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# VALUE IN USE OF CARILON POLYMERS

(August 1994)

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**SUMMARY**

A proposal for a technical-marketing publication on CARILON polymer is presented. It highlights key performance drivers in the industrial and consumer market sectors, which surfaced from perceived value in use of parts and components made from CARILON. It is aimed at generating the necessary interest in CARILON through publication in the relevant market-oriented media.

August, 1994.

# CONTENTS

## 1 BACKGROUND

Using standard laboratory-type test methods, the bottom-line thermal-mechanical performance level of CARILON polymers is easily characterised as "similar to other engineering thermoplastics (ETPs) such as nylons and polyacetals". Together with additional advantages, as perceived from such standard laboratory tests, one can generate a primary positioning of CARILON as a new ***material*** in the ETP market. Such primary positioning is test-sample related and mainly based on a (competitive) material database (Appendix 1).

A second step is to mould and test relevant end-products at end-users and converters active in the various ETP market sectors. If one focuses on the performance of the actual component, rather than on a set of material properties, and if one intelligently examines the current requirements and future trends in the specific sector, one can generate the value in use of CARILON as a new ***product***: what is the combination of advantages of a particular CARILON part worth to a particular customer ? Hence, the concept of value in use is related to sector specific tests and requirements, which may differ from sector to sector (Appendix 1). Within the same sector further differences may be encountered between e.g. conservative and more innovative end-users.

The value in use concept is directly linked to what an ***engineering*** thermoplastic actually means. By definition, parts and components made from ETPs fulfil a set of well-defined thermal-mechanical, dimensional and life requirements. The requirements for the component are an integral part of the total functionality of the (engineered) system of which it is part. The more requirements the component can fulfil, the more "engineering" it becomes. In this context, value in use of CARILON polymers relates to the ability to open-up the way to completely new applications or designs and to replace traditional materials like metals. It also relates to outperforming other ETPs in existing parts on the basis of better overall functionality, or because other ETPs are fully researched and offer no new opportunities.

Combined effort of marketing representatives, scouting the opportunities and establishing values and volumes, and R&D, providing the relevant technical toolbox, has in the last two years created a (probably small) part of what could be called a "value in use jig-saw puzzle". Now that the CARILON project is endorsed, the relevant CARILON marketing community has expressed a strong desire for publicity on the subject of CARILON polymers. In particular, CRCSL was requested to generate a draft technical presentation aimed at generating the necessary interest from companies active in the market sectors covered by CRCSL, i.e. the industrial, consumer and electrical sectors.

This report covers the relevant experiences as to the value in use of CARILON polymers, in particular in the industrial and consumer market sectors. These are presented in the form of a proposal for what could become, at a later stage, a technical marketing publication aimed at setting the scene and generating interest from companies active in these sectors. Key performance drivers in the two sectors are highlighted, accompanied by end-use examples that illustrate the value in-use of CARILON polymers, in the perception of our customers.

The current proposal clearly positions CARILON polymer in the higher end of the ETP market. Feed-back and comments (preferably in written form) will be greatly appreciated. With regard to the end-use examples described, relevant permission from our partners will be necessary in an eventual publication stage. Actions from the relevant marketing representatives here will be welcomed. It should also be noted that any such publication is still subject to agreed internal Shell clearance procedures.

## 2 DRAFT PUBLICATION

# CARILON polymer:

# A novel, robust engineering thermoplastic brings unique opportunities.

- A. Wakker, Shell Research S.A., Louvain-la-Neuve -

## Introduction

Nowadays, the development of a completely new polymer from its early laboratory invention towards reliable, quality end-products is without any doubt a challenging mission. Not only is the polymer supplier faced with tremendous research and market development costs. Also, today's polymer market is a very competitive one and increasingly operates on a global basis. Grade ranges are steadily diversifying to better fit the needs of demanding customers. Consistent manufacturing of reliable, easy-to-process base polymer together with high-quality customer service are today's prerequisite to successful partnership between supplier, converter and end-user.

In the market for engineering thermoplastics (ETPs), whilst growing at a steady rate of some 6% per annum, no truly new polymers emerged during the last decade(s). The major part of the ETP market was (and still is) the domain of the traditional polymers: nylons (PA6,66), polyacetals (POM), thermoplastic polyesters (PET, PBT), polycarbonate (PC) and polyphenyleneoxide (PPO). The higher end of the market is covered by more advanced ETPs like nylons 11 and 12, polyphenylenesulfide (PPS), polysulfone (PSU) and fluoropolymers. Reflecting upon recent history of the ETP market, the eighties would perhaps today be best characterised as relatively over-ambitious: Many new materials were explored through blending of pure polymers and through compounding with advanced fillers such as carbon fibres and liquid crystalline polymers. However, out of the many new formulations developed, only the Noryl grade range (blends of polystyrene and PPO, also with nylon) has possibly found a significant position in the ETP market. In the early nineties, with the downturn in the economic cycle, increasing competition from high performance polypropylene compositions and continuously improving product designs, the ETP market experienced a shift towards more realism, with a focus on the more established polymers. This is where today's ETP market approximately is, with prospects for an economic upswing on the horizon.

Not surprisingly, a truly successful new polymer must bring novel and unique value to users. It should open-up new opportunities for applications, outperform competing polymers, replace traditional materials or bring cost-savings. CARILON polymer does so. After the invention [1] by Dr. Drent at the Koninklijke Shell Laboratorium Amsterdam (KSLA), and the relevant process- and market development work, Shell Chemicals is now preparing for the commercialisation of CARILON. Market development quantities are readily available and commercial quantities will become available during 1996. With its broad and unique balance of performance and processing characteristics, this new semi-crystalline engineering polymer is expected to serve a major part of the ETP market in the automotive, industrial, consumer and electrical and electronic (E&E) sectors. The relevant market development programme has shown that CARILON grades have a robust thermal-mechanical ETP performance level. In addition, they offer unique, novel opportunities and add new value to end-products. This enables CARILON to be used in the high performance end of the ETP market. The present paper highlights the key performance drivers of CARILON polymer, accompanied by illustrative examples of end-uses, in particular in the industrial and consumer market sectors.

## The polymer

CARILON polymer is the product of a new, innovative process of Shell Chemicals, in which mixtures of carbon monoxide, ethylene and propylene are converted into perfectly alternating carbon monoxide/olefin terpolymers in which propylene units randomly replace ethylene units along the chain (Figure 1). CARILON is a high-melting, aliphatic polyketone. Historically, the polymerisation of this alternating polyketone has been of considerable interest to both scientific and industrial circles [2], but none of the identified catalyst systems satisfied the economic requirements for use in an industrial process. The new Shell technology is based on the invention at KSLA of an efficient palladium catalyst system, enabling for the first time actual production of the perfectly alternating terpolymer in economically suitable quantities.

CARILON is a semi-crystalline engineering polymer with a melting point of 220°C. Its grade range is optimised for the processing of injection moulded articles. Extrusion, blow moulding of small articles (e.g. bottles), film blowing and rotational moulding are also possible. CARILON DP P1000 is the natural, medium flow base grade (Figure 2). DP R1000 is a special high flow grade for the production of e.g. thin-walled mouldings. DP R1130 is a 30% short glass fibre reinforced grade. Flame retardant grades DP R2000 and R2120 are under development. These are being optimised to serve the E&E sector with appropriate halogen - and red-phosphorous free flame retardancy whilst maintaining a useful balance of mechanical and electrical properties.

Typical properties of the CARILON polymer grade range are shown in Figure 3. The density of the neat polymers lies in between those of nylons (1.14 g/cm$^3$) and polyacetals (1.4 g/cm$^3$). CARILON polymers have similar strengths and heat distortion temperatures as many other ETPs, but the neat grades have significantly higher elongations at yield and at break. At ambient conditions, stiffness of the neat grades is similar to that of nylons, and lower than those of polyacetals and polycarbonate. The continuous use temperatures [*] of CARILON grades are 90°C for DP P1000 and 120°C for DP R1130, respectively. Application for food-approval is pending and is expected to be granted.

## Key features

Whilst CARILON polymers have a robust thermal-mechanical performance level similar to those of other ETPs, they offer a unique combination of advantages:

- Insensitivity to water.
- Outstanding chemical resistance and barrier performance.
- Superior resilience and snappability.
- Excellent (low temperature) impact performance.
- Superior tribological performance in polymer pairings.
- Shortest injection moulding cycles as well as highest quality mouldings.

[*] Continuous use temperature or relative temperature index: half-value of mechanical properties after 11.000 hours ageing.

## Exposure to water

Because of their molecular architecture, nylons 6 and 66, thermoplastic polyesters and, to a lesser extent, nylons 11, 12 and polyacetals are subject to hydrolyses: they degrade upon prolonged exposure to water. Although CARILON absorbs a small amount of water (similar to nylon 11,12), which causes a minor plasticising effect (Figure 4), it is not degraded by it. Figure 5 shows the big difference in the plasticising effect of water between CARILON DP P1000 and nylon 66. The glass transition temperature of nylon drops by more than 30°C upon conditioning. It is well known that such severe water absorbtion and plasticisation limits the thermal dimensional stability of nylons subject to varying ambient conditions. The glass transition temperature of CARILON polymer is 15°C, well below the range of normal use temperatures, and is only slightly affected by water absorbtion. Consequently, CARILON polymers show excellent thermal dimensional stability in end-products exposed to varying ambient conditions.

Together with their mechanical performance level, their insensitivity to water make CARILON polymers in particular suitable for structural components in industrial and domestic cold water systems (fittings, valves, pumps and meters), filtration units, ultra-clean water systems, pool-cleaning equipment, industrial cleaning machines and domestic washing machines.

Figure 6(A) shows an injection moulded top-plate of a cold water meter from CARILON DP R1130. In the relevant stringent life tests, its performance was tested vis a vis three advanced ETPs: long glass fibre reinforced nylon copolymer (PA66.6 LGF60); glass- and mineral filled polyphtalamide (PPA GF40 MF25) and glass filled PPS (PPS GF60). Top-plates should withstand 25 bar cyclic pressure shocks also after accelerated ageing in 90°C hot water. Before ageing, all materials met the required lifetime (i.e. a certain number of cycles before failure). Figure 7 shows that after the accelerated water exposure, the materials performed quite differently. Polyphtalamide was quickly degraded. Nylon copolymer could not meet the relevant life criteria after 90 days exposure to hot water. Only PPS and CARILON DP R1130 showed acceptable performance after 90 days, but CARILON was clearly the least sensitive to exposure to water. CARILON, whilst having the lowest glass fibre loading, was considered the most suitable material for this new, metal-replacing part. In addition, compared to PPS, injection moulding cycle times were 30% shorter and part production was much easier.

## Chemical resistance and barrier performance

CARILON polymers have a relatively high melting point, are semi-crystalline and have chemical building blocks dissimilar to many chemicals and solvents. Therefore, CARILON polymers in general have an outstanding chemical resistance [3]. They can be exposed to a wide variety of industrial, consumer and automotive chemicals with a minimal effect on mechanical properties.

Mechanical properties are hardly affected upon immersion in industrial chemicals such as hydrocarbon solvents, aromatics, halogenated hydrocarbons, weak acids and bases and salts. In selected applications, extruded CARILON DP P1000 was found to meet the performance level of fluoropolymers in chemical pipes carrying e.g. hot bromines and hot caustic slurries. DP P1000 was also found to be a useful PA 11 replacement for housings of industrial batteries: life criteria for exposure to (relatively strong) sodium hydroxide solutions, as well as the relevant low temperature impact tests, were all met.

CARILON polymers are also not affected by detergent chemicals and bleach. Figure 6(B) shows a gas-injection moulded household oven door-handle from CARILON DP R1130. Here, high quality mouldings combine good thermal dimensional stability with resistance to hot, fatty water vapours and to household cleaning products. CARILON fulfils all requirements and moulds with 25% shorter cycle time than a currently used PBT grade.

Table 1 shows the barrier performance of blow moulded CARILON DP P1000 film for a range of industrial chemicals compared to high density polyethylene film. The differences are remarkable, with permeability being decreased up to a factor of 1000. Here, CARILON polymer offers new opportunities for chemical containment, for example as an internal liner of plastic drums.

| Chemical | Permeability ratio HDPE/CARILON |
|---|---|
| Butylacetate | 200 |
| Trichloroethane | 250 |
| White spirit | 1000 |
| Xylene | 1000 |

**Table 1:** Permeability ratios for liquid chemicals of typical 50 micron films.

CARILON polymers are also well suited for use in contact with automotive fuels (also oxygenated fuel formulations), cooling liquids (antifreeze), lubricants, oil and salts. In addition, CARILON polymers are perfectly impermeable to automotive fuel and are being used in new prototype fuel transfer hoses. With forthcoming new environmental legislation, CARILON is also extremely well suited for (complete) automotive fuel systems, details of which will be published later.

## Resilience and snappability

Whilst CARILON DP P1000 has a tensile strength similar to other ETPs, Figure 8 shows that its elongation at yield is exceptionally large, namely 25%. Consequently, CARILON can be subjected to much larger deformations than other ETPs before irreversible deformation occurs. It is resilient and very suitable for snap fit assembly. This is also illustrated by test results shown in Figure 9. CARILON DP P1000 and nylon were subjected to 100 repetitive stress loadings of 36 MPa, about half of the corresponding yield stresses. Whilst CARILON deforms more easily under the load, it shows much smaller unloaded, semi-permanent deformation than nylon. After the 100 test cycles, while CARILON samples completely recover to their undeformed initial shape, nylon does not.

In Figure 6(C) a clip of a vacuum cleaner tube from CARILON DP P1000 is shown. Interestingly, a well-defined clamping force, not too small and not too large, is needed to fit the clip on the tube and to keep it in place during service. Such clamping force should not be sensitive to varying ambient conditions. In addition, the clip should be able to accommodate dimensional tolerances in the tube and should offer sufficient impact performance, also at sub zero temperatures. None of the traditional ETPs fulfilled the requirements. Only CARILON polymer and PA12 passed all tests, but CARILON offered a 50% injection moulding cycle time advantage.

Figure 6(D) shows a joining collar from CARILON DP P1000. It is snapped with its four clamping arms onto an electric valve, and the complete assembly is mounted inside a domestic gas meter. This plastic part should be resistant against contaminants in gas (i.e. water, heptane and toluene) and should pass the relevant drop tests. Polyacetal was used for this part but was performing only marginally because too often clamping arms showed brittle failure upon the drop tests. CARILON DP P1000 failed as well in these tests because valves were simply ejected from the clamping arms, the simple reason being that CARILON has lower stiffness than polyacetal for which the collar was originally designed. This problem could however be easily overcome by addition of a minor amount of filler, thereby increasing the stiffness of CARILON DP P1000 sufficiently whilst maintaining the required snapability and drop test performance. Compared to polyacetal, CARILON parts were moulded here with a 25% cycle time reduction.

## Impact performance

Excellent impact performance is beneficial for almost all end-use applications. In general, the relatively high stiffness of semi-crystalline engineering polymers comes with relatively poor and brittle impact behaviour. Compared to other semi-crystalline ETPs, CARILON polymer has the advantage that the carbon monoxide/olefin polymer chain has a relatively flexible architecture, enabling the amorphous polymer matrix to absorb more energy. Figure 10 shows that, in falling weight impact testing, CARILON DP P1000 shows 100% ductile failure, both at room temperature and at temperatures as low as -30°C, with high impact energies which are only slightly lower than those of polycarbonate. Nylons show sizeable fractions of brittle failures at -30°C. Polyacetals are intrinsically brittle, irrespective of temperature.

## Tribological properties

Friction and wear depends upon many variables, including geometry, temperature, clearance, mating surface finish, pressure and velocity. Table 2 gives typical pin-on-disc results of coefficient of friction and wear factor against steel for CARILON DP P1000, polyacetals and nylons. When paired against steel, the performance of CARILON is superior to that of nylons and inferior to that of polyacetals. However, in most end-use applications pairing against steel requires lubrication, because of the high mechanical loads often encountered in the friction zone. No differences in performance are seen if the right lubricants are used. Appropriate Shell lubricants for use with CARILON polymer have been identified.

| | Coefficient of friction | Wear factor, $10^{-15}$ $m^3/Nm$ |
|---|---|---|
| CARILON DP P1000 | 0.3 | 17 |
| Polyacetals | 0.15-0.2 | 5-10 |
| Nylon 6 or Nylon 66 | 0.5-0.6 | 40-50 |

**Table 2:** Friction and wear against steel, unlubricated pin-on-disk test (speed 0.1 m/s, pressure 1.5 MPa)

Figure 6(E) shows a CARILON DP P1000 household mixer gear wheel. It runs against a steel worm wheel in a non-parallel, lubricated assembly. CARILON passed the relevant life test at a given load provided the appropriate grease was used. Lubricated polyacetal gears fulfil the requirements as well, but gears injection moulded from CARILON offer in this case a 50% cycle time advantage.

Whilst (lubricated) polymer-steel pairing will be needed in relatively high load-bearing applications, polymer-polymer pairing will be the preferred option where noise reduction, costs and weight savings are important. Table 3 gives the pin-on-disc results of the relative wear factors in polymer-polymer pairing, both of like and unlike polymers. Of the possible arrangements tested, CARILON DP P1000 with polyacetals was the best, showing no wear after 20 hours testing. In the case of like pairings CARILON-CARILON was the best choice.

| | CARILON DP P1000 | Polyacetals | Nylon 6 or Nylon 66 |
|---|---|---|---|
| CARILON DP P1000 | - | 0 | - |
| Polyacetals | 0 | - - - | - |
| Nylon 6 or Nylon 66 | - | - | - - |

- : unit of wear

**Table 3:** Relative wear factors, unlubricated pin-on-disk test (speed 0.25 m/s, pressure 5 MPa)

Plastic tribological arrangements with CARILON not only have the least wear but also generate the lowest noise. Therefore, CARILON is very well suited for gears and bearings in photocopying machines, laser printers, plotters, industrial conveying units and goods handling systems.

Figure 6(F) shows a cylindrical gear wheel from CARILON DP P1000. The cylindric part of this gear fits in an other cylindric plastic bearing, which is part of a conveyor unit. In the relevant life test, the cylindrical plastic surfaces slide against each other at a given speed and under a heavy load. With gears from polyacetal, contact surfaces melt. With gears from nylon, contact surfaces heavily wear. CARILON polymer does neither of those and shows very long life.

## Processing

Thanks to a very rapid mould set-up, CARILON injection mouldings are without exception moulded with shorter cycle times than existing high performance engineering polymers. Parts are opaque and have glossy, marr resistant surfaces with a high degree of mould definition. CARILON polymers mould well on most injection moulding equipment. Harmful or unpleasant flue gasses are not generated. Typical mould shrinkage of unfilled CARILON grades is 2% and fairly isotropic, with little or no after-shrinkage. Warp-free mouldings are easily produced and conditioning is not needed [4].

## 3 CONCLUSIONS

On the basis of both primary properties and value in use assessments of specific applications CARILON polymers have an exciting future ahead. The unique combination of properties, in particular the water insensitivity, the chemical resistance and barrier performance, the resilience, the ductility, the tribological performance and the processing characteristics, means there are numerous profitable opportunities in the industrial and consumer market sectors.

Louvain-la-Neuve, August 1994.

## *References*


1. E. Drent, J.A.M. van Broekhoven and M.J. Doyle, *J.Organomet.Chem*, **417** (1991).

2. Encyclopedia of Polymer Science and Engineering (John Wiley, NY 1987), Vol. 10, 369.

3. CARILON polymer chemical resistance databrochure.

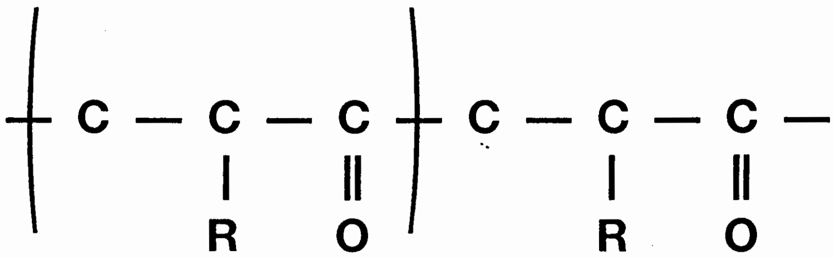
4. CARILON polymer injection moulding brochure.

**Figure 1:**
**Chemical structure of CARILON polymer**

## Chemical structure

Carilon
Polymer

**An aliphatic polyketone with a perfectly alternating aliphatic/carbon monoxide structure**



R = – H or – $CH_3$

Shell Chemicals

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LIB002 PR002

Figure 2:
CARILON grade range

## Product range

Carilon
Polymer

**CARILON polymer is a developmental product**

**The following development products (DP) can be made available:**

| | Unfilled | 30% GF | FR | FR/GF |
|---|---|---|---|---|
| Medium flow | DP P1000 | DP R1130 | — | DP R2120* |
| High flow | DP R1000 | — | DP R2000* | — |

*under development

Shell Chemicals


LIB007 PR007

Figure 3:
Typical properties of CARILON polymers

## Typical properties

Carilon
Polymer

| CARILON polymer DP grade reference | P1000 medium flow | R1000 high flow | R1130 30% GF |
|---|---|---|---|
| Melting temperature, °C | 220 | 220 | 220 |
| Density, g/cm³ | 1.24 | 1.24 | 1.45 |
| Melt flow rate (240°C/2.16kg), g/10 min. | 6 | 50 | 5 |
| Heat distortion temp. (1.82 MPa), °C | 90 | 90 | 215 |
| Tensile strength at yield, MPa | 60 | 60 | — |
| Elongation at yield, % | 25 | 20 | — |
| Tensile strength at break, MPa | 55 | 40 | 120 |
| Elongation at break, % | 350 | 350 | 3 |
| Flexural modulus, GPa | 1.4 | 1.4 | 7.0 |
| Notched Izod impact strength, kJ/m² | 15 | 8 | 8 |
| Mould shrinkage | ~2 | ~2 | ~0.3 (//)<br>~0.7 (⊥) |

Measured at 23°C, 50%RH, ISO standards

Shell Chemicals

**Figure 4:**
**Effect of water absorbtion**

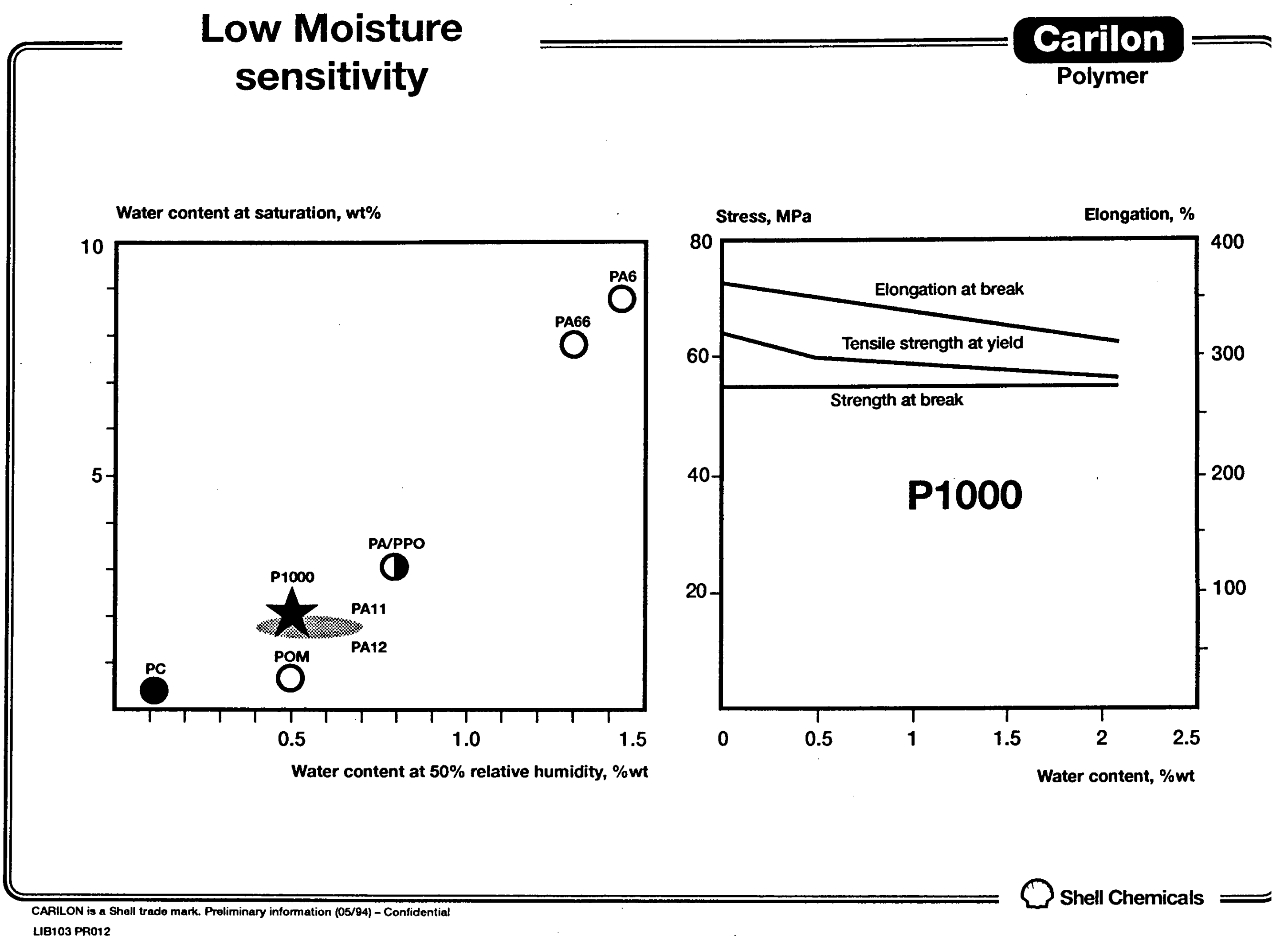


**Figure 5:**
**Influence of drying/conditioning on shear moduli of CARILON and nylon**

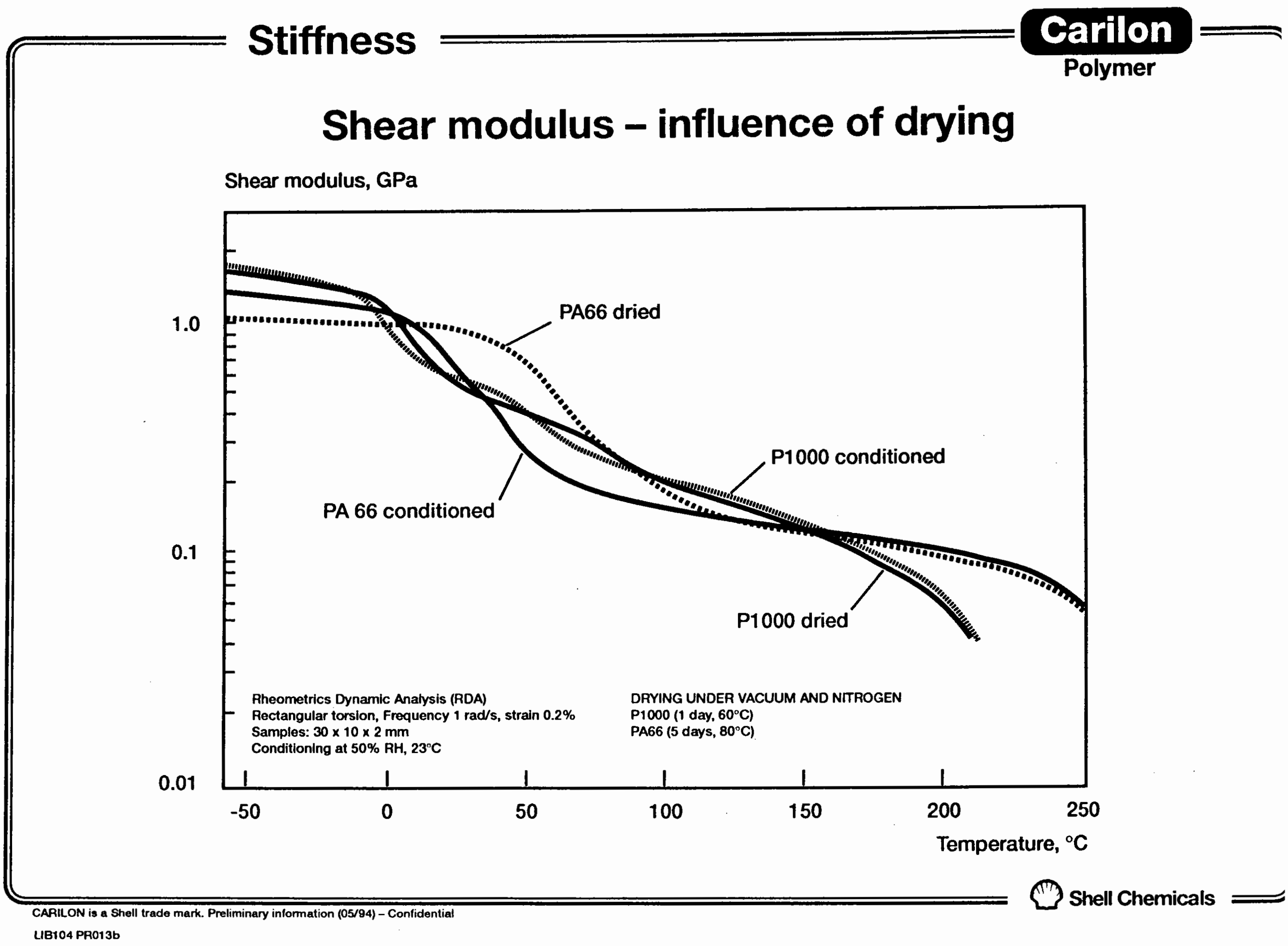


**Figure 6:**
**Injection mouldings from CARILON polymer**

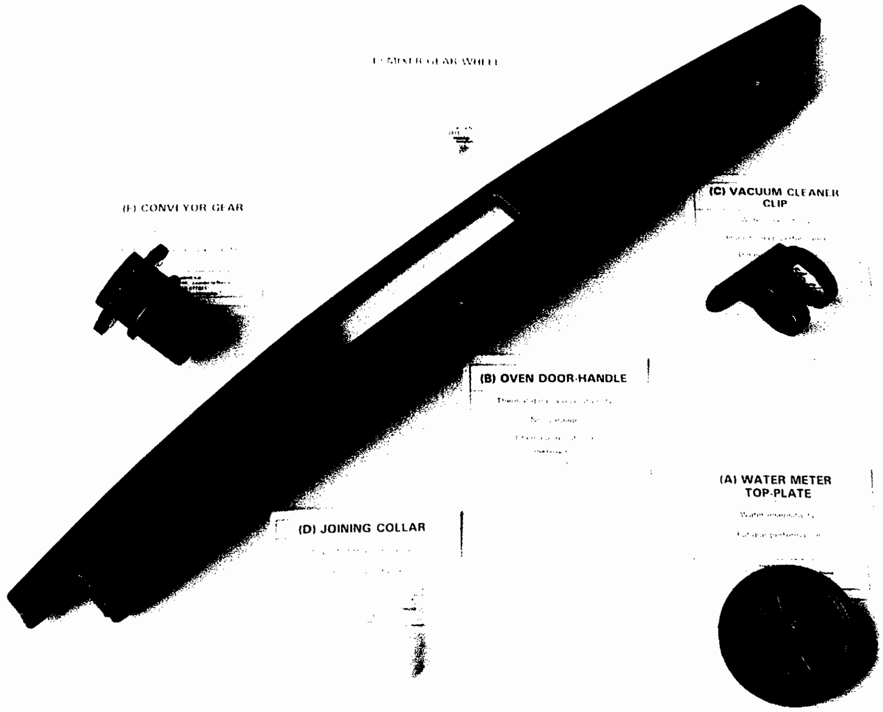


**Figure 7:**
**Life performance of water meter top-plates upon hot water ageing**

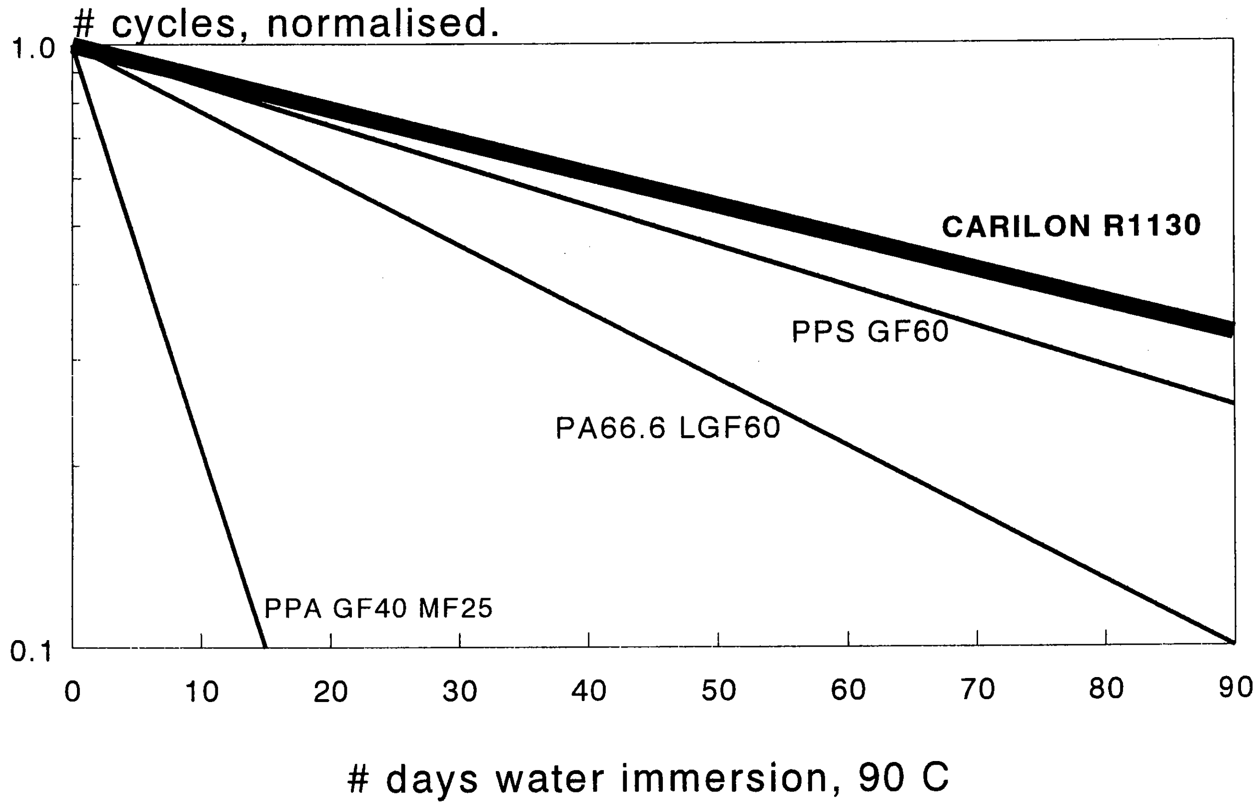
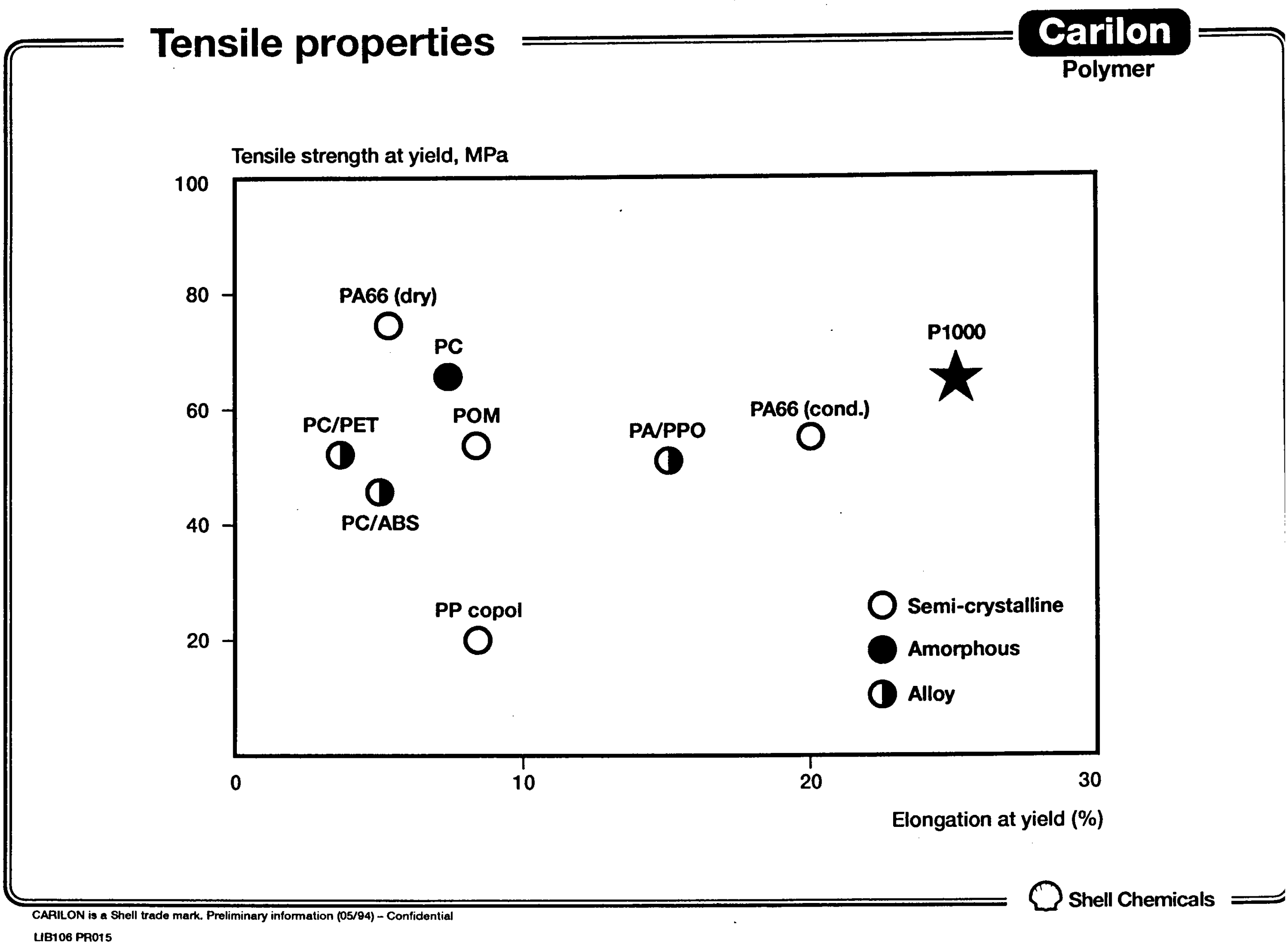
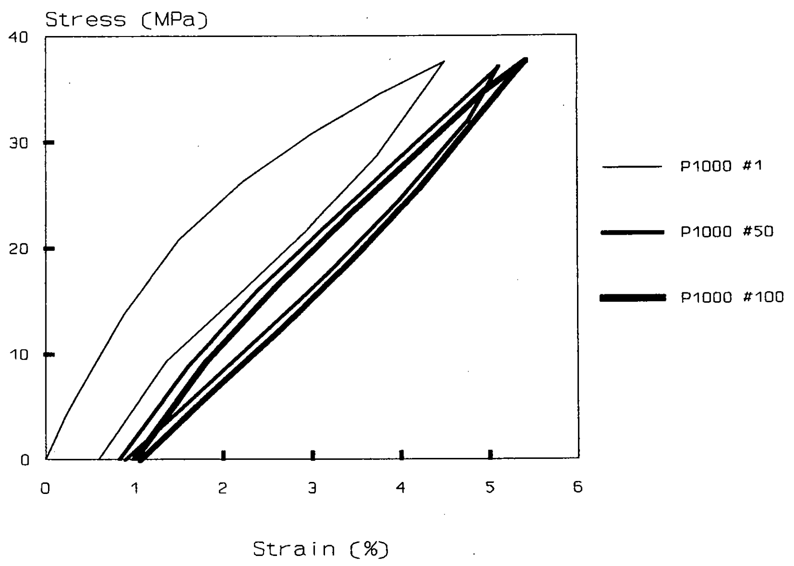


**Figure 8:**
**Tensile properties of CARILON and other ETPs**



## Figure 9:
## Cyclic stress loadings of CARILON and nylon tensile bars



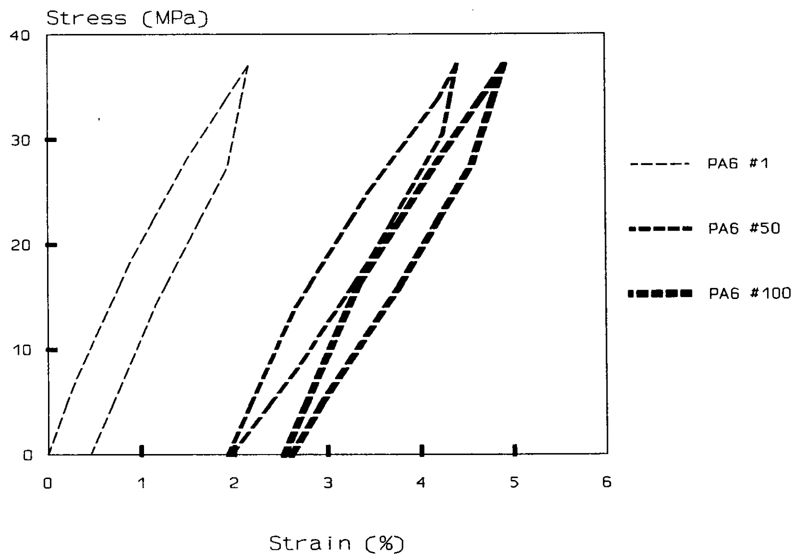
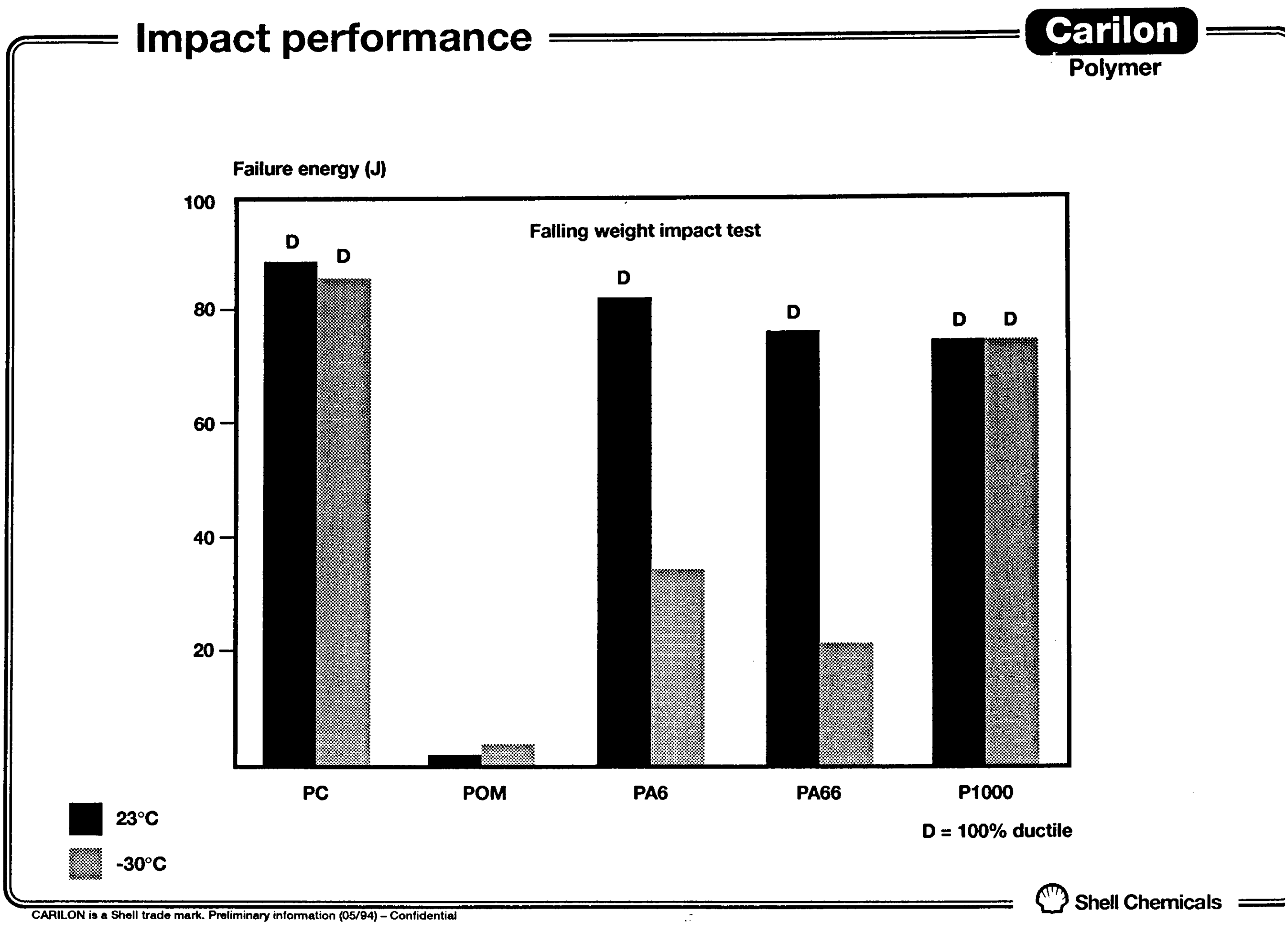



**Figure 10:**
**Impact performance of CARILON and other ETPs**

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LIB117 PR026

APPENDIX 1

# "Value" of CARILON polymers

| Primary Positioning | Value in Use |
|---|---|
| Material related. | Market sector specific. |
| Test sample related. | End-product related. |
| Standard test methods. | Sector specific testing. |
| RTI rating (UL). | Specific lifetime testing/modelling. |
| Material database | Application-specific database. |
| Material datasheets. | Sector-specific literature. |
| Material "image". | Market "image". |
| Bottom-line performance. | Down-scaling opportunities. |

## DISTRIBUTION

| | |
|---|---|
| **Central Offices, London** | |
| SIPC, ODLC/731 | 1 |
| SCEL, CBDC, CBDC/1 | 2 |
| SCEL, CBDC/2 | 6 |
| **Central Offices, The Hague** | |
| SICM, CMFS/223 | 5 |
| **Shell Research B.V.** | |
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