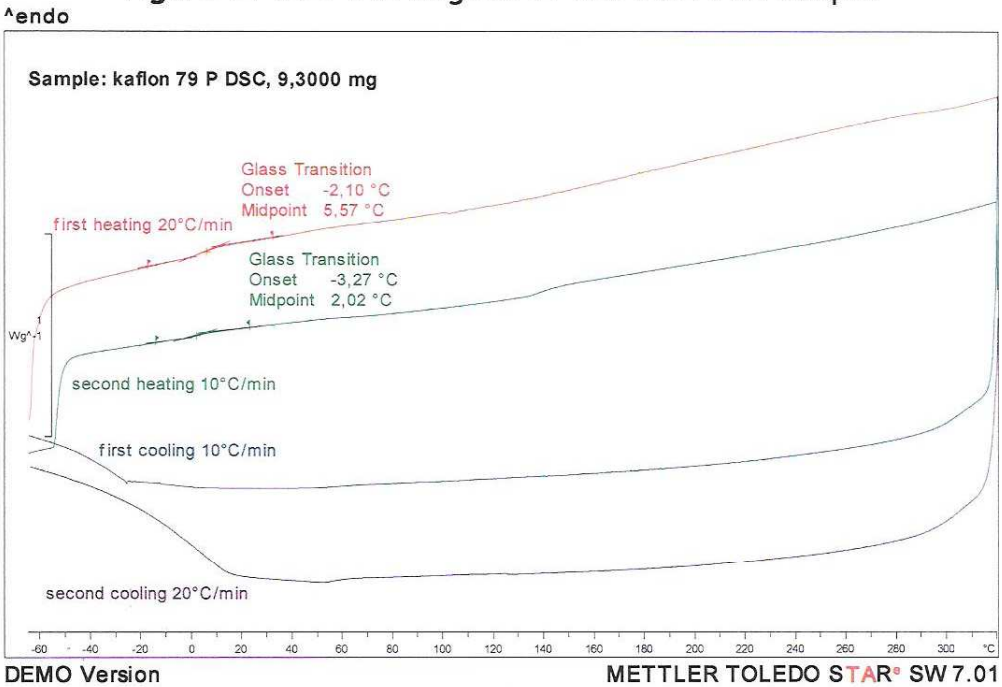

Figure 2. DSC thermogram of KAFLON 79P sample.

Figure 3 reports the overlap of first and second heating of KAFLON 72B and KAFLON 79P samples.

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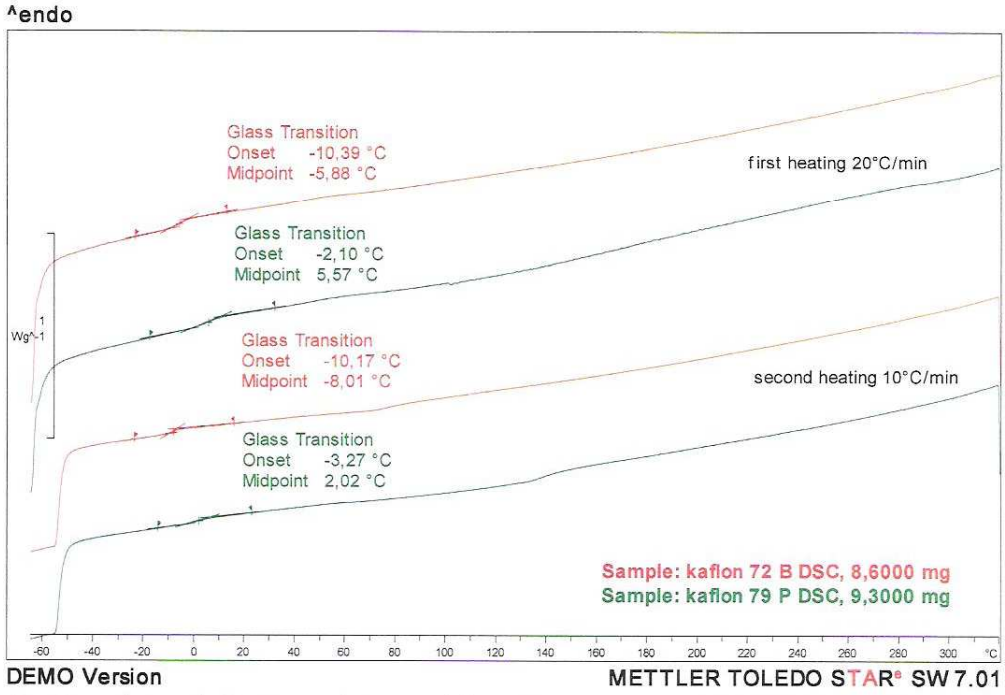

Figure 3. Overlap of first and second heating curves of KAFLON 72B (red curves) and KAFLON 79P (green curves).

In the DSC thermograms of both samples, only a step due to the glass transition is observed, which occurs at -5.9 °C (midpoint, at 20°C/min heating rate) and -8.0°C (midpoint, at 10°C/min heating rate) for sample KAFLON 72B and at 5.6 °C (midpoint, at 20°C/min heating rate) and 2.0°C (midpoint, at 10°C/min heating rate) for sample KAFLON 79P.

Thermogravimetric analysis of samples KAFLON 72B and KAFLON 79P

Figures 4-8 collect the TGA analyses of KAFLON 72B and KAFLON 79P samples recorded at 10°C/min heating rate from room temperature up to 1100°C, under nitrogen flow.

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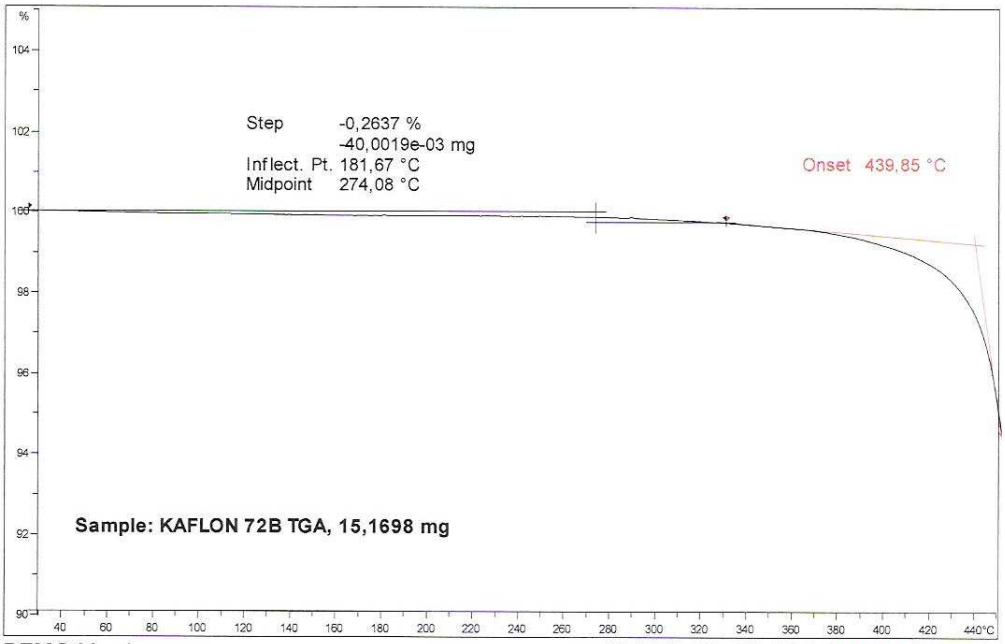

Figure 4. TGA analysis of KAFLON 72B samples under nitrogen flow.

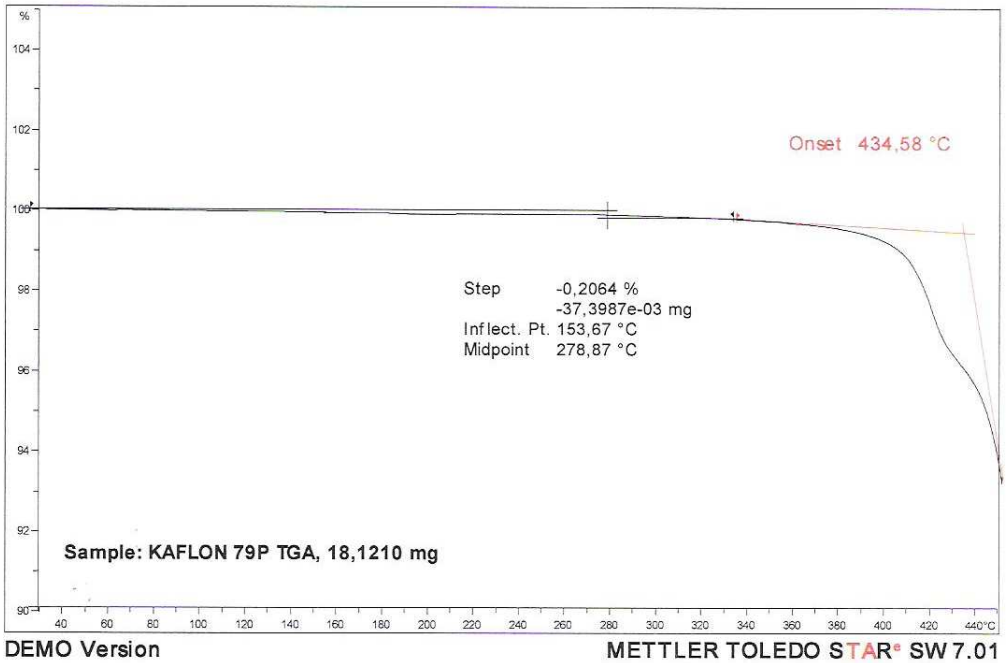

Figure 5. TGA analysis of KAFLON 79P samples under nitrogen flow.

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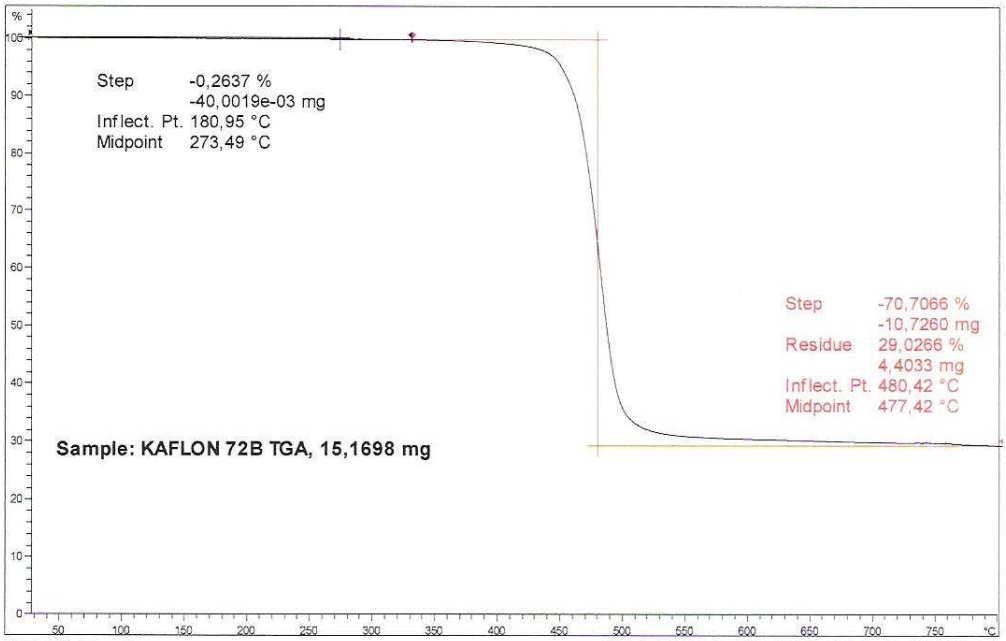

Figure 6. TGA analysis of KAFLON 72B samples under nitrogen flow.

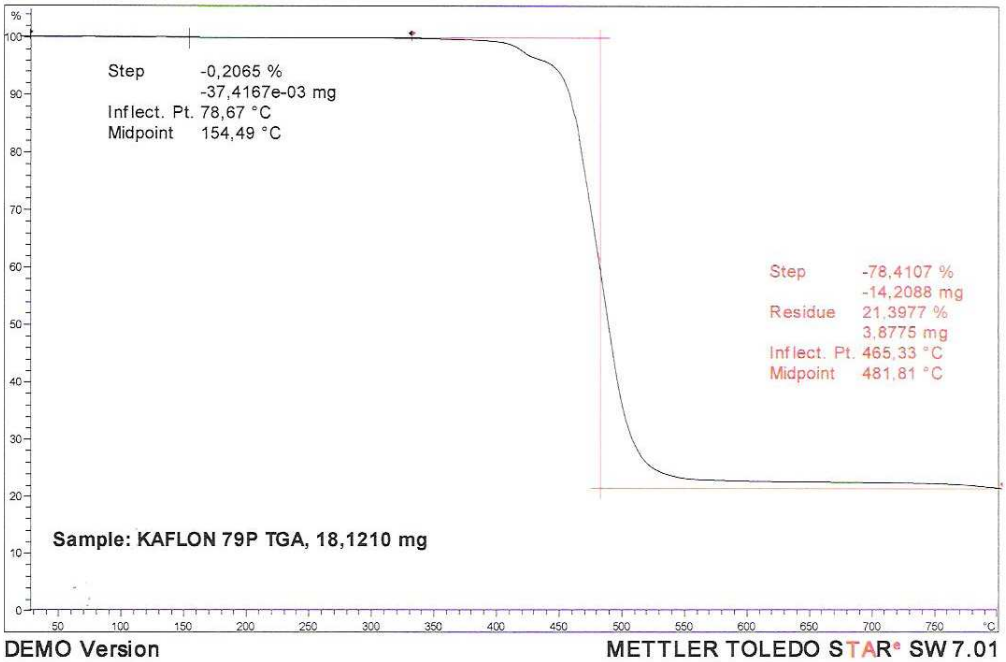

Figure 7. TGA analysis of KAFLON 79P samples under nitrogen flow.

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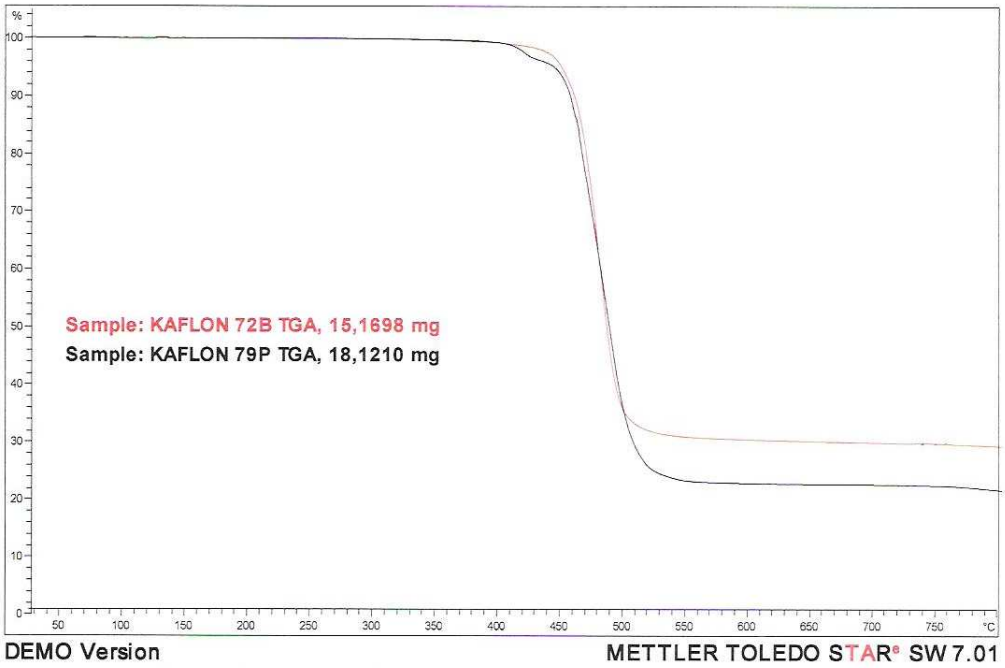

Figure 8. Overlap of TGA analysis of KAFLON 72B and KAFLON 79P samples under nitrogen flow.

KAFLON 72B and KAFLON 79P present very similar TGA curves with the main weight losses occurring at 440°C and at 435°C, respectively. In addition, for the latter sample, a slightly pronounced weight loss can be seen at about 410°C. Finally, the weight percent of the high temperature residue is higher for sample KAFLON 72B, possibly indicating an higher amount of inorganic fillers.

Mechanical analysis- KAFLON 72B

All the mechanical measurements were carried out using a dynamic-mechanical analyzer and employing the Three Point Bending geometry. The various strain-stress tests were performed at the frequency of 1 Hz and the strain amplitude was set in the region between 10^{-3} and 0.3 %.

As typical examples, Figures 9 and 10 report the stress-strain curve and the corresponding dynamic storage modulus (E')-strain curve for the as-received KAFLON 72B sample.

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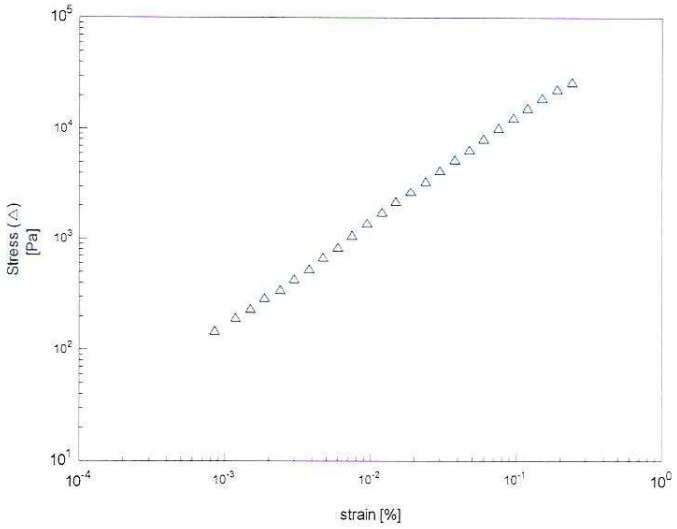

Figura 9. Stress-strain curve of KAFLON 72B sample.

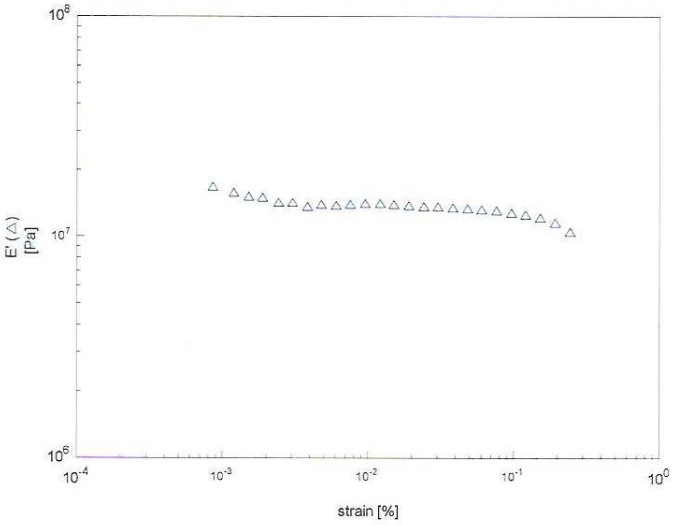

Figure 10. Dynamic storage modulus (E')-strain curve of KAFLON 72B.

KAFLON 72B sample, subjected to the stress-strain analysis, displays a linear behavior over the central region of the applied strain. In this central region, the strain is directly proportional to the applied stress (Figure 9), thus clearly defining the linear viscoelastic region. Consequently, in this strain region, the dynamic storage modulus E' is constant (Figure 10).

To evaluate the mechanical performances of KAFLON 72B subjected to annealing at 305°C for prolonged time periods, the E' modulus value was taken in this linear viscoelastic region in correspondence to the strain amplitude of 10^{-2} %, in agreement with the Report of 20/09/05.

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KAFLON 72B was aged at 305°C up to 240 h and the mechanical behavior was determined during this time period by subjecting the samples to the above described stress-strain analysis.

Figures 11-16 report the dynamic storage modulus (E') -strain curves of KAFLON 72B sample at different annealing time. In these Figures, the vertical red line corresponds to the strain amplitude of 10^{-2} %.

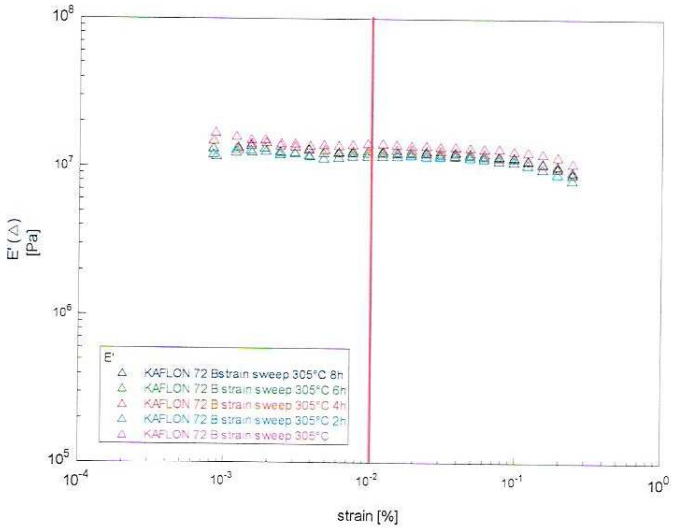

Figure 11. Dynamic storage modulus (E') as a function of strain amplitude at 305°C for KAFLON 72B sample in the time range 0-8 h.

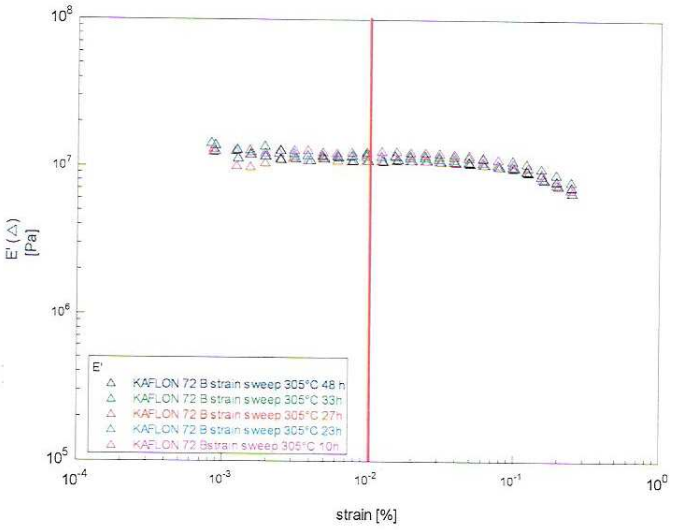

Figure 12. Dynamic storage modulus (E') as a function of strain amplitude at 305°C for KAFLON 72B sample in the time range 10-48 h.

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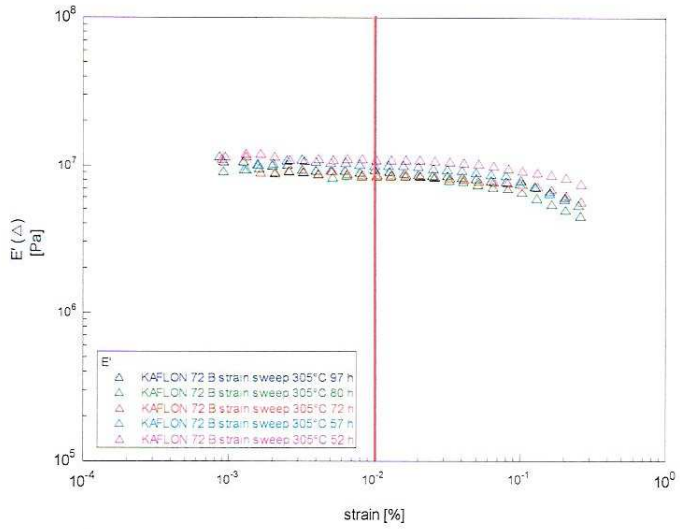

Figure 13. Dynamic storage modulus (E') as a function of strain amplitude at 305°C for KAFLON 72B sample in the time range 52-97 h.

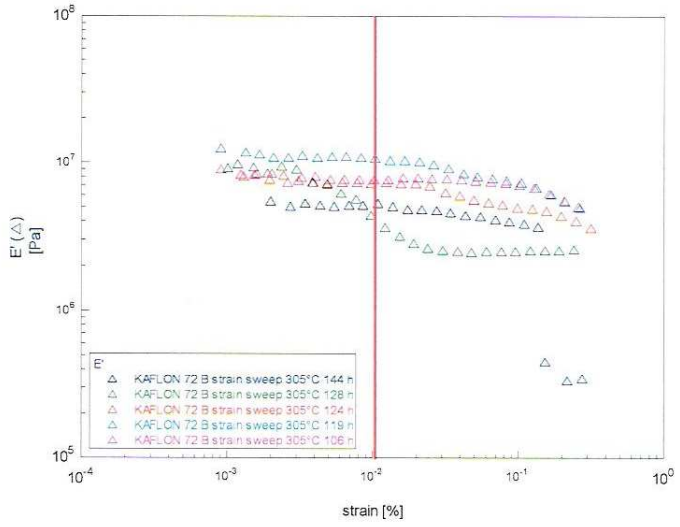

Figure 14. Dynamic storage modulus (E') as a function of strain amplitude at 305°C for KAFLON 72B sample in the time range 106-144 h.

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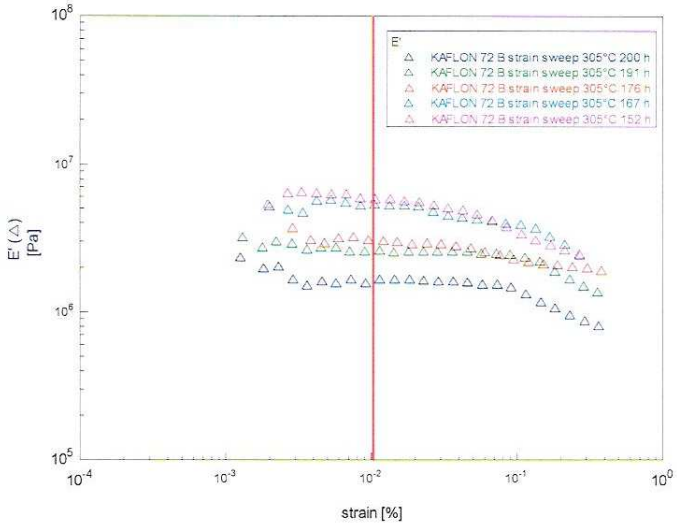

Figure 15. Dynamic storage modulus (E') as a function of strain amplitude at 305°C for KAFLON 72B sample in the time range 152-200 h.

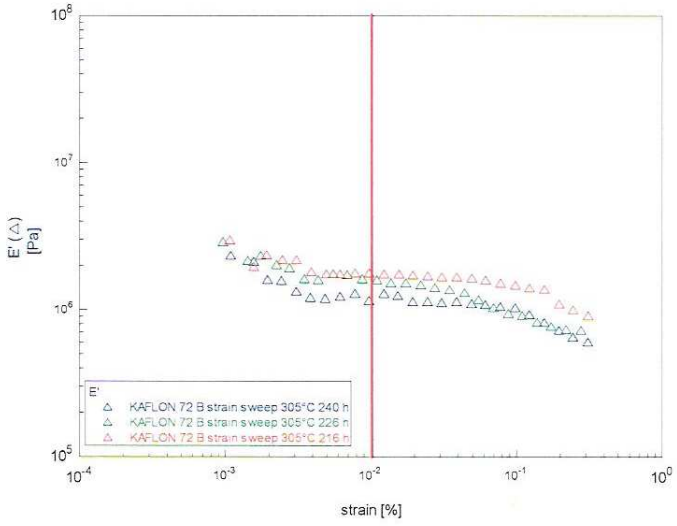

Figure 16. Dynamic storage modulus (E') as a function of strain amplitude at 305°C for KAFLON 72B sample in the time range 216-240 h.

At the beginning aging, the various mechanical curves appear very close each other. The curves are regularly translated toward lower modulus values along the modulus scale without changing their shape. As the annealing time increases, the shift extent is more pronounced and the shape of the E'-strain curves modifies with a slight reduction of the width of the linear viscoelastic region.

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Figure 17 reports the trend of dynamic storage modulus E' for KAFLON 72B as a function of annealing time at 305°C whereas the corresponding modulus values are collected in Table 1.

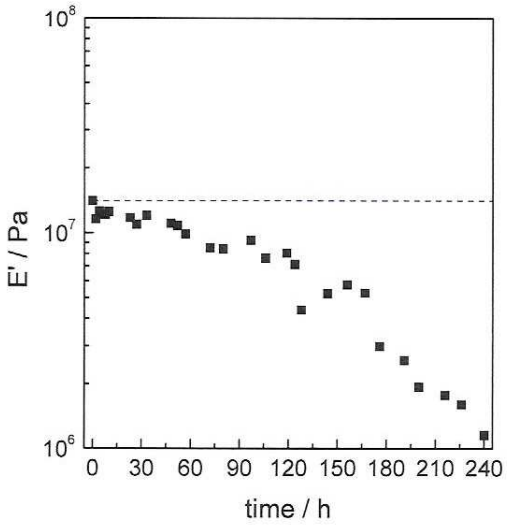

Figure 17. Dynamic storage modulus (E') as a function of the annealing time at 305°C of KAFLON 72B sample.

A regular modulus decrease as a function of time was observed.

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Table 1. Dynamic storage modulus (E') as a function of annealing time at 305°C for KAFLON 72B.

Annealing Time / h	Dynamic storage modulus E'/Pa
0	1,4053E7
2	1,1583E7
4	1,2576E7
6	1,2134E7
8	1,213E7
10	1,2506E7
23	1,1736E7
27	1,0946E7
33	1,2009E7
48	1,1059E7
52	1,0789E7
57	9,8462E6
72	8,517E6
80	8,3841E6
97	9,2209E6
106	7,6266E6
119	8,053E6
124	7,1256E6
128	4,3793E6
144	5,233E6
156	5,7394E6
167	5,2529E6
176	2,982E6
191	2,5633E6
200	1,9289E6
216	1,7739E6
226	1,6021E6
240	1,1542E6

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It is interesting to compare the mechanical behavior of the KAFLON 72B sample annealed at 305° with the behavior of the same sample subjected to annealing at 300 and 350°C, using the experimental results previously described (Report of 20/09/05).
Figure 18 illustrates the percent modulus decrease of KAFLON 72B as a function of time at 300, 305 and 350 °C.

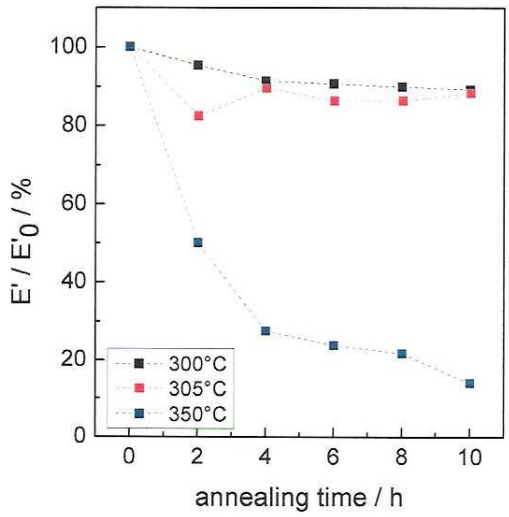

Figure 18. Percent modulus E' decrease of KAFLON 72B as a function of annealing time at 300, 305 and 350 °C.

Irrespective of the annealing temperature, the dynamic storage modulus decreases regularly as a function of time. The decrease is faster as the temperature increases. Although the data at 300 and 350°C were collected seven years ago, the modulus decrease sequence is correct and the overall mechanical behavior is perfectly reproduced. This indicates that the nature and quality of the material after all this time are unchanged.

Mechanical analysis- KAFLON 79P

KAFLON 79P was subjected to the same thermal and mechanical analysis above described for KAFLON 72B. Figures 19 and 20 report the stress-strain curve and the corresponding dynamic storage modulus (E')-strain curve for the as received KAFLON 79P sample.

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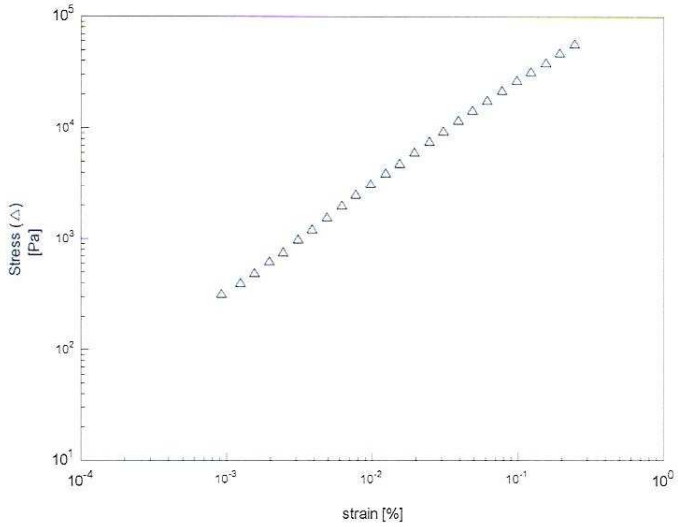

Figure 19. Stress -strain curve of KAFLON 79P sample.

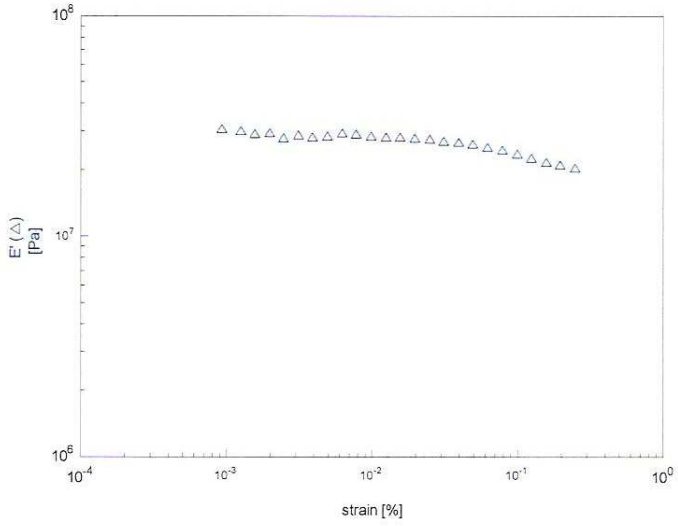

Figure 20. Dynamic storage modulus (E')-strain curve of KAFLON 79P.

The mechanical behavior of sample KAFLON 79P is very similar to KAFLON 72B. The stress-strain curves display a linear behavior over the central region of the applied strain range. In this central region, the strain is directly proportional to the applied stress with a constant dynamic storage modulus E' (Figure 20). Also for this sample, the E' modulus value was taken in this linear viscoelastic region in correspondence to the strain amplitude of 10^{-2} %, in agreement with the Report of 20/09/05.

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KAFLON 79P sample was aged at 305°C up to 240 h and the mechanical behavior was determined during this time period by subjecting the samples to the stress-strain analysis.
Figures 21-26 report the dynamic storage modulus (E') -strain curves of KAFLON 79P sample at different annealing time. In the Figures, the vertical red line corresponds to the strain amplitude of 10^{-2} %.

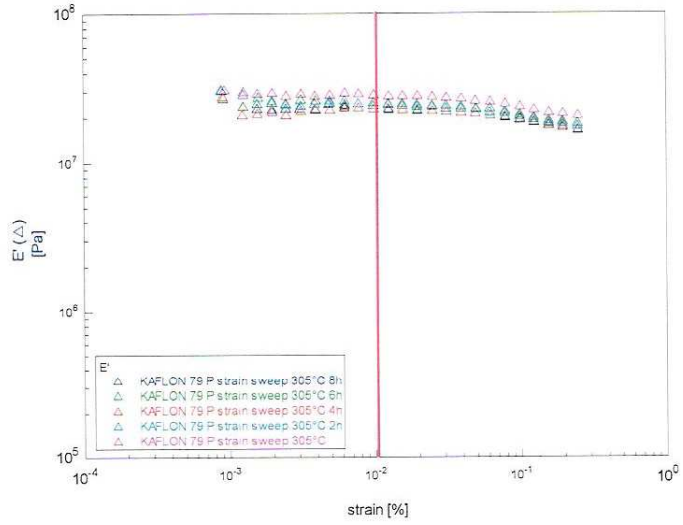

Figure 21. Dynamic storage modulus (E') as a function of strain amplitude at 305°C for KAFLON 79P sample in the time range 0-8 h.

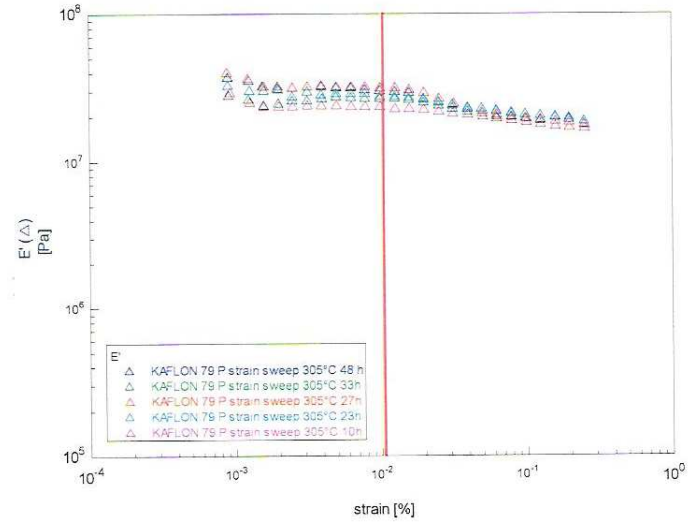

Figure 22. Dynamic storage modulus (E') as a function of strain amplitude at 305°C for KAFLON 79P sample in the time range 10-48 h.

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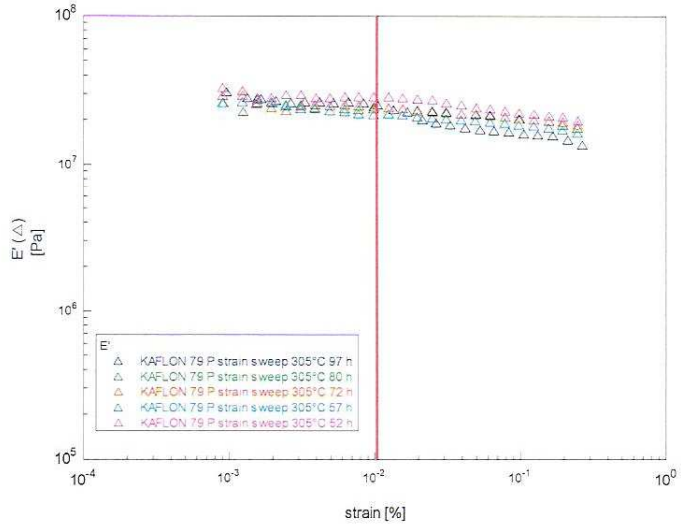

Figure 23. Dynamic storage modulus (E') as a function of strain amplitude at 305°C for KAFLON 79P sample in the time range 52-97 h.

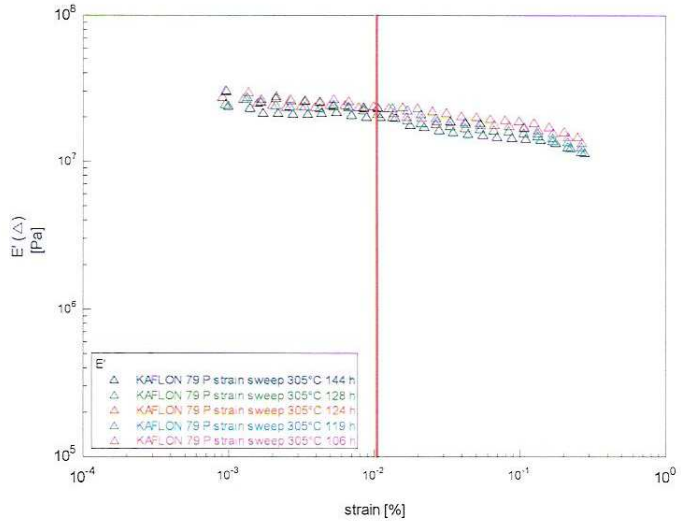

Figure 24. Dynamic storage modulus (E') as a function of strain amplitude at 305°C for KAFLON 79P sample in the time range 106-144 h.

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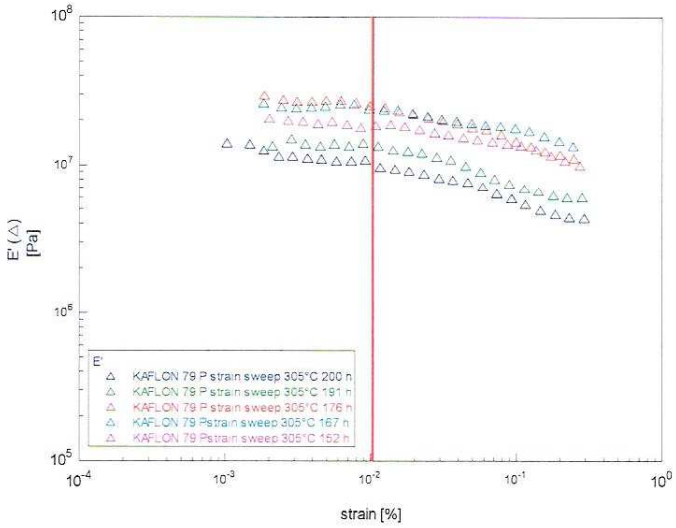

Figure 25. Dynamic storage modulus (E') as a function of strain amplitude at 305°C for KAFLON 79P sample in the time range 152-200 h.

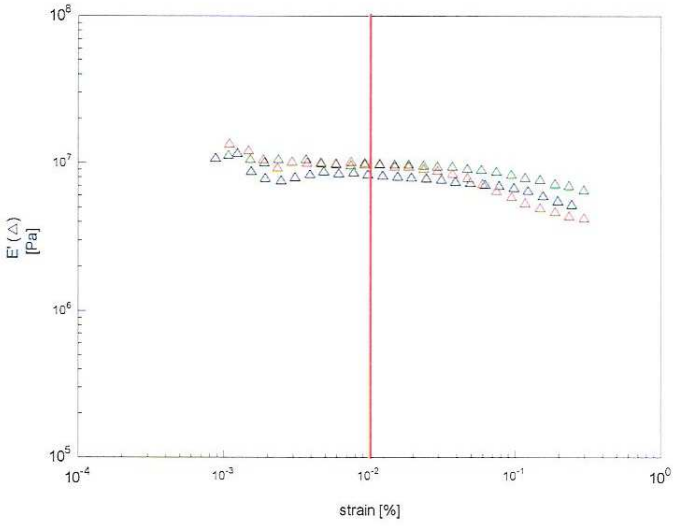

Figure 26. Dynamic storage modulus (E') as a function of strain amplitude at 305°C for KAFLON 79P sample in the time range 216-240 h.

The mechanical curves reported in Figures 21-26 are very close each other and do not change so much their shape with time. As the annealing time increases, the curves are first shifted toward higher values and then, after about 60 h annealing time, toward lower values along the modulus scale.

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Figure 27 reports the trend of storage dynamic modulus E' for KAFLON 79P sample as a function of annealing time at 305°C whereas the modulus data are collected in Table 2.

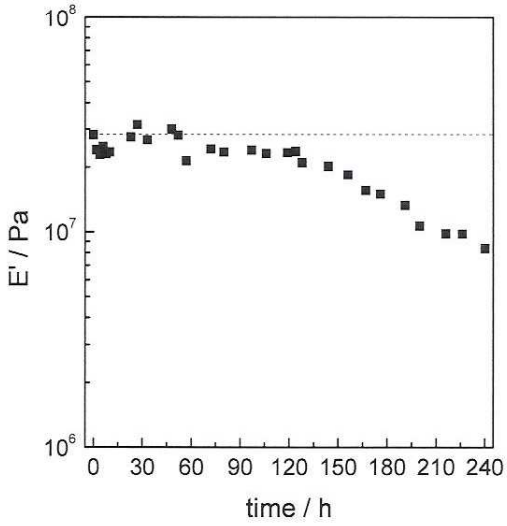

Figura 27. Dynamic storage modulus (E') as a function of the annealing time at 305°C of KAFLON 79P sample.

Table 2. Dynamic storage modulus (E') as a function of annealing time at 305°C for KAFLON 79P.

Annealing Time / h	Dynamic storage modulus E'/Pa
0	2,8339E7
2	2,404E7
4	2,2875E7
6	2,4934E7
8	2,2974E7
10	2,3475E7
23	2,7546E7
27	3,1526E7
33	2,675E7
48	3,0073E7
52	2,8101E7
57	2,1402E7
72	2,4311E7
80	2,3476E7
97	2,3955E7
106	2,3134E7
119	2,3392E7
124	2,3686E7
128	2,0954E7
144	2,013E7
156	1,8426E7
167	1,5583E7
176	1,4958E7
191	1,3264E7
200	1,0644E7
216	9,8009E6
226	9,756E6
240	8,3788E6

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A regular modulus decrease as a function of time was observed, but this decrease is definitely less pronounced in comparison with the one observed for KAFLON 72B (Figures 28 and 29).

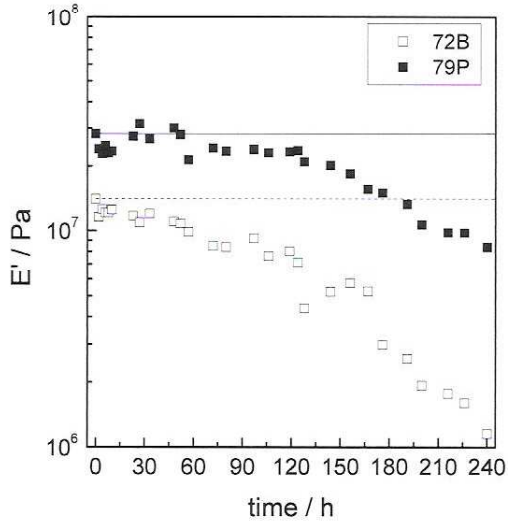

Figure 28. Dynamic storage modulus (E') as a function of the annealing time at 305°C of KAFLON 72B and 79P samples.

In particular, Figure 29 illustrates the percent modulus decrease of KAFLON 72B and 79P as a function of time at 305 °C.

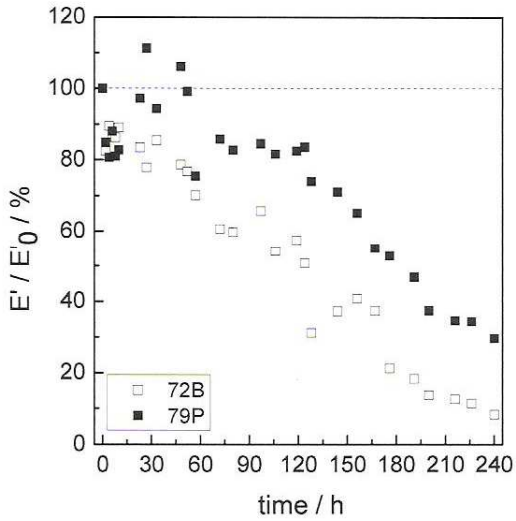

Figure 29. Percent modulus E' decrease of KAFLON 72B and 79P as a function of time at 305 °C.

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After 240 h annealing time at 305°C, the residual modulus for sample KAFLON 72B is about 10% of the initial one whereas in case of sample KAFLON 79P a residual modulus of 30% is observed.

CONCLUDING REMARKS

Two samples marked KAFLON 72B and KAFLON 79P were studied for their thermal behavior and mechanical performances once subjected to annealing at 305°C for time periods up to 240 h. The glass transition temperatures result -5.9°C for KAFLON 72B and 5.6°C for KAFLON 79P. Both samples display a very good thermal stability, once subjected to TGA analysis, with the main losses occurring at about 440°C.
To evaluate their mechanical performances, both samples were subjected to annealing at 305°C for prolonged time periods, and then the modulus E' was determined. In general, both samples display excellent mechanical performances after annealing at those severe conditions, as can be quantitatively substantiated by the observation that the residual modulus after 48 h annealing is 80% for KAFLON 72B whereas a slight modulus increase is observed for KAFLON 79P. In addition, the residual modulus after half total annealing time (120 h) at 305°C is 57% for KAFLON 72B and 83% for KAFLON 79P.
As a final point, it should be stressed that the results of the present mechanical analysis of KAFLON 72B subjected to annealing at 305°C are in perfect agreement with an analogous mechanical study for the same sample performed at different annealing temperatures (300 and 350°C) in the 'year 2005. This data coherence clearly indicates an outstanding quality constancy for KAFLON 72B with time.

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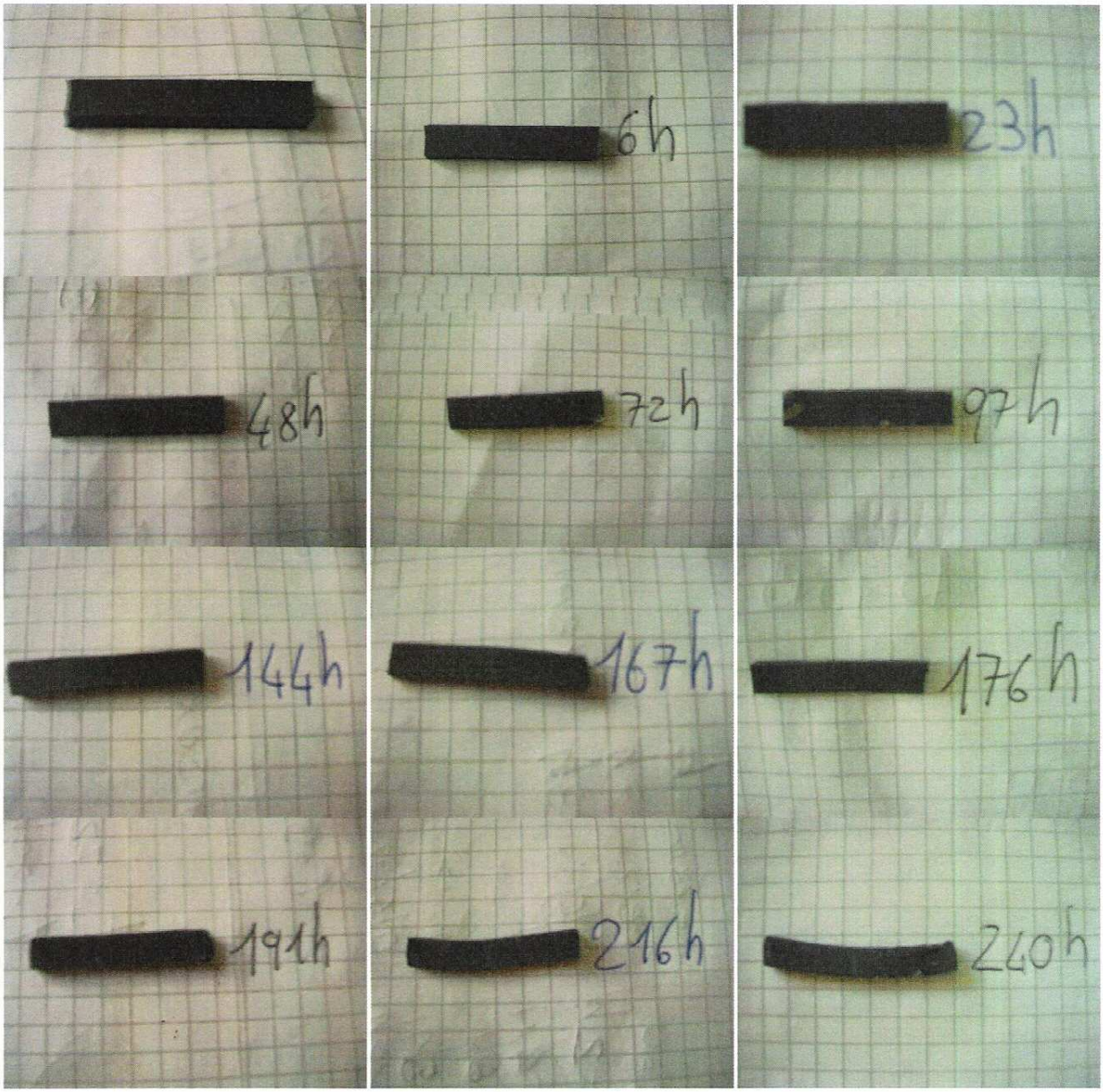
Appendix 1

Images of KAFLON 79P samples taken after various annealing time periods at 305°C.



KAFLON 79P

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