Shell Research
Louvain-la-Neuve

LVGR.95.191

Code 500.70.151 - PL5101
(Chemicals)

EVALUATION OF CARILON POLYMER P1000 AND R1000 BLENDED LOTS

by

P.Verbeke

LVGR.95.191

Code 500.70.151 - PL5101
(Chemicals)

EVALUATION OF CARILON POLYMER P1000 AND R1000 BLENDED LOTS

by

P.Verbeke

CONFIDENTIAL

LVGR.95.191

Code 500.70.151 - PL5101
(Chemicals)

EVALUATION OF CARILON POLYMER P1000 AND R1000 BLENDED LOTS

(January 1994 - October 1994)

by

P. Verbeke

Team members: K. Van Poppel
                A. Lacroix

Approved by: J.A. Verhave

SUMMARY

CARILON polymers are sampled to customers in the form of lots made up of batches physically blended together. Most of the recently produced lots were evaluated for a number of mechanical and rheological properties. Wherever possible the latest revisions of ISO test methods were used. From the limited data generated the best possible typical values for use in product literature were derived. A comparison of P1000 and R1000 properties showed indications of higher crystallinity in the lower molecular weight R1000 material.

October, 1995.

CONTENTS

EVALUATION OF CARILON POLYMER P1000 AND R1000 BLENDED LOTS

1   INTRODUCTION

The current.state of the CARILON polymer project requires the rapid build up of accurate product literature on a variety of subjects. Short introductory sheets and data sheets on several grades are already available. The data sheets for the base grades, P1000 and R1000, can already be considered out of date as manufacturing and marketing practices have changed drastically since their introduction. Also CARILON polymer testing practices at CRCSL are now in line with ISO testing standards, required by the industry.

Secondly a number of active development partners and regularly buying ones require information on product property variability. Thus far only a limited number of properties of batches produced at Moerdijk are being monitored. To date, no attempt to systematically characterise the variability of a full range of mechanical properties has been made. Therefore, an evaluation of all currently sampled P1000 and R1000 material was considered useful. Most of the data were generated according to the ISO/CAMPUS specifications, the test results may therefore also prove useful to fill a first CARILON polymers CAMPUS template.

2   MATERIALS

The marketing development unit in Moerdijk produces batches of approximately 1000 Kg of P1000 and approximately 800 Kg of R1000. Although the process control is reasonable, an inevitable batch variability exists. To make larger quantities of polymer with homogeneous properties available, physical blending of batches is used. The selection process for blending of batches into one lot is based on a carefully designed specification including nib properties, molecular weight, melt stability and impact behaviour. The lots are then dried, physically blended and bagged in aluminum lined bags to prevent moisture pick up.

Four P1000 lots were evaluated viz. lot 21, 22, 30 and 33. The materials were produced in the period '92 - '94. R1000 materials, including lot 20, 28 and 32, were produced more recently ('93 - '94). The materials were taken straight from unopened bags and not preconditioned before use.

3   METHODS

Samples were moulded on a Netstal HP1200 machine equiped with a CAMPUS-ISO mould. Typical moulding conditions for both grades are shown in Table 2.

All tests were performed, after a three day conditioning period at 23°C and 50% R.H., according to the relevant ISO standards. Specific description can be found elsewhere[1]. Less frequently employed methods are described below.

The falling weight impact energy was measured on a Rosand instrumented impact tester. A full description of the device and the test method can be found elsewhere[2]. Test results are reported as the median and interquartile distance. It is felt that these non-parametric quantities characterise the distribution of the impact energy better than a simple average[3].

Density measurements were performed using an Accupic gas displacement apparatus. Measurements were repeated three times, final accuracy is better than 0.001 g/cm^3. DSC measurements were done according to draft SMS method 2816.
Flow curves of both R and P1000 materials have been measured on a Rosand twin barrel capillary rheometer. The test method used was reported earlier[4].

The stability data were gathered on the same apparatus, a report describing the method is in preparation[5].

4   RESULTS

Some characteristics of the lots tested are shown in Table 1. Mechanical properties can be found in Tables 3 and 4, standard deviations of mechanical tests are presented in Table 5. Two measures of crystallinity: heat of fusion and density can be found in Table 8. Typical flow behaviour of P and R1000 as a function of shear rate is presented in Figure 4 and Table 9. Also a measure of polymer melt stability is presented in Figure 5 and Table 11.

The standard deviations for mechanical properties were calculated using data for lots 22-33 (Tables 3 and 4). Lots 19 to 21 were excluded from calculations because of the historical nature of the data. Their properties were measured piecemeal over a long period of time, moulding and conditioning of samples was, sometimes intentionally, different. Variability for falling weight impact is not given as this property is not distributed normally.

A priori one can not assume that the standard deviation of a mechanical property is equal for P1000 and R1000. However no differences could be found when comparing the standard deviations calculated separately for P1000 and R1000 properties. Hence an averaged standard deviation for R1000 and P1000 results is shown in Table 5.

The standard deviations provide an estimate of the spread in generated test data if a new lot were moulded using similar conditions as stated in Table 2 and tested according to the described test methods. As such they can be used in establishing significant differences between lots. If differences are found however, it is not possible to attribute this to manufacturing, moulding or testing separately! Table 5 simply offers a general description of the variability of the testing process.

Lately ISO/527 used for tensile testing was revised. The test method now includes a well defined method to establish the value of the modulus. In earlier revisions a choice of methods was presented to the user. CRCSL, after some initial testing, has always adopted the chord modulus between 0.2 and 0.3% strain. The current method requires the determination of the chord modulus between 0.05 and 0.25%. Data for three lots has been reanalysed using the test protocol as defined in the new revision. A comparison between old and new data is shown in Table 7. From this data and taking into account a standard deviation of 0.05 GPa (Table 5) no differences between both test methods can be found. Although the new revision will be used in future, comparisons with old CRCSL data can be made without problems.

Similar to the Tensile test method also the ISO HDT method was revised. Currently very little comparative data is available. First indications are that slightly lower HDT values will be found for similar product. This is not unreasonable, because the latest revision lowers the necessary deformation with the samples used from 0.33 mm to 0.32 mm. However some further testing will be necessary.

5   DISCUSSION

5.1   Variability in Mechanical Properties

Comparing data, especially on physical properties, can be a daunting task. This however can be simplified considerably by using the correct statistical tool. In the present work we want to compare average properties with an associated estimate of the standard deviation. This is most appropriately done using a standard students t-test[6], implying that results from tested properties are assumed to be normally distributed.

Additionally we assume that the standard deviation of different lots is equal, in line with results reported in Table 5. The result of a two sided t-test at the five percent level is shown in the last column of Table 5. Here we chose to represent the maximum not significant absolute value of a difference of two means at the five percent level. This means that when comparing two means with a difference in value larger than the number noted in the last column of table five, the difference can be considered significant.

When comparing P1000 lots it becomes apparent that each property shows variations larger than the testing variability i.e. when testing the largest differences these appear to be significant. Possibly the water content of samples could have an influence. It has already been established[7] previously that the glass transition temperature and hence the stiffness can shift due to the water content. Assuming however that this is not the case, for which the R1000 data described below offer some indirect evidence, one can conclude that the current pick and choose strategy does not lead to a "zero" variability product. In itself this result is not necessarily negative, in that the product variations must be confronted with customer reactions. To date, and based on limited experience in the market place, there has not been a single case were product variability has lead to a customer reaction.

For R1000, where only two lots can be compared, none of the properties show a significant difference. It is however far to early to conclude that R1000 is less variable than P1000 product.

5.2   Comparison of P1000 and R1000 Product

For the comparison of P1000 and R1000 product the typical data from Table 6 were used as representing "the best possible" at this point in time. Typical properties for P1000 and R1000 product were calculated by averaging lot 22-33 data from Tables 3 and 4.

Differences between properties of P1000 and R1000 are theoretically all linked with the difference in molecular weight. It is not unreasonable, for example, to expect a slightly higher crystallinity in the lower molecular weight R1000 CARILON polymer. The significance of the difference have again been tested with a t-test as described in section 5.1. The significance of P1000 - R1000 differences is noted as a y(es) or n(o) in the last column of Table 6. As can be seen all mechanical properties were judged significantly different at the five percent level.

The tensile stress and strain at yield indicate that R1000 is the stiffer material. Typically P1000 shows a four MPa lower strength, but a two percent higher strain at yield. Surprisingly enough the tensile modulus of P1000 is higher than that of R1000. A comparison of the tensile stress-strain curves (Figure 1) reveals a rather peculiar fact. Over most of the deformation range R1000 shows consistently higher stresses than P1000, however in the first percent of strain this situation is reversed. The ISO standard prescribes a number of ways to determine the modulus however all methods are based on low deformation (<1%) data. Consequently higher moduli are measured for P1000 material. Currently we can offer no explanation for this behaviour. This phenomenon, although not documented in this work, seems quite repeatable over different lots.

The flexural modulus of P and R1000 product on the other hand is quite similar. Stress-strain curves (Figure 2) show again that P1000 and R1000 are similar in behaviour for the first percent of deformation, but higher stresses can be noted for R1000 material in the rest of the deformation domain. Further substantiation of a higher stiffness of the R1000 material is offered by the shear modulus - temperature curves (Figure 3). Here R1000 shows a higher stiffness than P1000 over the whole temperature domain.

Although there is only a small difference between heat distortion temperatures (HDT) for P and R1000 and the HDT values show considerable spread, it is clear that R1000 shows a slightly higher HDT. This is consistent with the shear modulus results. Recently a relation between vicat temperature and shear modulus measurements was established[8]. The authors argued that the vicat temperature was simply the temperature at which the material reached a particular modulus. Similarly one could argue that the HDT is a test to determine the temperature at which the material reaches a certain modulus. Assuming simple elastic behaviour, the deformation will only reach the preset maximum at a particular value of the modulus. From the data represented in Figure 3 a ten degree difference in HDT for P and R1000 can be roughly estimated. The latter value corresponds well with the six degree difference in Table 6.

The difference in falling weight and izod impact energy of P1000 and R1000 product can easily be correlated to the lower molecular weight of the latter. Usually the influence of the molecular weight is explained in terms of the average number of entanglements per polymer chain. The more entanglements the higher the resistance to rupture. The latter is only true up to a critical average molecular weight.

5.3   CARILON Polymer Crystallinity

The differences between P and R1000 product presented in the previous section indicate quite clearly that the level of crystallinity in R1000 material is higher. It therefore seems quite useful to study this phenomenon in a more detailed way.

Semi-crystalline polymers show three distinct morphological regions: a crystalline or spherulitic zone, an interfacial zone and an amorphous zone. The crystalline zone is characterised by nicely ordered polymer chains, whereas no ordering is present in the amorphous zone. The interfacial zone shows some degree of ordering as it is made up of polymer chain segments extending from spherulites. Crystallinity is usually determined indirectly by density measurements, enthalpy of fusion or spectroscopic techniques (i.e. Raman). Only one direct method to establish polymer crystallinity exists: X-ray diffraction. Unfortunately the latter is quite tedious and difficult to calibrate. The indirect methods show another disadvantage: typically the relative influence of the morphological regions is different for each technique. As a consequence small differences between results have been found.

In the present work CARILON polymer crystallinity has been determined using heat of fusion and density (Table 8). It is quite clear that P1000 shows a lower heat of fusion than R1000. Density measurements on the other hand show very similar results for both grades. This type of inconsistency has been interpreted in terms of the influence of the interfacial zone[9]. The heat of fusion is generally accepted as a pure measurement of crystallinity[9], whereas the ordering in the interfacial zone also influences the density of the bulk polymer. Following this line of thought it seems therefore that R1000 has a somewhat higher crystallinity and P1000 a higher fraction of interfacial material. Assuming a similar average spherulite size for both grades, the results suggest a CARILON polymer chain can only make a limited number of folds to form crystalline matter. With P1000 having the longer average chain length, this would result in longer segments extending from the spherulites and hence a more pronounced interfacial zone. Although the above is presently a theory supported by a limited amount of evidence, it may be important to pursue a more detailed study of CARILON polymer morphology. The interfacial zone could play an important role in physical ageing: i.e. higher ordering with time or other long term properties.

5.4   P1000 and R1000 Shear Rheology

For use in processing problems the flow behaviour of P1000 and R1000 material are also included (Table 9, Figure 4). Using an Ellis model (Equation 1) the flow behaviour as a function of temperature was fitted.

$$\eta = \frac{\eta_0 e^{\left(\frac{Ea}{RT}\right)}}{\left(1 + \left(\sigma/\sigma_{\frac{1}{2}}\right)^{\left(\frac{1}{n}-1\right)}\right)} \tag{1}$$

Non linear least squares were used to fit the data in Table 9 to equation 1. Model parameters and some relevant statistics are noted in Table 10. A detailed discussion of CARILON rheology can be found in reference 4. The activation energy of flow is the parameter of interest here. The latter has been reported to be quite low and slightly different for P1000 and R1000. This is not confirmed by the data in Table 10. For comparison flow activation energy of P1000 and R1000 was reported as 17 and 30 kJ/mole respectively[4]. Current product shows a similar activation energy both for P and R1000 product of about 30kJ/mole. This is also supported by recent work at WTC, where 25 kJ/mole was reported for both grades[10]. No solid explanation for the difference with the previously reported data can be offered. Most probably improved stability allowed a more accurate measurement of the temperature dependence of flow.

Also for use in practical processing work, some stability data is noted in Table 11. Interpretation is straightforward, leaving CARILON material in the melt for ten minutes at the respective temperatures will increase the viscosity, due to cross linking. Current indications are that a viscosity rise as small as twenty percent can affect mechanical properties, especially impact behaviour at low temperature.

6   CONCLUSIONS

- A comprehensive overview of mechanical and rheological properties of CARILON polymer P1000 and R1000 is presented. Based on all available commercial lots variations in all the mechanical properties could be noted.

- The data presented can currently be considered the best possible on sampled P1000 and R1000 product. Use of the typical properties (Table 6) in the product literature, confidential presentation and open literature publications is therefore recommended.

- Consistent small differences in mechanical properties of P and R1000 product indicate a higher crystallinity level for the lower molecular weight R1000 material. This was confirmed with indirect measures of crystallinity. A theory attributing an (important) role to the interfacial zone was proposed.

- Flow rheology of current product was shown to be consistent with older '92 materials. Especially the low activation energy for flow was confirmed. As a result of this, increasing the temperature considerably for enhanced flow is still counter indicated, and this not only for reasons of stability!

7   FURTHER WORK

Although all properties were measured according to the latest revisions of the ISO standards, the moulding conditions and the pre test conditioning could still be a possible source of variation in the results. This is clearly an area were further work is required and essential for entrance into the Campus system.

Some fundamental work in the area of polymer crystallinity and morphology is required for a better understanding of the differences in properties between P1000 and R1000. Notably this understanding could lead to new product development.

Louvain-la-Neuve, October, 1995.

References

1.   A. Lacroix, LVGR in preparation

2.   A. Wakker, P. Verbeke, T. Schoolenberg, "The falling weight impact strength of CARILON EP polymer", LVGR.92.074

3.   P. Verbeke, "Impact strength of CARILON EP polymers", LVRS.92.05

4.   J. De Clippeleir, P. Verbeke,"Rheological characterisation of CARILON polymers: Rheotens and capillary rheology", LVGR.93.029

5.   P. Verbeke, LVGR in preparation

6.   C. Bennett, N. Franklin, "Statistical analysis in chemistry and the chemical industry", Wiley, New York, p. 153

7.   A. Lacroix, A. Wakker, "The shear modulus of CARILON EP polymer and competing engineering thermoplastics", LVGR.93.128

8.   S.P. Namhata, L. Santolini, G. Locati, Polymer testing 12(1993) 75

9.   L. Mandelkern, A.J. Peacock, Stud. in phys. and theor. Chem., 54(1988),201-227

10   J.M. Machado, M. Londa, A. Verbeke, W.P. Gergen, ANTEC 95, p. 2335

Lot	Official designation	Nr of batches blended	Date available	COT (min)
19	27-P1000-1000 lot 11PMA0019	13	nov 92	27
20	27-R1000-1000 lot 11PMA0020	15	nov 92	75
21	27-P1000-1000 lot 01QMA0021	6	march 93	23
22	27-P1000-1000 lot 02QMA0022	7	march 93	39
28	27-R1000-1000 lot 08QMA0028	9	sept 93	79
30	27-P1000-1000 lot 10QMA0030	20	jan 94	27
32	27-R1000-1000 lot 02RMA0032	36	feb 94	94
33	27-P1000-1000 lot 06RMA0033	30	june 94	50

Table 1: Characteristics of lots

Barrel temperature,	°C	240
		250
		250
Nozzle temperature,	°C	250
Mould temperature,	°C	80
Injection speed, mm/min		15

	Holding pressure (bar)	Holding time (sec)	Cooling time (sec)	Cycle time (sec)
Flex bar/ HDT bar	470	15	10	32
Tensile bar	700	15	15	34
FWIS plate	500	7	7	20
Izod bar	520	14	10	29

Table 2a: Typical R1000 moulding conditions

Barrel temperature,	°C	240
		250
		250
Nozzle temperature,	°C	250
Mould temperature,	°C	80
Injection speed, mm/min		20

	Holding pressure (bar)	Holding time (sec)	Cooling time (sec)	Cycle time (sec)
Flex bar/ HDT bar	694	10	10	27
Tensile bar	847	10	10	24
FWIS plate	723	9	7	22
Izod bar	675	11	10	26

Table 2b: Typical P1000 moulding conditions

Property		Lot 33	Lot 30	Lot 22	Lot 21	Lot 19
TENSILE						
Stress @ yield,	MPa	57	61	59	60	-
Strain @ yield,	%	23	24	22	23	-
Modulus,	GPa	1.47	1.52	1.37	1.39	-
FLEXURAL						
Flexural strength at 3.5%,	MPa	40.5	41.4	38.8	40.5	-
Modulus,	GPa	1.49	1.60	1.45	1.46	-
FWIS 23°C						
Median,	J	61	48	37	70	69
IQR (75 -25 percentile),	J	24	32	23	4	17
# samples ductile		17	18	15	20	20
# samples nippy		3	0	5	0	0
# samples brittle		0	2	0	0	0
FWIS -30°C						
Median,	J	27	62	40	57	79
IQR (75 -25 percentile),	J	52	51	60	56	38
# samples ductile		5	9	6	7	13
# samples nippy		5	4	5	4	3
# samples brittle		10	7	9	9	4
NOTCHED IZOD						
Impact energy @ 23°C,	kJ/m²	21	20	18	20	21
Heat deflection temp.,	°C	87	93	100	92	-

Table 3: Mechanical properties of P1000 lots

Property		Lot 32	Lot 28	Lot 20
TENSILE				
Stress @ yield,	MPa	63	63	61
Strain @ yield,	%	21	21	20
Modulus,	GPa	1.31	1.31	1.49
FLEXURAL				
Flexural strength at 3.5%,	MPa	43.6	44.1	-
Modulus,	GPa	1.53	1.55	-
FWIS 23°C				
Median,	J	30	34	-
IQR (75 -25 percentile),	J	13	19	-
# samples ductile		8	14	-
# samples nippy		4	3	-
# samples brittle		8	3	-
NOTCHED IZOD				
Impact energy @ 23°C,	kJ/m²	-	-	11.3
Heat deflection temp.,	°C	101	97	-

Table 4: Mechanical properties of R1000 lots

- : Not determined

Property		Test Method	Number of samples	Standard deviation	Maximum allowable difference at the 5% level
TENSILE		ISO 527/R	5		
Stress @ yield,	MPa			0.25	0.37
Strain @ yield,	%			0.6	0.9
Modulus,	GPa			0.05	0.07
FLEXURAL		ISO 178	5		
Flexural strength at 3.5%,	MPa			0.3	0.4
Modulus,	GPa			0.01	0.015
FWIS 23°C		-	20	-	-
NOTCHED IZOD		ISO 180/1A	12		
Impact energy @ 23°C,	kJ/m^2			0.4	0.34
Heat deflection temp.,	°C	ISO 75/A	3	3	6.8

Table 5: Test method specifications and experimental error

Property		P1000	R1000	Difference significant at the 5% level
TENSILE				
Stress @ yield,	MPa	59	63	y
Strain @ yield,	%	23	21	y
Modulus,	GPa	1.45	1.31	y
FLEXURAL				
Flexural strength at 3.5%,	MPa	40	44	y
Modulus,	GPa	1.50	1.54	y
NOTCHED IZOD				
Impact energy @ 23°C,	kJ/m^2	20	11	y
Heat deflection temp.,	°C	93	99	y

Table 6: Typical properties for P1000 and R1000 product

Lot	Old modulus	New modulus
28	1.31	1.33
32	1.31	1.33
30	1.52	1.53

Table 7: Comparison of revision 1966 and 1-1993 ISO/527 tensile modulus

Lot	Heat of fusion (J/g)	Density (g/cm^3)
P1000/30	84.5	1.245
P1000/33	83.5	1.245
R1000/28	91.1	1.244
R1000/32	90.6	1.242

Table 8: Indirect measures of CARILON EP crystallinity

Shear rate (s^{-1})	viscosity at 240°C (Pa.s)	Shear rate (s^{-1})	viscosity at 260°C (Pa.s)	Shear rate (s^{-1})	viscosity at 280°C (Pa.s)
14.98	1510	68.05	799	291.4	401.6
21.16	1418	94.16	740.8	418.7	345.6
29.93	1278	135.5	653.9	603.1	285.8
46.88	1104	195.2	575.6	869.2	240.6
66.81	995.4	282.4	500.6	1255	196.7
94.80	879.5	408.8	417.6	1815	159.4
134.5	772.4	594	340.5	2630	126
66.96	993.1	865.2	274.7	3818	99.23
96.18	888.9	999	219.1	5559	76.76
138.6	762.3	1266	172.6	8090	59.17
199.8	646.9	1860	134.3	11891	44.62
289.3	548.8	2749	101.5		
419.2	454.4	4092	75.6		
609.8	366.9	6151	55.03		
889.5	300.0	9322	38.99		
1303	237.1	14470			
1918	183.1				
2840	139.7				
4236	105.6				
6381	77.42				

Table 9a: Flow behaviour as a function of temperature of P1000/Lot 30

Shear rate (s^{-1})	viscosity at 240°C (Pa.s)	Shear rate (s^{-1})	viscosity at 260°C (Pa.s)	Shear rate (s^{-1})	viscosity at 280°C (Pa.s)
1052	72.73	11425	24.53	580.9	60.14
588.6	82.35	6542	32.33	323.9	63.46
329.4	91.05	3598	42.16	180.6	64.48
184.4	97.09	1983	52.26	56.28	68.83
103.2	102.8	605.9	67.77	31.43	70.5
32.37	117.1	1921	51.97	17.55	68.58
18.13	125.9	1062	60.48	612.2	62.66
1074	71.04	588.5	69.11	1104	51.18
1977	60.32	326.3	75.44	1993	42.85
3669	45.69	181.2	77.76	3605	35.01
12498	24.61	100.7	82.05	6527	27.57
		56.02	85.08	11348	21.54

Table 9b: Flow behaviour as a function of temperature of R1000/Lot 28

15

Parameter		P1000	R1000
Ea	(kJ/mole)	29	28
η_0	(Pa.s)	1269	90
$\sigma_{1/2}$	(MPa)	94	120
n		0.41	0.48
asymptotic R^2		0.99	0.98

Table 10: Ellis model parameters for P and R1000 melts (See Equation 1)

Temperature (°C)	P1000/ Lot 30	R1000/ Lot 32
240	1.10	1.01
260	1.22	1.08
280	1.35	1.27

Table 11: Typical stability behaviour (Viscosity increase after 10 min)
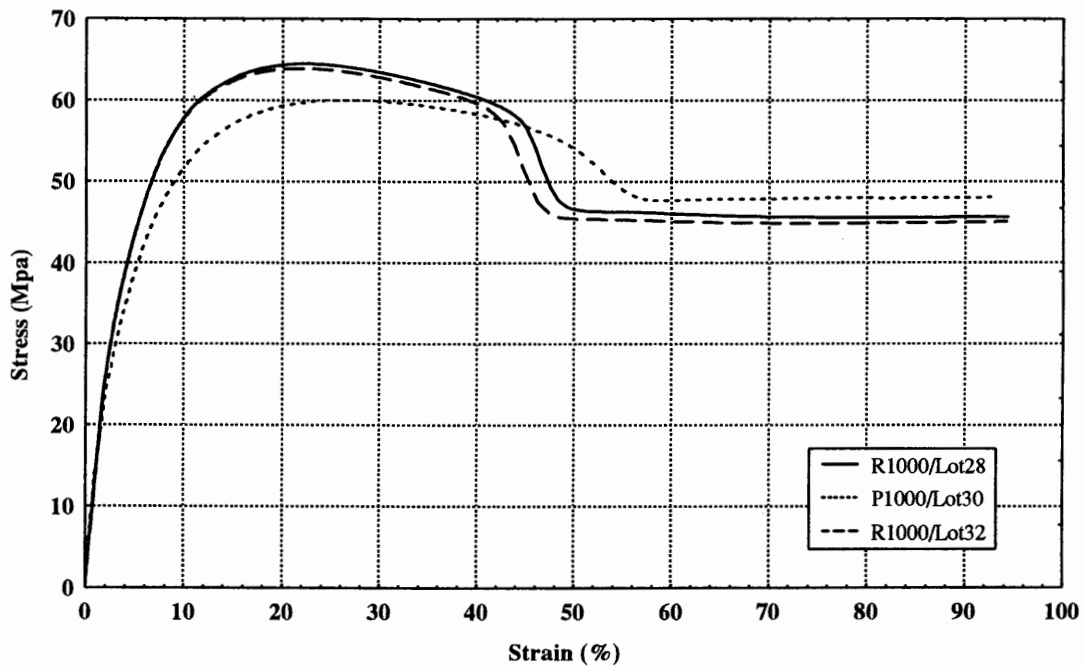
Figure 1: Typical tensile behaviour
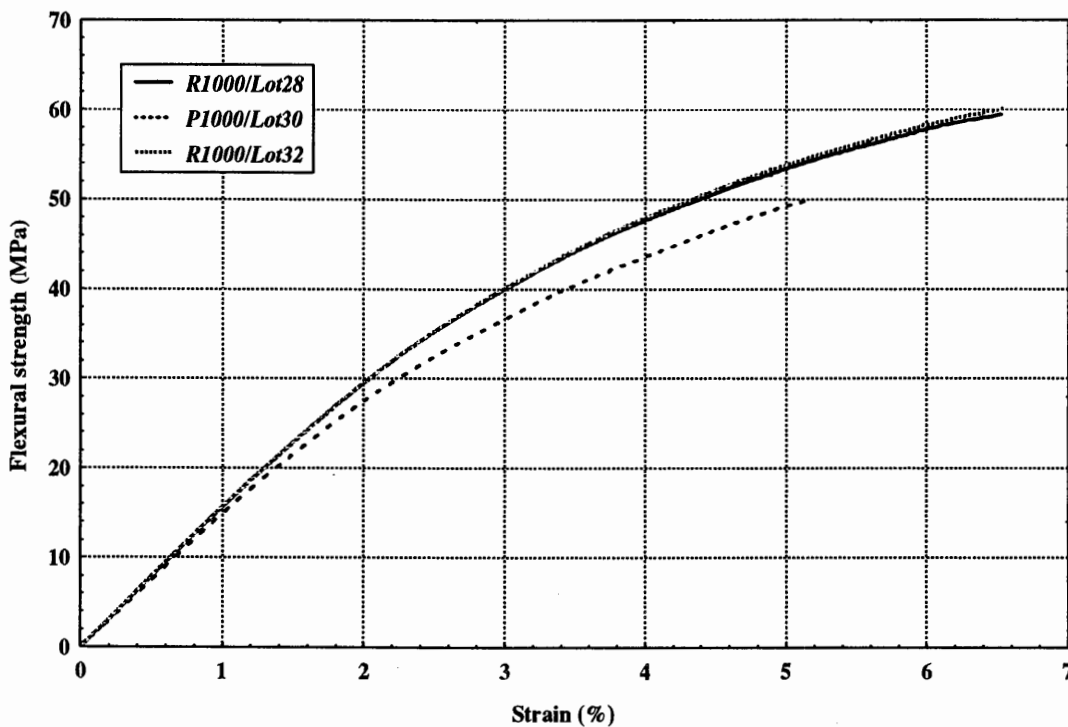
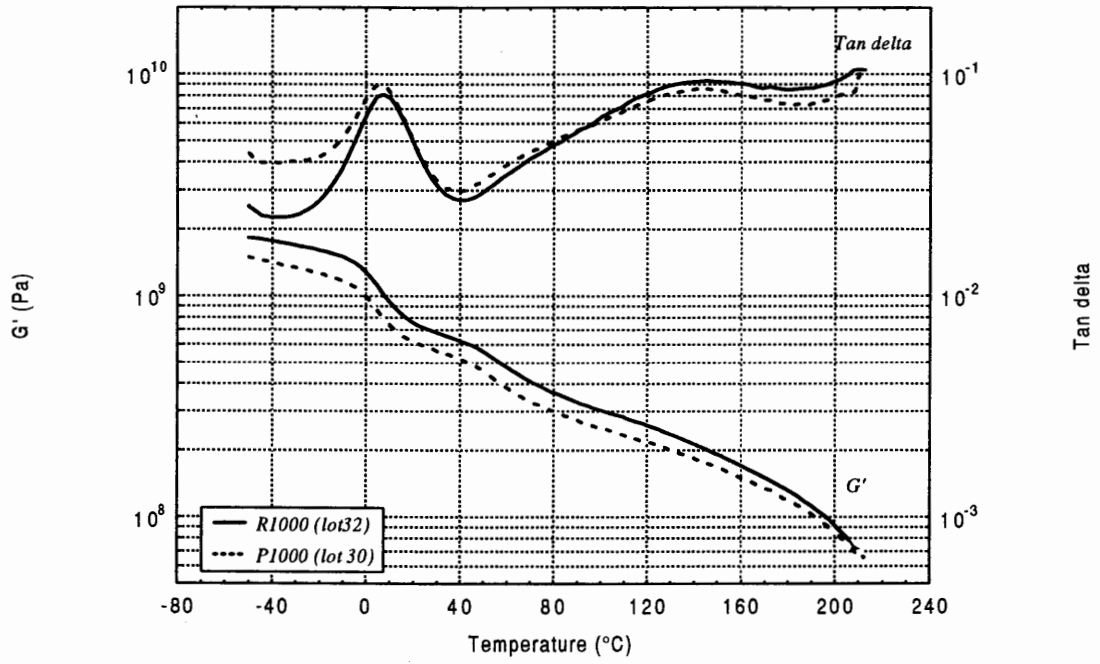
Figure 2: Typical flexural behaviour

Figure 3: Typical shear modulus as a function of temperature
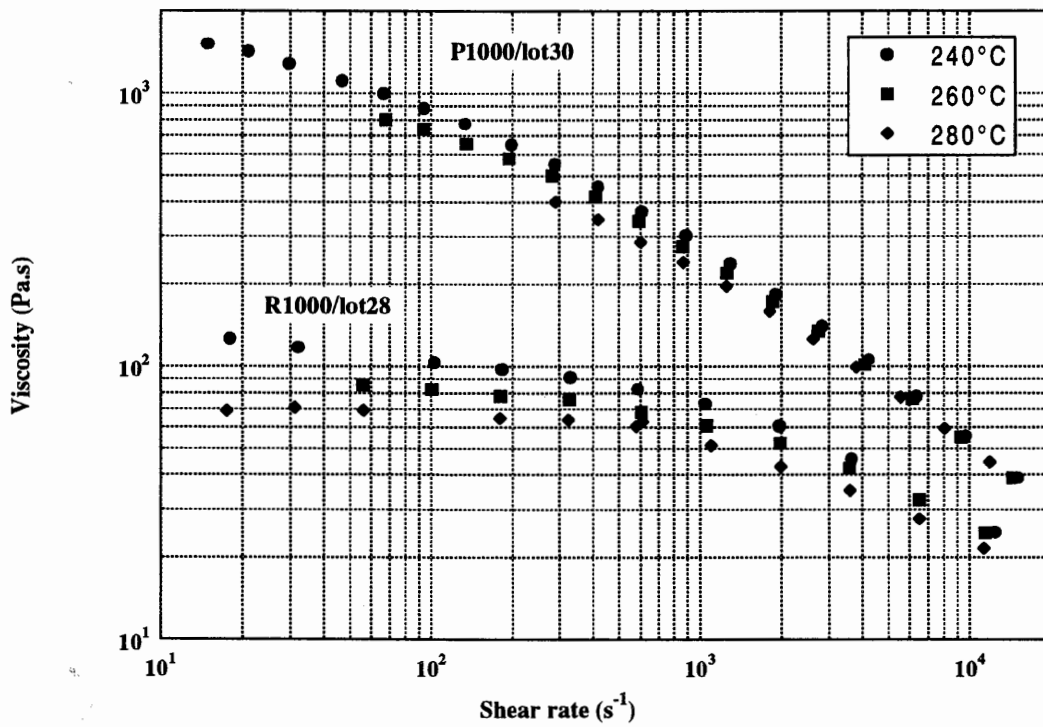

Figure 4: Typical flow behaviour

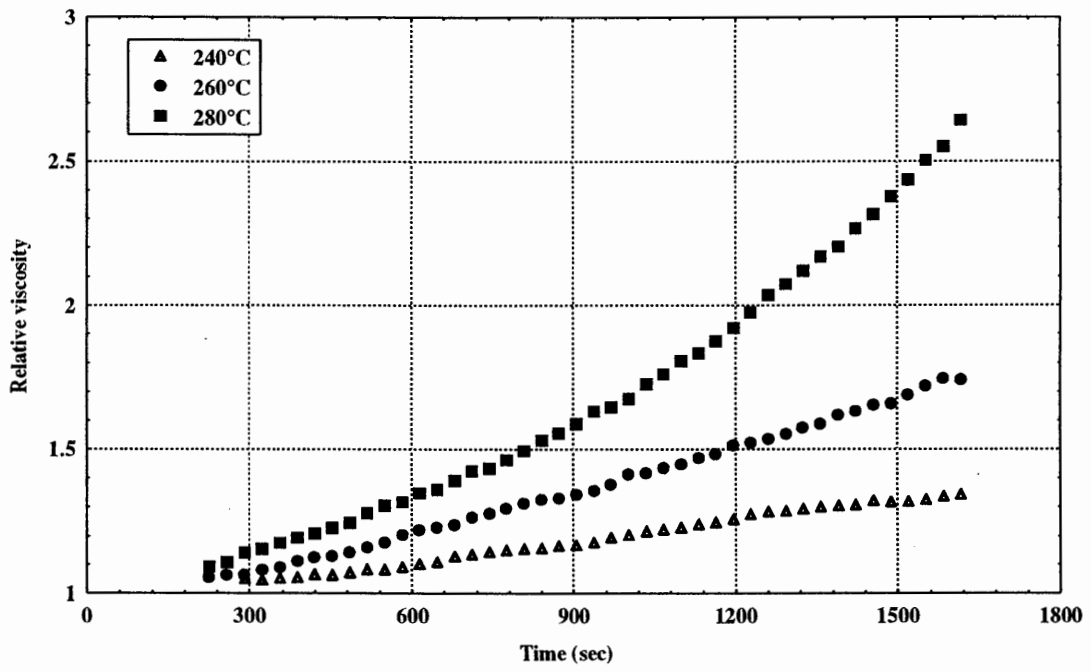**Figure 5:** Lot 30 viscosity increase as a function of time and temperature

DISTRIBUTION

Central Offices, London

SICL, CBDC	1
SICL, CBDC/1	1
SICL, CBDC/2	1
SIOPL, ODLC/731	1

Central Offices, The Hague

SICH, CMFS/223	5

Shell Research BV

KSLA, ICS/1	3

Shell Research S.A.

CRCSL, GAI	5

Shell Nederland Chemie B.V.

Pernis, FKD/61	2
Klundert, NMT/3	1

Shell Development Company

WTC	6