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(Chemicals)

AGEING OF CARILON POLYMER DP P1000 AND DP R1130 IN BOILING WATER AND COMPARISON WITH OTHER ENGINEERING THERMOPLASTICS

(October 1994 - October 1996)

by

B. Rompato

[redacted]

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Owner: SRTCL-CTCAR/4

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Shell Research and Technology Centre, Louvain-la-Neuve

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Approved by: A. Noordam

SUMMARY

Because of their chemical and thermal resistance, mechanical performance and tribological properties, Engineering Thermoplastics (ETPs) are being frequently used in Consumer/Appliances/Medical and Industrial market sectors. To support the application development programme on CARILON Polymer in these market sectors, its competitive positioning to other ETPs with regard to chemical resistance needs to be well understood. To this end, a programme has been initiated to study the effect of boiling water on the performance of CARILON Polymer in comparison with other ETPs.

CARILON Polymer grades DP P1000 and DP R1130 have been aged in boiling water for one year. Tensile properties as well as weight changes have been recorded and compared with those of the major competitors including polyacetal homopolymer (POM), polyamides (PA66 and PA12), polybutylene terephthalate (PBT), polyvinylidene fluoride (PVDF), polysulphone (PSU) and polypropylene homo (PP). The present study confirms that neat CARILON Polymer (DP P1000) appeared to have a better hydrolytic stability than PBT, POM, PA66 and PA12. However, PVDF, PSU and, to some extent PP, were found to perform better than DP P1000. 30% w/w glass-reinforced CARILON Polymer (DP R1130) offers a better retention of tensile properties upon ageing than 30% w/w glass reinforced PBT and 40% w/w glass reinforced PPS. As for CARILON DP R1130, 30% w/w glass reinforced PA66 retains its strength at break but shows a larger decrease in elongation at break.

Both CARILON Polymer grades discolour upon prolonged exposure to hot water (starting after 1 month). Compared to other ETPs, CARILON Polymer DP P1000 and DP R1130 show the largest discoloration. However, the discoloration does not affect the mechanical properties of CARILON Polymer.

November, 1997.

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AGEING OF CARILON POLYMER DP P1000 AND DP R1130 IN BOILING WATER AND COMPARISON WITH OTHER ENGINEERING THERMOPLASTICS

1. INTRODUCTION

The Consumer/Appliances/Medical (CAM) and Industrial market sectors have been identified as potential application areas for CARILON Polymer. The 1996 CAM market for Engineering Thermoplastics (ETPs) is estimated at 330 kton in Europe (EU) and North America (NA), growing at an average rate of 3% per annum.

Because of their chemical and thermal resistance, mechanical performance and tribological properties, ETPs are being frequently used in the CAM and Industrial market sectors. To support the application development programme on CARILON Polymer in these market sectors, its competitive positioning to other ETPs with regard to chemical resistance needs to be well understood. To this end, a programme has been initiated to study the effect of boiling water on the performance of CARILON Polymer in comparison with other ETPs. In this programme, neat (DP P1000) and glass reinforced (DP R1130) CARILON Polymer have been aged in boiling water for one year. Tensile properties as well as weight changes have been recorded in comparison with those of the main competitors including polyacetal homopolymer (POM), polyamides (PA), polybutylene terephthalate (PBT), polyvinylidene fluoride (PVDF), polysulphone (PSU) and polypropylene homo (PP). PP was also included because it generally offers good resistance to hot water ageing.

The current report finalises the comparative study. The preliminary results up to six months have already been part of a previous report [1] but for the sake of completeness the results are summarised in this report as well. Tensile properties are discussed in comparison with other ETPs. CARILON Polymer strengths and weaknesses are highlighted.

2. EXPERIMENTAL

This section details the ageing procedure; i.e. the materials used, the injection moulding parameters, the ageing protocol and the testing procedure.

2.1. Materials

Neat CARILON Polymer DP P1000 has been compared with polyamide 66 (PA66), polyamide 12 (PA12), polybutylene terephthalate (PBT), polypropylene homopolymer (PP), polyacetal homopolymer (POM), polyvinylidene fluoride (PVDF) and polysulphone (PSU). Details on the tradenames, suppliers and grades are listed in Table 1.

The glass-reinforced CARILON Polymer grade containing 30% w/w of the Owens Corning 429YZ fibre type (DP R1130) was evaluated with 30% w/w glass-reinforced-grades of PA66, PBT (PA66-GF30 and PBT-GF30) and with 40% w/w glass-reinforced polyphenylene sulphide (PPS-GF40). More details can be found in Table 1.

Both CARILON Polymer grades contain the additive package number 27; i.e. Irganox 1330 0.2%, Nucrel 535 0.3% and CaHAP 0.2%.

2.2. Injection moulding

Standard tensile bars (ISO 527-1993, type 1A) have been injection moulded on a Netstal HP1200 equipped with a multi-cavity CAMPUS mould under the conditions listed in Table 2 for the virgin polymers and in Table 3 for the glass-reinforced grades.

2.3. Ageing protocol

2.3.1. Ageing up to 6 months

At the start of the experiment, the ageing time was planned to last upto 6 months. Therefore, exposure times varied from 1, 3, 7, 14, 28 days up to 181 days (Table 4). CARILON Polymer DP P1000 and DP R1130 were aged in the same container with PA66, PA66-GF30, PA12, POM, PBT, PBT-GF30, PPS-GF40 and PP. The glass container was filled with fresh demineralized water and 5 tensile bars of each polymer. After each ageing step, the container was emptied and all test specimens were collected and tested. The container was then cleaned and refilled with clean water and unaged tensile bars for another exposure time.

2.3.2. Ageing up to 1 year

After 6 months of ageing, CARILON Polymer was found to fully retain tensile properties. It was therefore decided to continue the ageing experiment. CARILON DP P1000 and DP R1130 were aged with PP and PA66-GF30. PVDF and PSU were also included. In order to safe time, another ageing protocol was applied: all samples were immersed in boiling water at the beginning of the ageing experiment and test specimens were removed at appropriate time intervals (see Table 5 - second set-up).

Prior to the testing, samples were cooled down for a period between one and seven hours in a conditioned room (23°C / 50% RH). The weight and the dimensions were recorded prior to the tensile test.

All materials were aged in the same container (see Figure 2). After one month, PPS was aged in a separate container since it discoloured severely. The boiling water was yellow with brown particles in suspension.

2.4. Testing

The materials were evaluated on the basis of relative weight changes, tensile strength and elongation at yield and at break following ISO-527 (1993) with a testing speed of 50 mm/min. The number of test specimens was limited to 5. The tensile modulus was calculated from the above-mentioned tensile test results. It is assumed that the calculated value is somewhat higher than the modulus that would have been obtained if test method ISO 527 (1 mm/min) had been followed. An automatic extensiometer was chosen for measuring the elongation of neat polymers. This extensometer was not appropriate for glass-filled materials since it slipped and instead a clip-on extensiometer was used.

The percentage weight change was obtained by weighing 5 tensile bars prior to and after exposure to boiling water. As the samples were fully immersed into water, we assumed that the weight gain was mainly due to water.

During the first set-up, i.e. up to 6 months, width, thickness and length changes were also recorded but the results were not accurate enough for any significant conclusions and are therefore not included in the report.

The water conductivity as well as the visual colour of the water were recorded.

3. RESULTS AND DISCUSSIONS

Raw data are presented in Tables 6, 7 for neat polymers and in Table 8 for glass-reinforced types. Results have been, as much as possible, compared with literature data [3].

3.1. Weight change

Tables 6, 7 and Figure 1 show the average water content of neat polymers as a function of time. Figure 1 shows that all polymers studied reached an equilibrium concentration after one day in boiling water. The neat CARILON Polymer absorbs less water than PA66, i.e. +4% versus +7%. Compared to the other ETPs, the weight change recorded can be ranked as follow: CARILON DP P1000> POM > PA12 > PSU > PBT > PVDF > PP, in decreasing order. These results are in line with the findings of work previously done on the influence of water on the mechanical and the physical properties of CARILON Polymer [2].

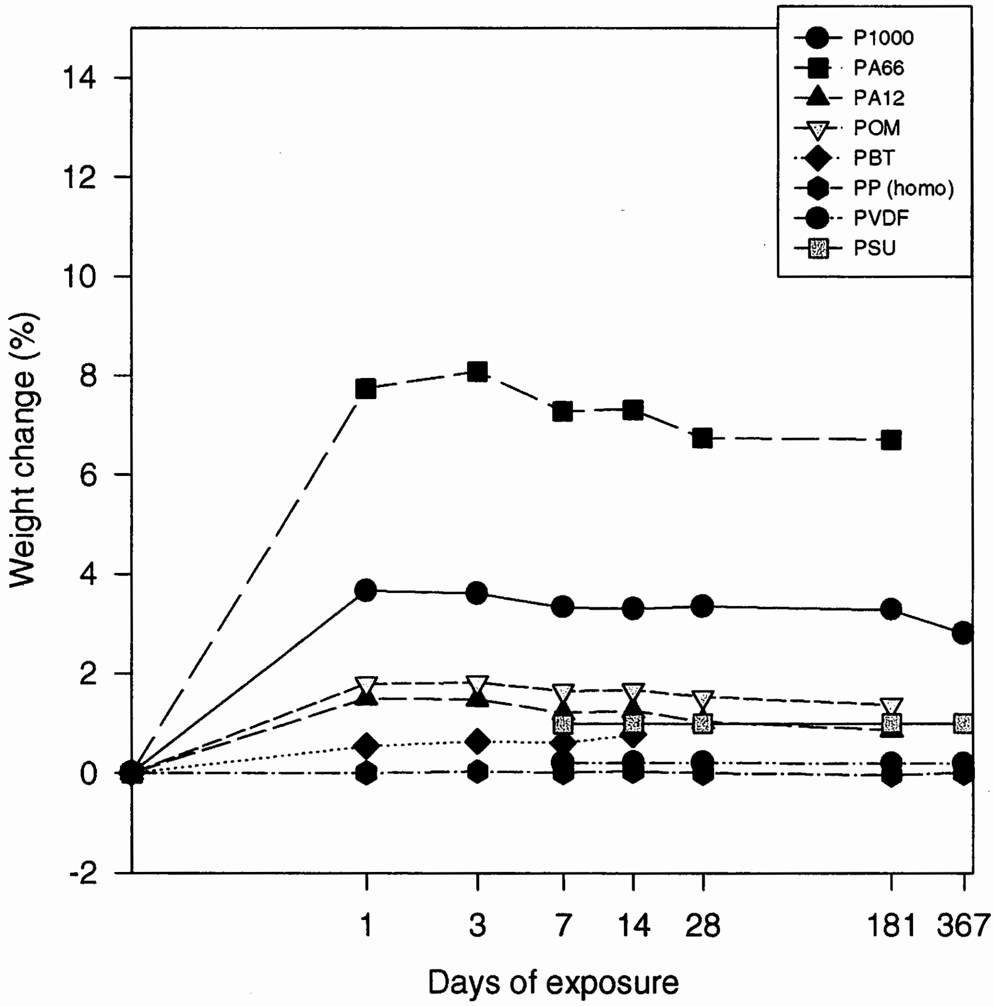

Figure 1: Weight change of neat CARILON Polymer vs competing ETPs

Table 8 and Figure 2 present the water take up of the glass-reinforced CARILON Polymer (DP R1130) as well as that of other reinforced ETPs. Weight change recorded for DP R1130 follows the same trend as for the neat materials. PA66-GF30 absorbs more water than DP R1130 viz. +4% versus +2%. PBT-GF30 and PPS-GF40 absorb less than DP R1130; around +1%.

After one day immersion, CARILON DP R1130 increases about +2% in weight and maintains the same level upto 6 months. After 6 months, a weight loss from +2% to +0.7% is found. Possibly this finding can be related to enhanced degradation at the glass-fibre matrix interface. However, further investigation is required.

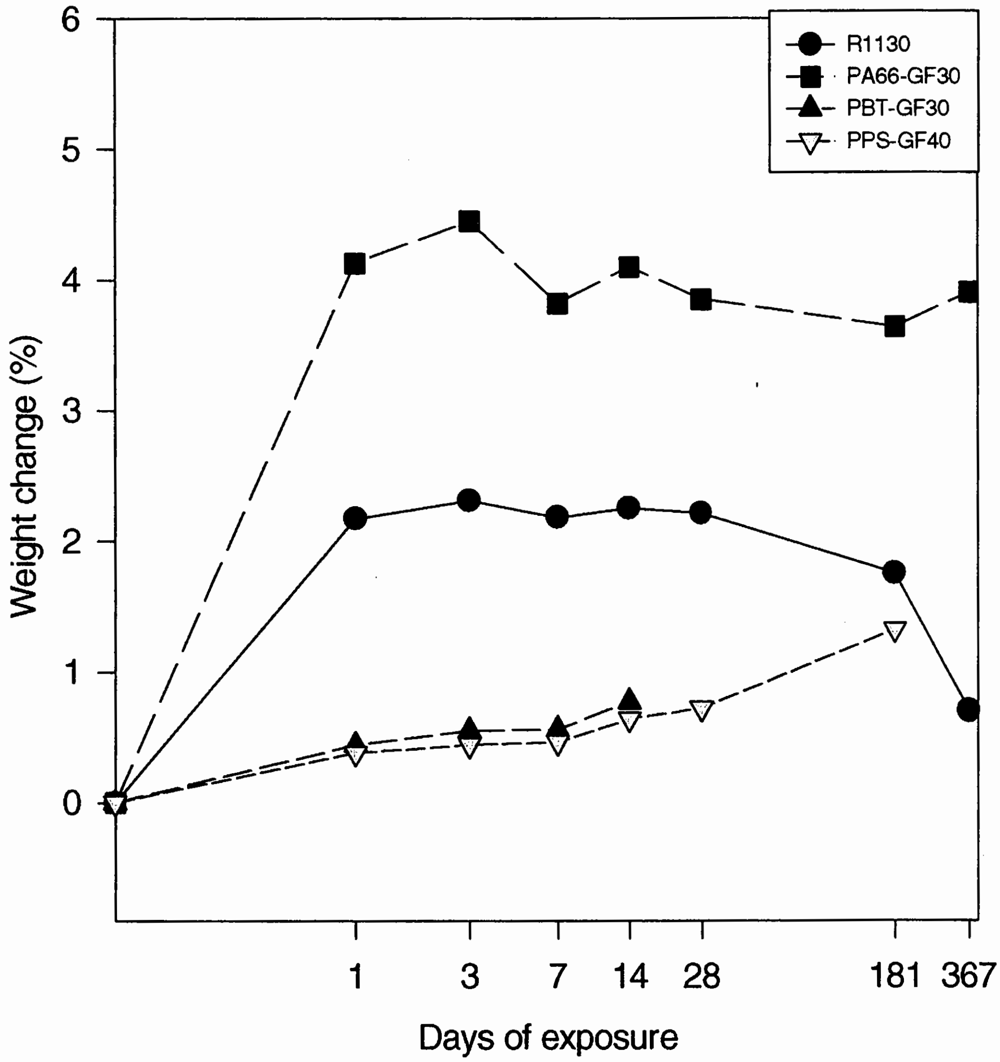

Figure 2: Weight change of glass-fibre reinforced CARILON Polymer vs competing ETPs

3.2. Tensile strength at yield

Tensile strength at yield as a function of exposure time is plotted in Figure 3 for CARILON DP P1000 and competing materials.

CARILON DP P1000 shows no significant variations on the strength at yield. A level of around 56 MPa is maintained during the whole ageing period. The same conclusion can be drawn for PSU, PVDF and PP. Values of 80 MPa, 58 MPa and 35 MPa are found respectively.

However, the condensation polymers like PBT, POM and to a lesser extent PA66 and PA12 are very sensitive. Unaged PBT has a tensile strength at yield of 61 MPa. Already after one day exposure to boiling water, PBT doesn't yield anymore. POM keeps its tensile strength at yield of 64 MPa up to 14 days exposure. After 28 days, POM has a brittle failure behaviour. PA66 and PA12 show a similar tensile strength at yield upon exposure to boiling water. A strength of around 38 MPa is maintained upto 28 days.

Glass reinforced grades do not show yielding.

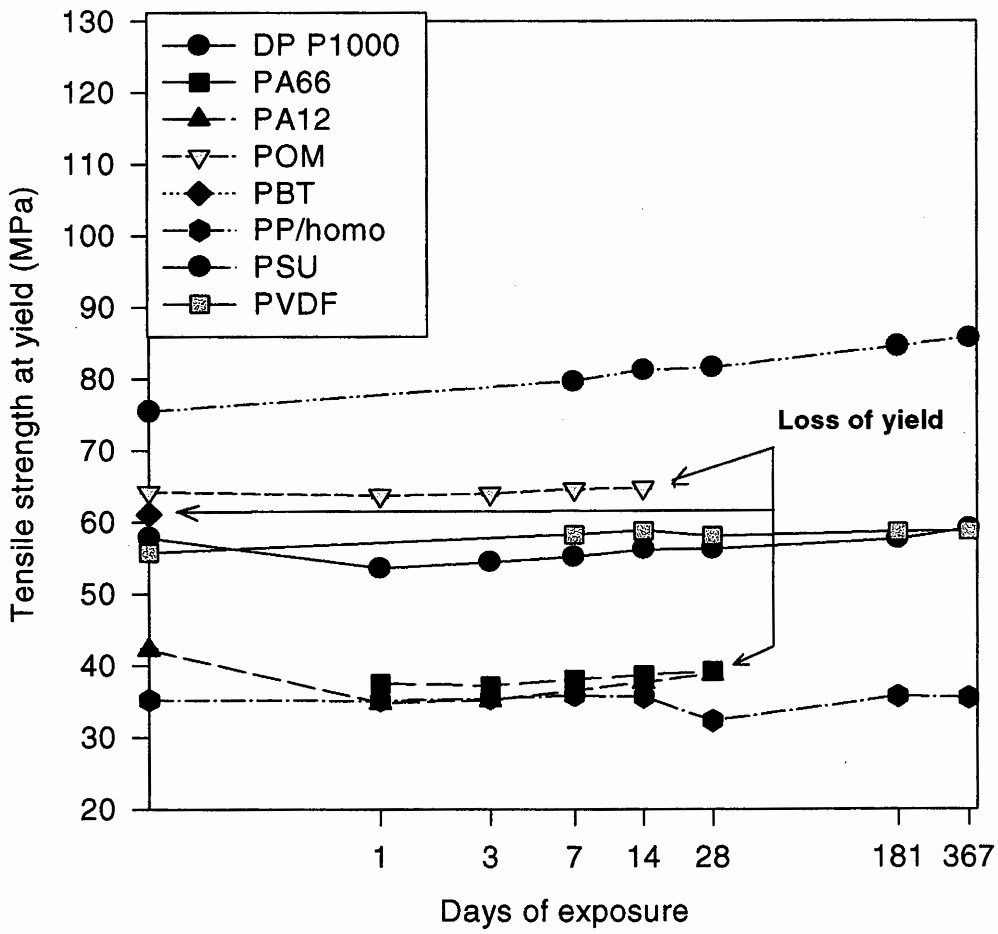

Figure 3: Effect of ageing in boiling water on tensile strength at yield of neat CARILON Polymer vs competing ETPs

3.3. Elongation at yield

Figure 4 shows the elongation at yield of CARILON DP P1000 and that of neat competitors as a function of exposure time.

After one day, CARILON DP P1000, PA66, PA12 and POM, show an increase in elongation at yield; i.e. +5%, +20%, +10% and +3% respectively. A plateau is reached and maintained up to 14 days for POM, up to 28 days for PA66 and PA12 and, up to one year for CARILON DP P1000. PSU, PVDF and PP hardly show any differences in the elongation at yield. PSU maintains an elongation at yield of around 5% whereas PVDF has 9% and PP 10%.

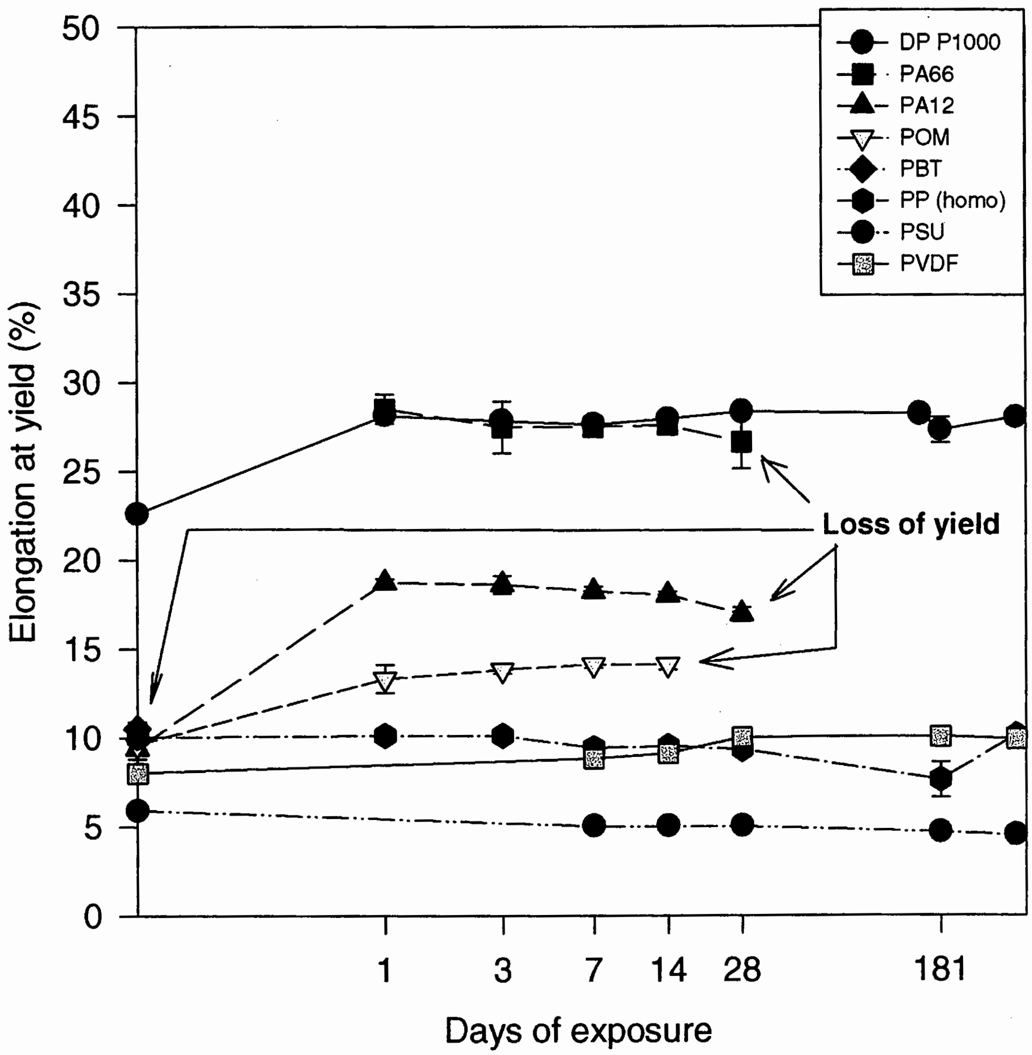

Figure 4: Effect of ageing in boiling water on elongation at yield of neat CARILON Polymer compared to competing ETPs

3.4. Tensile strength at break

In Figure 5, CARILON DP P1000 maintains a strength at break between 70 and 80 MPa up to 28 days. After 6 months (181 days), the tensile strength at break drops to 45 MPa. This level is maintained up to the end of the ageing period (1 year).

The condensation polymers show poor performances. PBT keeps a strength of around 60 MPa up to 3 days. A dramatic decrease to around 15 MPa occurred after 14 days in-line with literature [3]. The failure behaviour was completely brittle and it was decided to discontinue the testing of PBT. Like CARILON polymer, POM does not show any decrease before 28 days. The strength at break is maintained at a level of 60 MPa. However, after 6 months, it decreases to 50 MPa with a big scatter in the results (see standard deviation) which on top of a lower elongation at break led us to stop the ageing programme. PA66 presents a big decrease in tensile strength at break from the 'dry' state at day 0 to the 'wet' state of day 1 in boiling water. A drop from 80 MPa to 50 MPa has been recorded. Larger exposure to boiling water results in a further decreases to around 30 MPa after 6 months. PA12 maintains a strength at break of around 40 MPa up to 14 days. After 14 days of exposure, the tensile strength at break further shows a slight decrease. The ageing behaviour is comparable to PA66.

PSU, PVDF and PP do not show any differences in the strength at break. PSU keeps a value of around 50 MPa whereas PVDF has 36 MPa and PP 15 MPa.

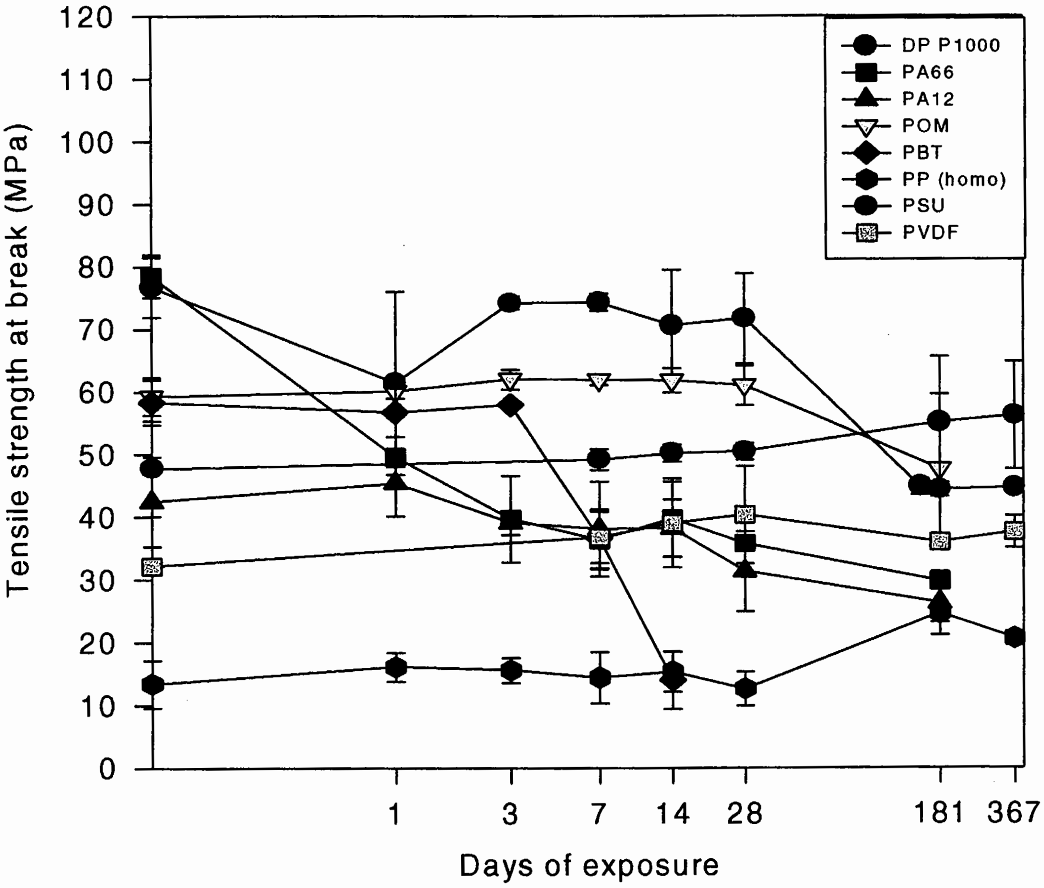

Figure 5: Effect of ageing in boiling water on tensile strength at break of neat CARILON Polymer vs competing ETPs

The glass-reinforced CARILON polymer (DP R1130) and competing materials are plotted in Figure 6.

CARILON DP R1130, like neat DP P1000, shows a continuous decrease in tensile strength at break up to one year, i.e. from 125 MPa to 90 MPa. PA66-GF30 shows a similar behaviour except for the 'dry' state data. The tensile strength decreases from 160 MPa at the dry state to 77 MPa after one year of ageing.

PBT-GF30 shows a bigger decrease. It gives a higher initial value than CARILON DP R1130; i.e. 140 MPa compared to 125 MPa respectively. But a dramatic failure occurs after 14 days for PBT-GF30 while DP R1130 shows a value of 100 MPa compared to 40 MPa for PBT-GF30.

The reduction of the tensile strength of PPS-GF40 shown in Figure 6 is also high. After 6 months, PPS-GF40 shows a completely brittle behaviour without any strength at break anymore. It drops from around 160 MPa down to 40 MPa. The ageing programme was ended.

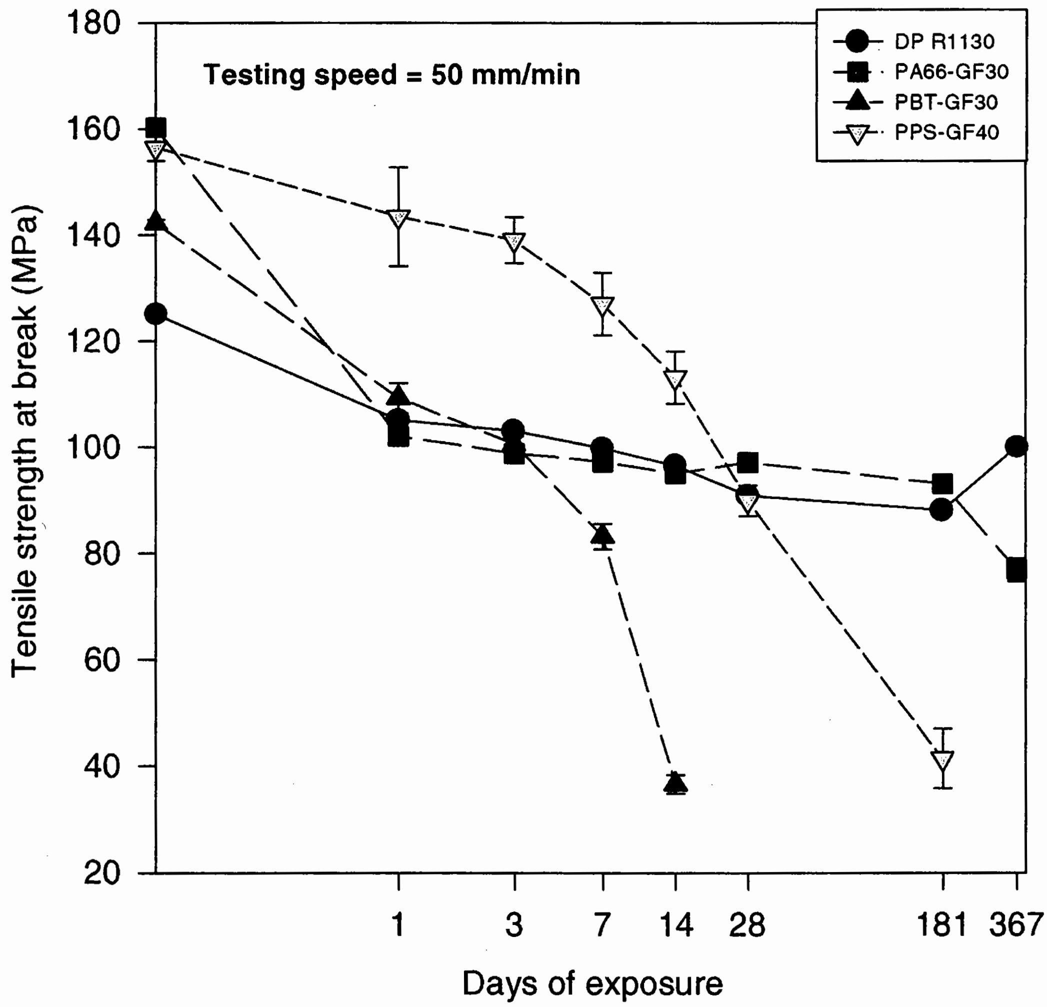

Figure 6: Effect of ageing in boiling water on tensile strength at break of glass fibre reinforced CARILON Polymer vs competing ETPs

3.5. Elongation at break

CARILON DP P1000 maintains an elongation at break higher than 300% up to 28 days in boiling water; it decreases to 75% after 6 months and after one year still has 50% elongation at break.

The results measured with PA66 show large standard deviations (see error bars on Figure 7). After one day, PA66 contains absorbed water and shows an elongation at break of around 250%. This elongation drops to 0% after 6 months. PA66 was not aged any further. PA12 behaves similarly except for the 'dry' state of 200% at the beginning of the ageing. The elongation at break of PBT drastically decreases from 16% down to 0.5% after 14 days. The ageing experiment was ended after that. The elongation at break of POM was maintained at around 30% up to 14 days. After 28 days, the elongation at break started to decrease and after 6 months, POM showed a completely brittle failure behaviour accompanied by a low strength at break after which the experiments were stopped.

PSU shows a decrease in elongation at break from 50% unaged to 11% after one year in boiling water. The standard deviation seems to decrease with ageing time. PVDF and PP do not show significant changes in elongation at break upon ageing, i.e. 40% and 50% respectively. This property clearly shows that CARILON DP P1000 surpasses all its competitors.

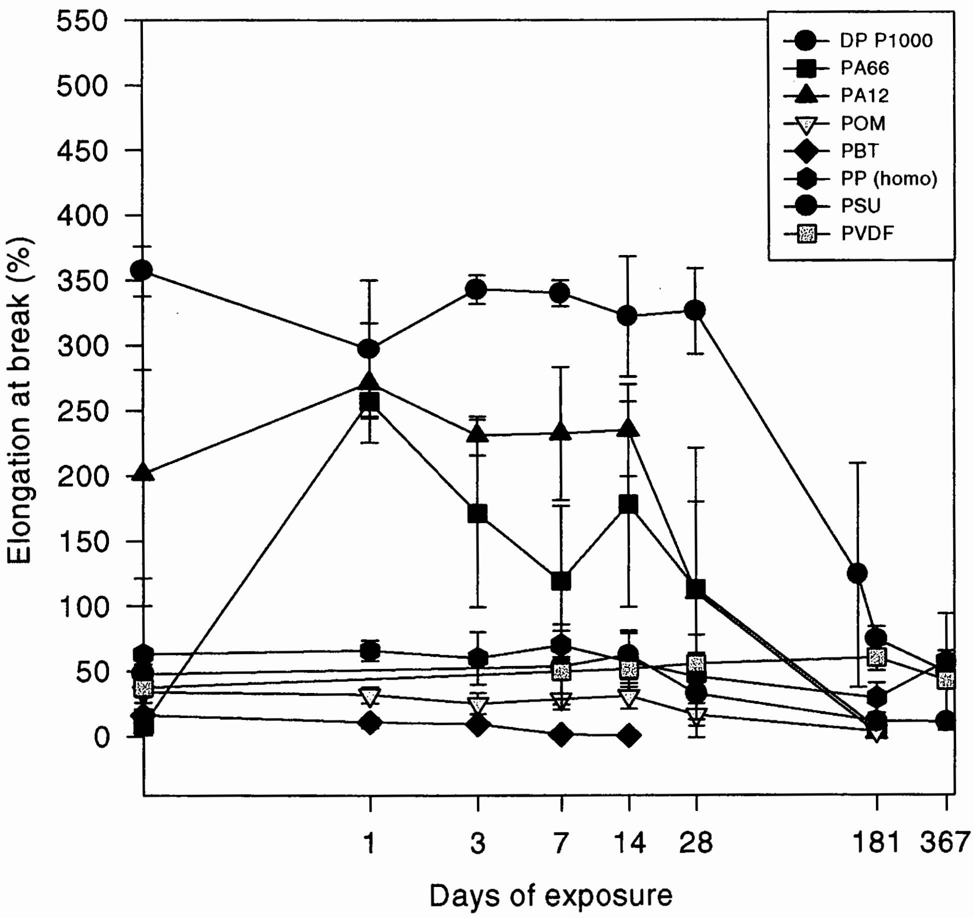

Figure 7: Effect of ageing in boiling water on elongation at break of neat CARILON Polymer vs competing ETPs

CARILON DP R1130 hardly shows any change in elongation at break up to 28 days of exposure. Elongation at break remains at a level of 2.8%. After 6 months, elongation at break slightly drops to around 2%. This level is maintained upto the end of the ageing time (1 year).

PA66-GF30 shows an increase from 3.6% in the 'dry' state to around 5.5% after ageing as expected by the water take up. An elongation at break of 2% is recorded after one year.

A larger decrease is found for PBT-GF30 and PPS-GF40 as already mentioned for the strength at break results. PBT-GF30 starts with the same level of elongation at break as DP R1130, i.e. 2.6%. After 1 day, a reduction to half of that value is found (1.4%) and no elongation is recorded after 14 days. The elongation at break of PPS-GF40 is also affected upon ageing in boiling water. The initial value is lower than that of the other polymers tested but it reflects the higher glass fibre content, 40% w/w in place of 30% w/w for the others. After 6 months, the elongation at break drops to nearly 0%. The ageing programme was ended.

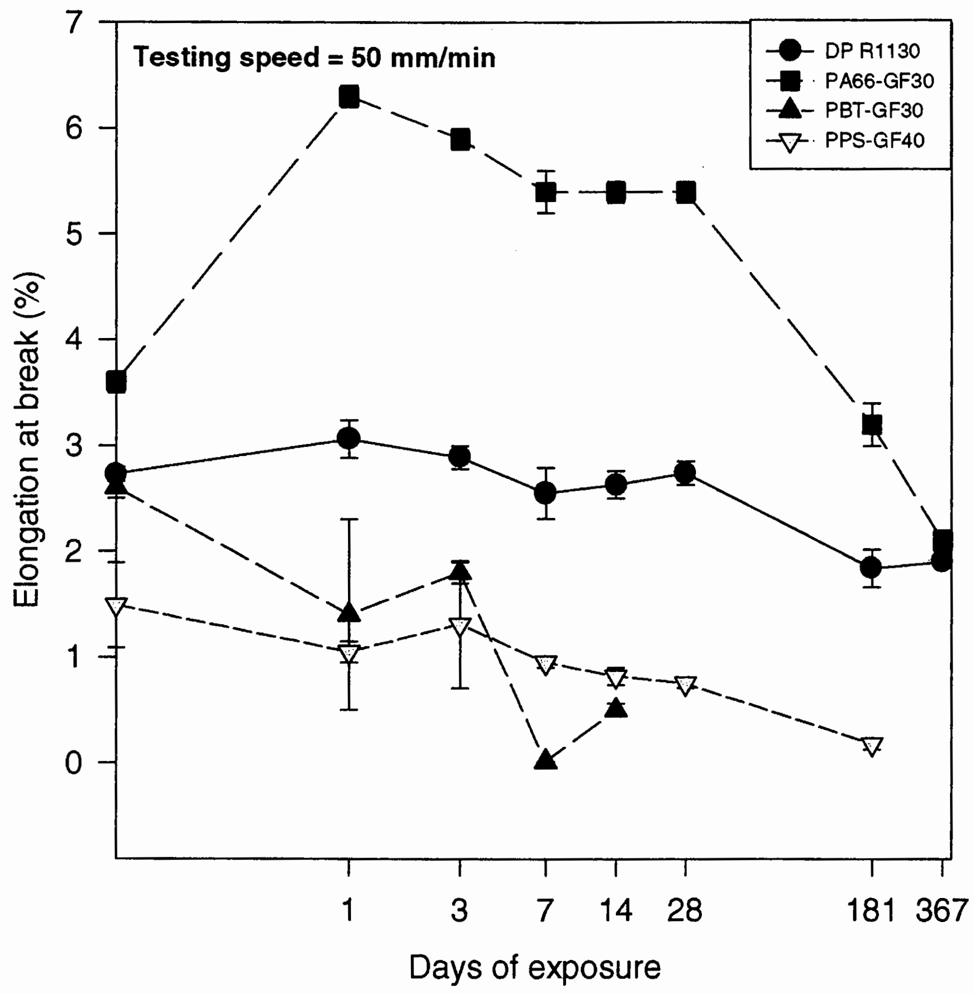

Figure 8: Effect of ageing in boiling water on elongation at break of glass fibre reinforced CARILON Polymer vs competing ETPs

3.6. Tensile Modulus

Figure 9 plots the modulus as function of the ageing time. It is assumed that the modulus is higher than the modulus described in the ISO-527 method (see Section 2.4. Testing).

After one day, CARILON DP P1000 shows a decrease in modulus which is maintained until the end of the ageing program. It drops from 1.7 GPa to 0.9 GPa after one day.

PA66 shows a bigger decrease in modulus than DP P1000. This is mainly due to the initial value which is taken 'dry'. After one day, a modulus of 0.8 GPa is found. This modulus value is maintained upto the end of the ageing program. No initial value of modulus for PA12 has been recorded. A similar trend as one obtained for PA66 is found. Modulus remains at 1 GPa during the whole ageing period. POM gives a slightly lower decrease than DP P1000. At the beginning, a modulus of 3.1 GPa is found. It drops to around 2.2 GPa. This value is maintained upto 28 days. At 6 months ageing, the modulus suddenly increases upto the initial value of 3.1 GPa. No explanations have been found for this phenomenon. The modulus of PBT is initially 3 GPa. It decreases to around 2.5 GPa after ageing. This value is maintained upto the end of the ageing program.

The modulus of PVDF, PSU and PP do not show any big changes upon ageing, i.e. 1.9 GPa, 2.8 GPa and 2.3 GPa respectively.

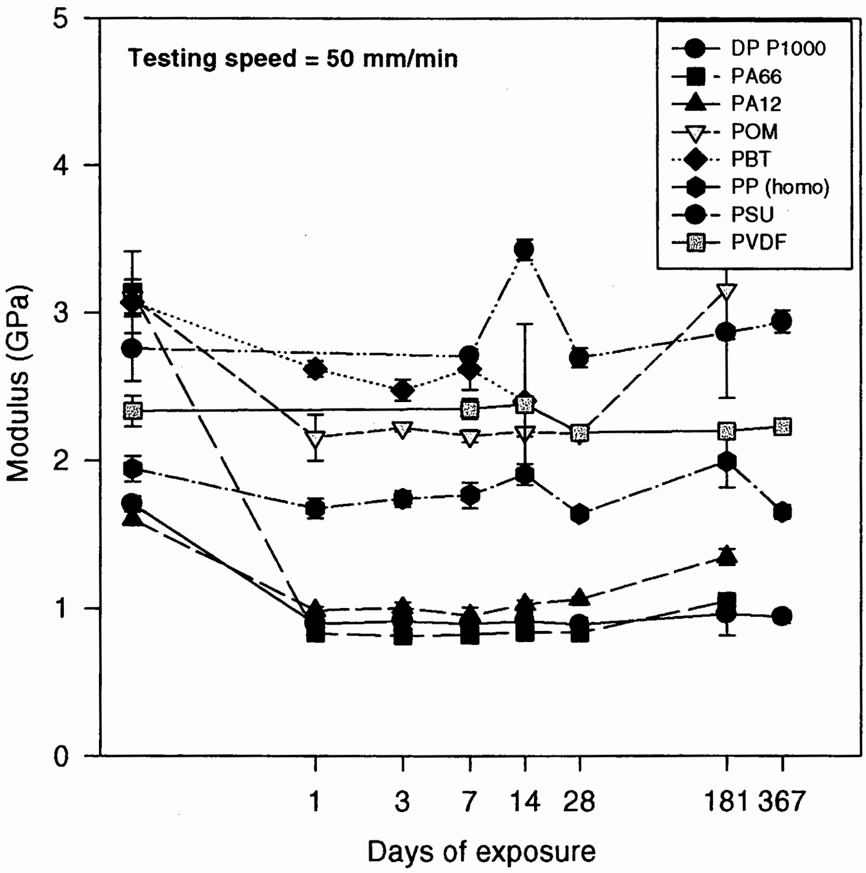

Figure 9: Effect of ageing in boiling water on tensile modulus of neat CARILON Polymer vs competing ETPs

The modulus of DP R1130 decreases after 1 day in boiling water from 8.4 GPa to 6 GPa. After 6 months of ageing, a value of 8 GPa has been measured for the tensile modulus. This represents an increase by 2 GPa compared to the last previous measurement (28 days). Modulus further increases to 9 GPa after 1 year of exposure. This is probably related to degradation phenomena at the glass fibre-matrix interface. However, more investigation needs to be carried out to prove these statements.

As for the neat polymers, PA66-GF30 shows the biggest change in modulus. It is followed by CARILON DP R1130, PBT-GF30 and PPS-GF40. PBT-GF30 shows the same slow decrease as for the neat version. A value of 10 GPa at day 0 is reduced to 8.8 GPa after 14 days of ageing. PPS-GF40 does not show a big variation in modulus upon ageing. An initial value of 15.6 GPa is reduced to 13 GPa after 28 days.

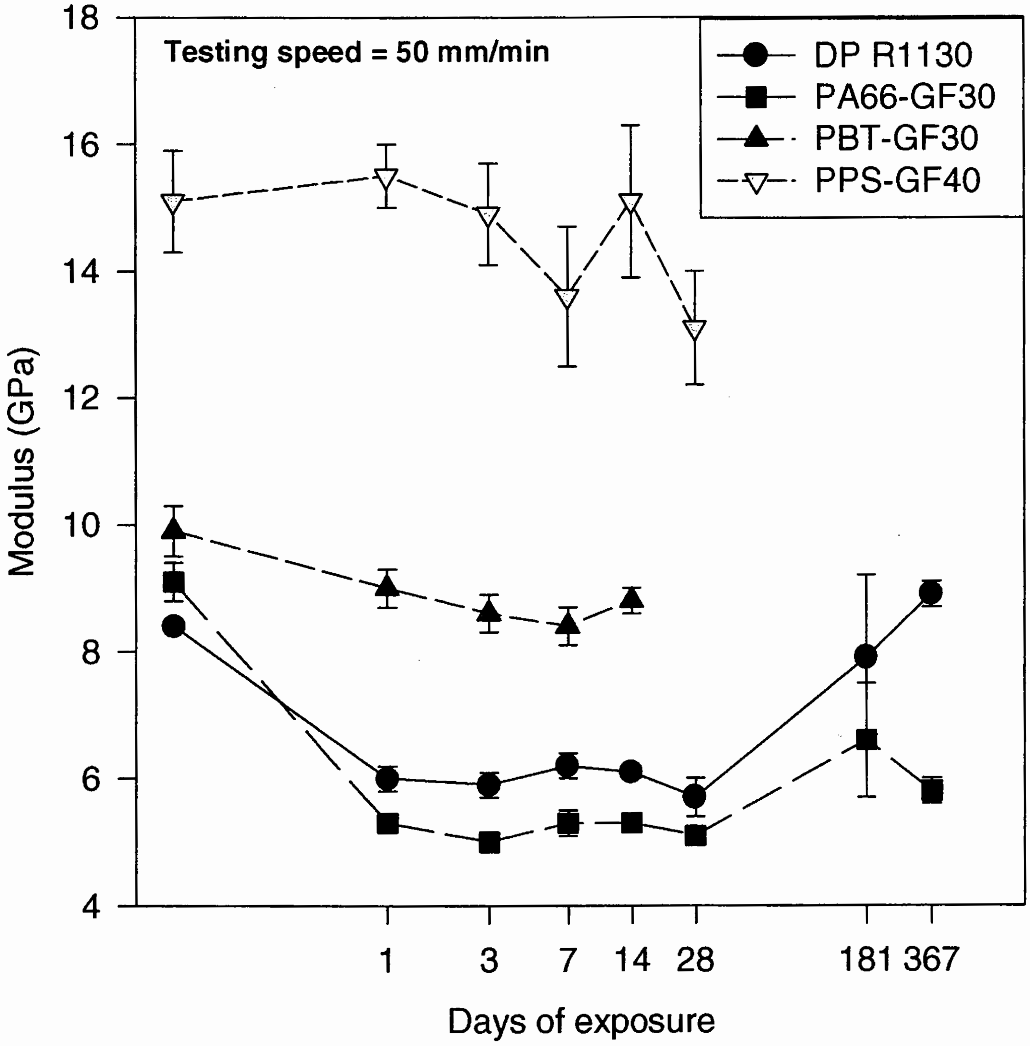

Figure 10: Effect of ageing in boiling water on tensile modulus of glass fibre reinforced CARILON Polymer vs competing ETPs

3.7. Discoloration effects

Figures 12 to 21 show the effect of discoloration on all aged samples.

Compared to neat competitors, CARILON DP P1000 shows the largest discoloration (Figure 12). It starts at 1 month ageing towards a yellow colour; turns to brown after 6 months and to dark brown after one year. However, it only appears at the surface; the central core of the one year aged sample is still white. This discoloration is mainly due to chemical mechanisms of ionic nature and does not affect the mechanical properties which is in line with previous findings [4] .

PA66-neat shows also surface discoloration (Figure 13) but less than CARILON DP P1000. PA12, POM, PBT, PP, PSU and PVDF only present a yellowish discoloration on the surface (Figures 14 to 18). This effect may be due to other samples like PPS-GF40 which was aged in the same container until 1 month.

CARILON DP R1130 also presents a large discoloration. As for the neat DP P1000, it starts at 1 month of ageing (Figure 19) towards a yellow colour but it already turns to dark brown after 6 months. Contrarily to DP P1000, it is seen through the bulk of the material.

PA66-GF30 behaves like the neat polymer: after 6 months, it turns into a brown coloured sample (Figure 20). This is only a surface phenomenon. PBT-GF30 does not show discoloration but it has only been aged during 14 days. PPS-GF40, on the other hand, discolours from dark brown to greyish brown already after one day in boiling water (Figure 21). The discoloration is seen through the bulk of the material.

3.8. Water conductivity and colour

The conductivity and the colour of the boiled water have been recorded in Tables 4 and 5.

Demineralized water with an initial conductivity of 1.5 µS/cm has been used. After each ageing time the conductivity increased more and more (180 µS/cm after 1 year). This means that more ions are presents in the water. Further investigations should be done in order to determine the nature and origin of these ions.

The boiled water turned yellow after 28 days for the first set-up. This was mainly due to PPS-GF40 samples. In the second set-up, the water turned yellow only after 6 months; here, no PPS-GF40 samples were present but the CARILON Polymer test samples started to discolour.

4. CONCLUSIONS

After one year of ageing in boiling water, five main conclusions are drawn:

- Neat CARILON Polymer has a better hydrolytic stability than condensation polymers like PBT, POM and to a lesser extent PA66 and PA12.
- PVDF, PSU and, to some extent, PP-homo retain their tensile properties better than neat CARILON Polymer.
- CARILON Polymer DP R1130 performs better than PBT-GF30 and PPS-GF30 in terms of retention of tensile properties. PA66-GF30 retains its strength at break but shows a big decrease in elongation at break after one year.
- CARILON Polymer DP R1130 shows a decrease in weight accompanied by a limited increase in modulus after one-year ageing. This is most likely related to enhanced degradation at the glass-matrix interface. However further investigations should be performed.
- Neat CARILON Polymer as well as the glass-reinforced grade show the highest level of discoloration when compared to other ETPs. In CARILON Polymer DP P1000, the discoloration is only a surface effect; the bulk of the polymer does not discolour. The discoloration does not affect directly the mechanical properties of CARILON Polymer. CARILON DP R1130 discolours through out the bulk of the material.

5. RECOMMENDATION FOR FURTHER WORK

No investigations have been done on the effect the different polymers could have had on each other. Ageing data on PA66, PBT, PA12, POM, PPS-GF40 were found to be similar to those reported in literature. This leads to the suggestion that the increased water conductivity should not have a significant effect on the data measured for the competitors in this study. However, to validate the results as obtained for CARILON Polymer, additional ageing test are being performed on DP R1130 and DP P1000 in separate vessels.

Further investigations are required to understand the weight loss and modulus increase found after one year on CARILON DP R1130. During the additional ageing test, more data are being collected between 6 months and 1 year. Rheology and analysis of the additives residue will be performed on the aged sample.

Louvain-la-Neuve, November, 1997.

6. REFERENCES

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2. P. Verbeke and A. Lacroix: "The influence of water on the mechanical and physical properties of CARILON EP polymer", *CL.96.50029*.

3. *Chemical Resistance*, Second Edition, Plastic Design Library **Volume I - Thermoplastics**.

4. A.A. Smaardijk: "Discoloration of CARILON Polymer", *CTCAR2/1358/96*.

Type	Trade name	Manufacturer
PK	CARILON DP P1000-1000	Shell Chemicals (lot 06RMA0033)
PK-GF30	CARILON DP R1130-1000	" (lot 10QED0133 ex. DSM and lot 09RKD0001 for 1 year ageing)
PA66	Ultramid A3K	BASF
PA66-GF30	Ultramid A3EG6	"
PA12	Vestamid L1940	Hüls
POM homo	Hostaform C1921	Hoescht
PBT	Pocan B1305	Bayer
PBT-GF30	Ultradur B4300G6	BASF
PPS-GF40	Ryton R4	Phillips Petroleum
PP homo	Polypropylene JY6100	Shell Chemicals
PVDF	Solef 1008	Solvay
PSU	Ultrason S2010	BASF

Table 1: Polymers grades used for the ageing

	DP P1000	PA66	PA12	POM	PBT	PP	PSU	PVDF
Temperatures (°C)								
Mould	60	70	80	85	80	60	85[a]	75
Melt	250	270	225	200	240	225	340	210
Nozzle	250	285	230	210	-	230	350	220
Metering zone	245	275	230	210	-	230	350	220
Compression zone	240	265	210	200	-	220	350	210
Feed zone	240	255	190	190	-	210	350	190
Times (s)								
Metering	7.06	8.65	6.42	4.81	6.71	5.25	5.10	5.09
Injection	6.06	5.1	3.80	4.04	1.87	4.89	5.23	4.65
Holding	10.31	9.66	20	14.31	12	24.86	12	29.27
Cooling	10	30	30	10	10	25	20	20
Cycle	29.61	47.8	57.55	31.85	31.0	61.95	40.62	58.71
Pressure (bar)								
Injection (in mould)	361	330	375	330	450	361	361	389
Injection (hydrol.)	721	677	778	749	1200	808	1150	957
Holding	694	681	768	753	1500	795	1130	971
Back	2	5	2	5	10	5	5	5
Speeds								
Injection (mm/s)	15	10	15	15	18	10	10	10
Screw (rpm)	80	120	80	120	35	120	100	120

[a] ; following datasheet it should be 120°C but it was impossible to go at higher temperatures at that time

Table 2: Injection moulding conditions of CARILON Polymer DP P1000 and competing ETPs

	DP R1130	PA66-GF30	PBT-GF30	PPS-GF40
Temperatures (°C)				
Mould	90	80	80	85[a]
Melt	240	290	260	300
Nozzle	250	NR[b]	NR	300
Metering zone	250	NR	NR	300
Compression zone	250	NR	NR	300
Feed zone	240	NR	NR	270
Times (s)				
Metering	5.36	NR	NR	6.39
Injection	0.67	NR	NR	5.21
Holding	10.08	8	10	6.08
Cooling	10	NR	NR	30
Cycle	24.32	NR	NR	44.57
Pressure (bar)				
Injection (in mould)	NR	278	361	375
Injection (hydrol.)	860	636	801	802
Holding	730	660	816	809
Back	5	NR	NR	5
Speeds				
Injection (mm/s)	75	15	20	10
Screw (rpm)	20	NR	NR	120

[a] : according datasheet it should be 120°C but it was impossible to go at higher temperatures at that time

[b] : Not recorded

Table 3: Injection moulding conditions of CARILON DP R1130 and competing glass-reinforced ETPs

1 st set up - up to 6 months P1000; R1130; PA66; PA66-GF30; PA12; POM; PBT; PBT-GF30; PPS-GF40; PP		
Ageing time day	water conductivity µS/cm	Remarks
0	1.5	each time fresh water
1		
3		
7	36	water clear
14	39	water clear
28	48	water colour yellow Brown particles in suspension
181 (6 months)	118	
	136*	*PPS aged in a separate container

Table 4: Timing protocol during the ageing in boiling water (1st set-up)

2d set up - up to 1 year P1000; R1130; PA66-GF30; PP; PVDF; PSU		
Time day	water conductivity µS/cm	Remarks
0	1.5	run for 1 year
7	ND	water clear (PVDF,PSU removed tested)
14	ND	idem
28	ND	idem
181 (6 months)	ND	water slightly yellow (PVDF, PSU and P1000 as reference tested)
367 (1 year)	179	All samples tested water colour yellow

Table 5: Timing protocol during the ageing in boiling water (2d set up)

	Ageing time (days)	Weight change (%)	Yield[a] Elongation (%)	Yield[a] Strength (MPa)	Break[a] Elongation (%)	Break[a] Strength (MPa)	Modulus[a] (GPa)
DP P1000	0		22.6 ± 0.3	57.8 ± 0.2	357 ± 19	76.7 ± 4.8	1.70 ± 0.05
	1	3.66	28.1 ± 0.2	53.6 ± 0.1	297 ± 53	61.4 ± 14.6	0.90 ± 0.03
	3	3.61	27.8 ± 0.3	54.4 ± 0.1	343 ± 11	74.2 ± 1.1	0.91 ± 0.02
	7	3.33	27.6 ± 0.5	55.2 ± 0.3	340 ± 10	74.3 ± 1.4	0.90 ± 0.03
	14	3.30	27.9 ± 0.3	56.2 ± 0.1	322 ± 46	70.6 ± 8.9	0.91 ± 0.06
	28	3.35	28.3 ± 0.3	56.3 ± 0.1	326 ± 33	71.7 ± 7.2	0.89 ± 0.05
	150	2.98	28.2 ± 0.2	58.2 ± 0.2	123 ± 86	44.8 ± 1.2	0.88 ± 0.02
	181	3.28	27.3 ± 0.7	57.6 ± 0.2	74.1 ± 9.7	44.3 ± 1.1	0.96 ± 0.14
	367	2.81	28.0 ± 0.3	59.1 ± 0.4	49.3 ± 3.2	44.6 ± 0.7	0.94 ± 0.04
PA66	0		- (5)	- (82)	9.1 ± 7.9	78.5 ± 3.4	3.14 ± 0.28
	1	7.7	28.5 ± 0.8	37.5 ± 0.2	257 ± 12	49.5 ± 1.5	0.83 ± 0.03
	3	8.1	27.5 ± 1.5	37.2 ± 0.4	171 ± 72	39.7 ± 6.9	0.81 ± 0.02
	7	7.3	27.5 ± 0.5	38.1 ± 0.2	119 ± 58	36.4 ± 4.7	0.82 ± 0.05
	14	7.3	27.6 ± 0.4	38.7 ± 0.2	178 ± 79	39.7 ± 6.0	0.84 ± 0.02
	28	6.8	26.6 ± 1.5	39.2 ± 0.4	113 ± 67	35.8 ± 4.6	0.83 ± 0.03
	181	6.7	-	-	5.7 ± 0.2	29.8 ± 0.8	1.05 ± 0.00
	367	STOPPED	STOPPED	STOPPED	STOPPED	STOPPED	STOPPED
PA12	0		9.4 ± 0.6	42.2 ± 0.2	201 ± 80	42.5 ± 0.6	-
	1	1.5	18.7 ± 0.2	34.8 ± 0.2	271 ± 46	45.4 ± 5.2	0.98 ± 0.03
	3	1.5	18.6 ± 0.5	35.2 ± 0.3	231 ± 15	39.1 ± 1.9	1.00 ± 0.04
	7	1.2	18.2 ± 0.3	36.5 ± 0.2	232 ± 51	38.1 ± 7.6	0.95 ± 0.06
	14	1.3	18.0 ± 0.2	37.7 ± 0.2	235 ± 36	38.2 ± 4.6	1.03 ± 0.03
	28	1.0	16.9 ± 0.4	38.8 ± 0.3	110 ± 111	31.3 ± 6.4	1.06 ± 0.02
	181	0.9	(3.0)	(28.7)	2.6 ± 0.8	26.2 ± 5.1	1.35 ± 0.05
	367	STOPPED	STOPPED	STOPPED	STOPPED	STOPPED	STOPPED
POM	0		9.6 ± 0.2	64.2 ± 0.1	34.2 ± 13.2	59.3 ± 3.0	3.10 ± 0.13
	1	1.8	13.3 ± 0.8	63.8 ± 0.3	31.8 ± 6.3	60.1 ± 1.2	2.16 ± 0.16
	3	1.8	13.8 ± 0.2	64.0 ± 0.2	25.2 ± 8.0	62.0 ± 1.6	2.22 ± 0.02
	7	1.7	14.1 ± 0.2	64.6 ± 0.1	28.5 ± 4.1	61.9 ± 0.8	2.17 ± 0.04
	14	1.7	14.1 ± 0.3	64.8 ± 0.1	31.0 ± 9.6	61.8 ± 1.9	2.19 ± 0.03
	28	1.5	(14.4)	(64.8)	16.5 ± 8.7	61.0 ± 3.2	2.18 ± 0.04
	181	1.4	-	-	3.3 ± 3.5	47.6 ± 12.0	3.16 ± 0.74
	367	STOPPED	STOPPED	STOPPED	STOPPED	STOPPED	STOPPED

a: testing speed : 50 mm/min

Table 6: Results of CARILON DP P1000 aged in boiling water up to 1 year versus competing ETPs - part 1

	Ageing time (days)	Weight change (%)	Yield[a] Elongation (%)	Yield[a] Strength (MPa)	Break[a] Elongation (%)	Break[a] Strength (MPa)	Modulus[a] (GPa)
PBT	0		10.5 ± 0.4	61.1 ± 0.3	16.3 ± 4.2	58.3 ± 3.6	3.07 ± 0.08
	1	0.5	-	-	10.7 ± 4.2	56.7 ± 3.9	2.62 ± 0.05
	3	0.6	-	-	9.2 ± 0.7	57.9 ± 0.5	2.48 ± 0.07
	7	0.6	-	-	1.3 ± 0.4	36.6 ± 4.7	2.62 ± 0.14
	14	0.8	-	-	0.54 ± 0.19	14.0 ± 4.6	2.40 ± 0.52
	28	STOPPED	STOPPED	STOPPED	STOPPED	STOPPED	STOPPED
PP	0	0.00	10.0 ± 0.1	35.2 ± 0.1	63.0 ± 37.2	13.4 ± 3.8	1.94 ± 0.09
	1	0.04	10.1 ± 0.1	35.1 ± 0.1	66.0 ± 8.0	16.1 ± 2.3	1.68 ± 0.07
	3	0.01	10.1 ± 0.1	35.4 ± 0.2	60.4 ± 20.0	15.6 ± 2.0	1.74 ± 0.05
	7	0.04	9.4 ± 0.2	35.8 ± 0.0	69.8 ± 10.6	14.4 ± 4.1	1.77 ± 0.09
	14	0.00	9.5 ± 0.1	35.6 ± 0.1	56.7 ± 22.0	15.3 ± 3.2	1.91 ± 0.07
	28	0.04	9.3 ± 0.0	32.3 ± 0.1	45.6 ± 17.5	12.6 ± 2.7	1.64 ± 0.02
	181	0.00	7.6 ± 1.0	35.7 ± 0.1	29.3 ± 11.4	24.6 ± 1.4	1.99 ± 0.17
	367		10.2 ± 0.0	35.5 ± 0.1	56.9 ± 8.4	20.6 ± 1.1	1.65 ± 0.05
PSU	0		5.9 ± 0.1	75.5 ± 0.1	47.7 ± 7.6	50.9 ± 1.0	2.8 ± 0.2
	1		ND	ND	ND	ND	ND
	3		ND	ND	ND	ND	ND
	7	1.0	5.0 ± 0.1	79.7 ± 0.1	53.3 ± 32.5	49.2 ± 1.7	2.7 ± 0.0
	14	1.0	5.0 ± 0.1	81.3 ± 0.0	62.4 ± 18.6	50.2 ± 1.3	2.7 ± 0.1
	28	1.0	5.0 ± 0.1	81.6 ± 0.0	32.7 ± 18.0	50.5 ± 1.3	2.7 ± 0.0
	181	1.0	4.7 ± 0.1	84.6 ± 0.3	11.2 ± 3.1	55.0 ± 10.5	2.9 ± 0.0
	367	1.0	4.5 ± 0.1	85.8 ± 0.1	10.7 ± 1.1	56.2 ± 8.6	2.9 ± 0.1
PVDF	0		8.0 ± 0.2	55.8 ± 0.1	37.4 ± 6.9	32.2 ± 0.4	2.3 ± 0.1
	1		ND	ND	ND	ND	ND
	3		ND	ND	ND	ND	ND
	7	0.2	8.8 ± 0.1	58.3 ± 0.1	49.6 ± 21.0	36.8 ± 4.1	2.3 ± 0.1
	14	0.2	9.1 ± 0.2	58.8 ± 0.2	51.4 ± 13.3	39.1 ± 7.1	2.4 ± 0.0
	28	0.2	10.1 ± 0.1	58.1 ± 0.2	55.6 ± 21.9	40.4 ± 7.8	2.2 ± 0.0
	181	0.2	10.1 ± 0.1	58.7 ± 0.2	60.1 ± 9.9	35.9 ± 1.0	2.2 ± 0.0
	367	0.2	9.9 ± 0.6	58.8 ± 0.5	42.6 ± 2.7	39.0 ± 2.3	2.2 ± 0.0

a: testing speed : 50 mm/min

Table 7: Results of CARILON DP P1000 aged in boiling water up to 1 year versus competing ETPs - part 2

	Ageing time (days)	Weight[c] change (%)	Break[c] Elongation (%)	Break[c] Strength (MPa)	Modulus[c] (GPa)
DP R1130	0	0	2.7 ± 0.1	125 ± 1	8.4 ± 0.1
	1	2.2	3.1 ± 0.2	105 ± 1	6.0± 0.2
	3	2.3	2.9 ± 0.1	103 ± 1	5.9 ± 0.2
	7	2.2	2.5 ± 0.2	100 ± 1	6.2 ± 0.2
	14	2.2	2.6 ± 0.1	96.5 ± 0.8	6.1 ± 0.1
	28	2.2	2.7 ± 0.1	90.9 ± 0.6	5.7 ± 0.3
	181	1.8	1.8 ± 0.2	88.0 ± 0.8	7.9 ± 1.3
	367	0.7	1.9 ± 0.0	100 ± 0.2	8.9 ± 0.2
PA66-GF30	0	0	3.6 ± 0.1	160 ± 1	9.1 ± 0.3
	1	4.1	6.3 ± 0.1	102 ± 0.4	5.3 ± 0.1
	3	4.5	5.9 ± 0.1	98.8 ±0.7	5.0 ±0.1
	7	3.8	5.4 ± 0.2	97.2 ± 0.2	5.3 ± 0.2
	14	4.1	5.4 ± 0.1	95.0 ± 0.2	5.3 ± 0.1
	28	3.9	5.4 ± 0.1	97.1 ± 0.8	5.1 ± 0.1
	181	3.6	3.2 ± 0.2	93.1 ± 0.2	6.6 ± 0.9
	367	3.9	2.1 ± 0.1	76.9 ± 2.2	5.8 ± 0.2
PBT-GF30	0	0	2.6 ± 0.1	142 ± 0.5	9.9 ± 0.4
	1	0.44	1.4 ± 0.9	109 ± 3	9.0 ± 0.3
	3	0.55	1.8 ± 0.04	101 ± 3	8.6 ± 0.3
	7	0.56	0.014 ± 0.0004 [a]	83.2 ± 2.4	8.4 ± 0.3
	14	0.77	0.50 ± 0.06	36.6 ± 1.8	8.8 ± 0.2
	28	STOPPED	STOPPED	STOPPED	STOPPED
PPS-GF40	0	0	1.5 ± 0.4	156 ± 3	15.1 ± 0.8
	1	0.38	1.0 ± 0.1	143 ± 9	15.5 ± 0.5
	3	0.44	1.3 ± 0.6	139 ± 4	14.9 ± 0.8
	7	0.46	0.95 ± 0.05	127 ± 6	13.6 ± 1.1
	14	0.64	0.82 ± 0.08	113 ± 5	15.1 ± 1.2
	28	0.72	0.74 ± 0.04	89.9 ± 2.9	13.1 ± 0.9
	181	1.32	0.18 ± 0.05 [a]	41.4 ± 5.6	b
	367	STOPPED	STOPPED	STOPPED	STOPPED

[a] : n = 2
[b]: no modulus calculated due to elongation at break too short
c: testing speed = 50 mm/min

Table 8: Results of DP R1130 aged in boiling water versus competing glass-reinforced ETPs

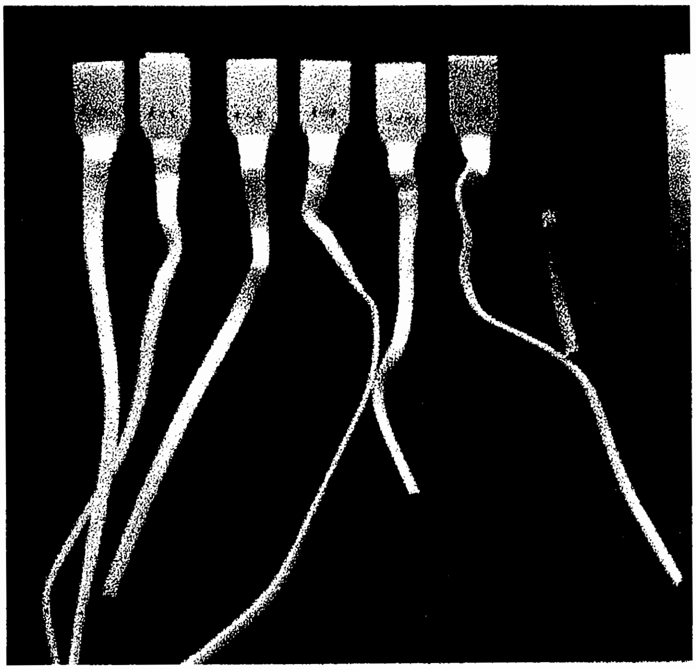

Figure 12: Aged sample of CARILON DP P1000 from 0 day up to 1 year.

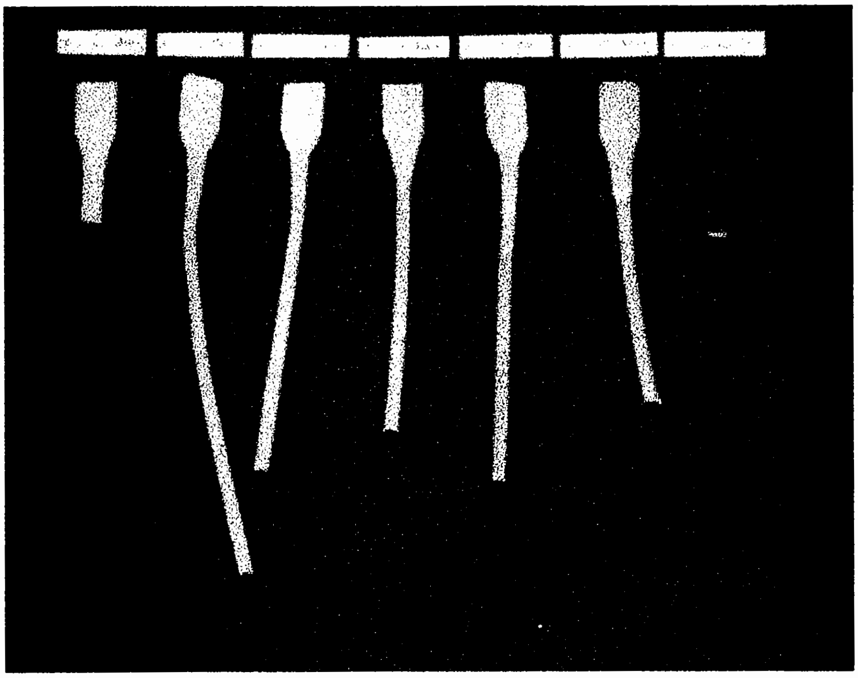

Figure 13: Aged sample of PA66 neat from 0 day up to 6 months

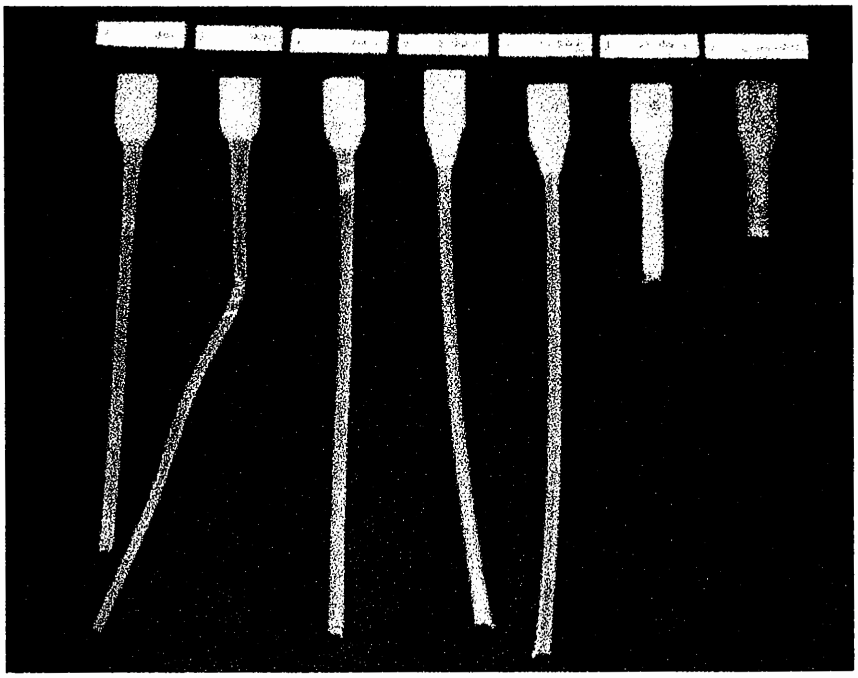

Figure 14: Aged sample of PA12 neat from 0 day up to 6 months

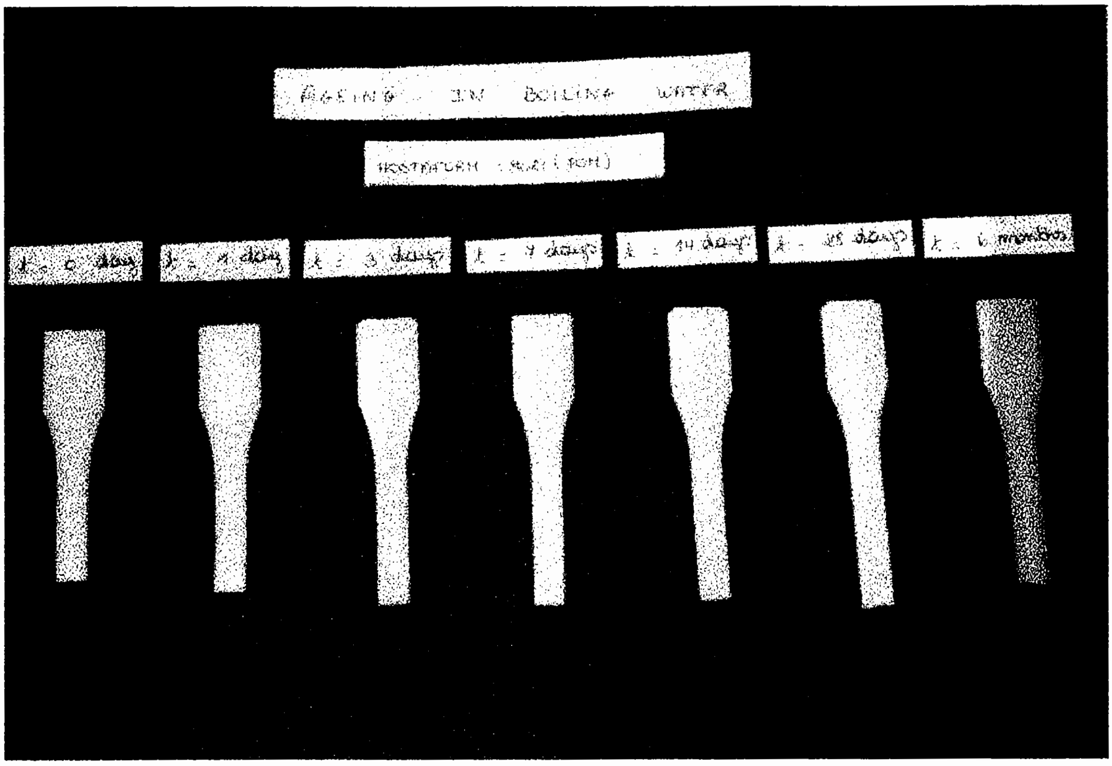

Figure 15: Aged sample of POM neat from 0 day up to 6 months

Figure 16: Aged sample of PP neat from 0 day up to 1 year

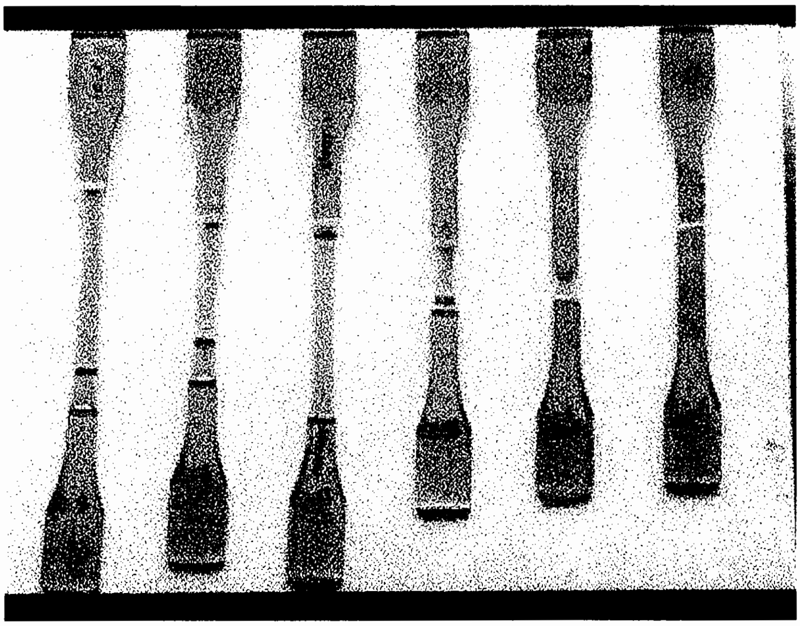

Figure 17: Aged sample of PSU neat from 0 day up to 1 year

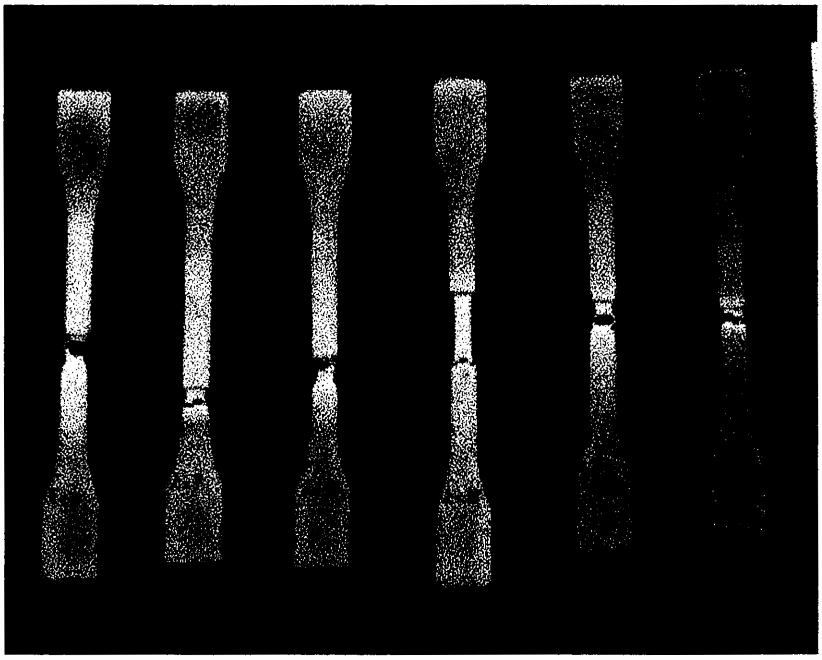

Figure 18: Aged sample of PVDF neat from 0 day up to 1 year

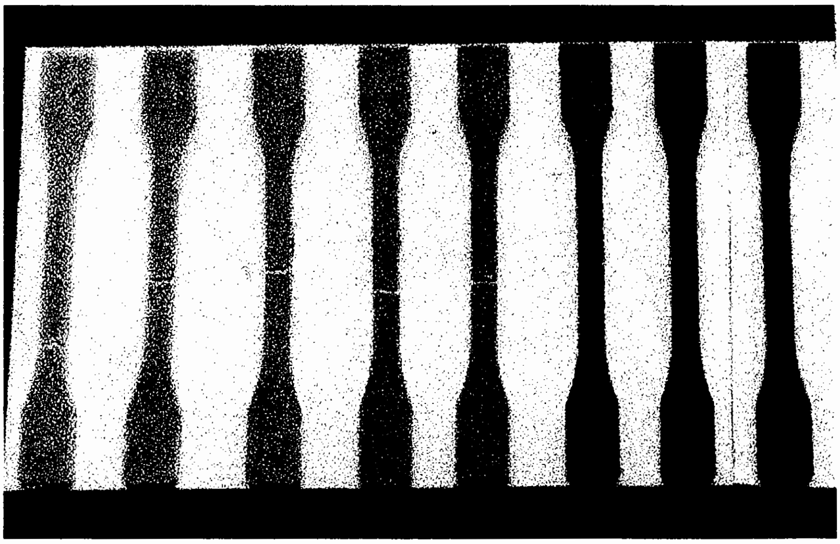

Figure 19: Aged sample of CARILON DP R1130 from 0 day up to 1 year

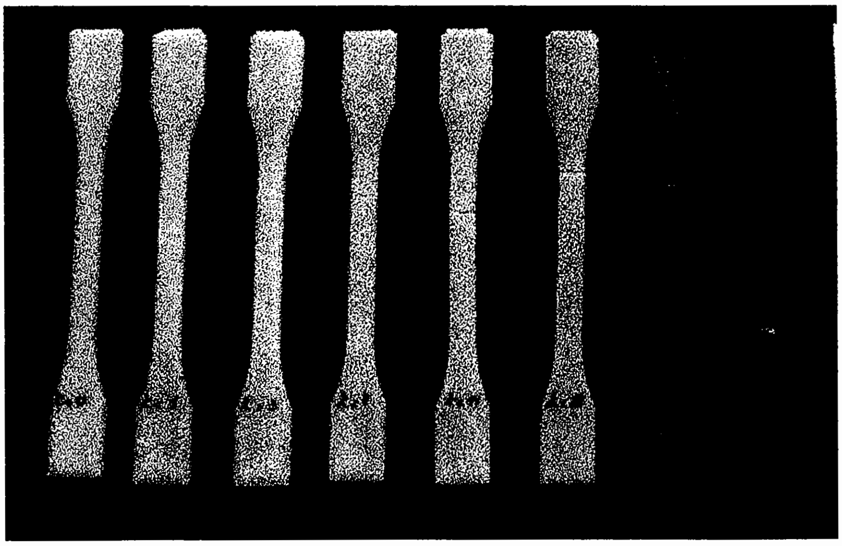

Figure 20: Aged sample of PA66-GF30 from 0 day up to 1 year

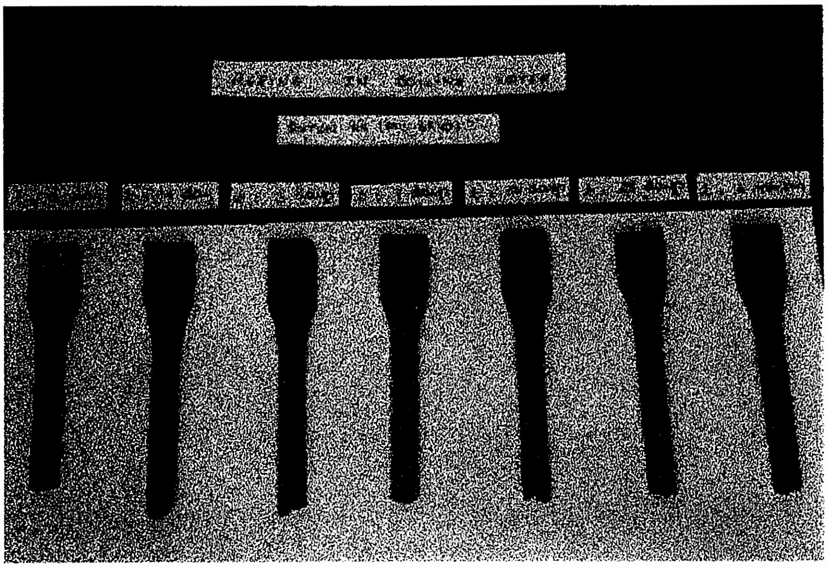

Figure 21: Aged sample of PPS-GF40 from 0 day up to 6 months

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