CENTRAAL LABORATORIUM T.N.O.

Rapport

Mechanical properties of
highly filled elastomers II

Appendices

TNO

Julianalaan 134 - Delft - Telefoon 20130*

Nijverheidsorganisatie T.N.O.

CENTRAL LABORATORY T.N.O.
DELFT
(The Netherlands)

MECHANICAL PROPERTIES OF HIGHLY FILLED ELASTOMERS II

Influence of particle size and content of filler on tensile properties and shear moduli.

APPENDICES

Office of Naval Research
Contracts N 62558-2822 and N 62558-3243
Technical Report No. 2
April, 1963

APPENDIX A CORRELATION BETWEEN DENSITY AND COMPOSITION

Table A 1 Composition, density and volume content of the filled urethane rubbers prepared

sample no.	weight		density d_4^{20}	filler content in per cent. by vol.			particle size NaCl
	rubber component (g)	filler component (g)	(g/cm^3)	as calculated from weight ratios of components *)	as calculated from correlation with density **)	as given in Table 2	μ
41	-	0	1.0724	-	-	0	-
43	344	740	1.6237	50.2	50.3	50	300 - 480
44	324	700	1.6365	51.7	51.5	52	"
47	406	580	1.5274	41.4	41.5	42	"
52	471	430	1.4243	31.1	32.1	32	"
48	354	760	1.6436	51.5	52.1	52	210 - 300
49	345	490	1.5332	41.1	42.0	42	"
53	451	410	1.4235	31.0	32.1	32	"
55	537	280	1.3041	20.5	21.1	21	"
58	355	625	1.5911	46.6	47.3	47	125 - 150
78	379	670	1.5873	46.7	46.9	47	"
59	431	495	1.4736	36.2	36.6	37	"
61	500	355	1.3621	26.0	26.4	26	"
63	569	210	1.2441	15.5	15.7	16	"
60	395	564	1.5269	41.4	41.5	42	90 - 105
62	463	423	1.4158	31.1	31.4	31	"
64	533	282	1.3002	20.7	20.8	21	"
65	604	141	1.1856	10.4	10.4	10	"
66	395	564	1.5257	41.4	41.4	41	50 - 60
67	462	423	1.4133	31.1	31.1	31	"
68	532	282	1.2928	20.8	20.1	20	"
69	603	141	1.1854	10.4	10.3	10	"
70	397	554	1.5217	40.8	41.0	41	33 - 40
71	462	423	1.4163	31.1	31.4	31	"
75	463	423	1.4122	31.1	31.0	31	"
76	533	282	1.2985	20.7	20.7	21	"
77	604	141	1.1857	10.4	10.4	10	"

*) density of rubber component d_r^{20} = 1.0724 g/cm^3
density of filler component d_f^{20} = 2.169 g/cm^3

**) see formula (2.1) of the report proper, page 8

APPENDIX B SWELLING IN SOLVENTS

From the sample a specimen of 50 mm length and 3.5 x 7 mm^2 cross-section was machined. The specimen was mounted in a wide test tube (Ø 40 mm) with stopper and provided with two short pins at a mutual distance of 35 mm. After conditioning at 23° C the distance between the centre of the two pinheads was measured by means of a cathetometer. The swelling liquid was put in the test tube and after certain time intervals the distance between the marks was measured again. From the data, volume per cent. increase S_v was calculated as a function of swelling time.

In the determination of the volume swelling of sodium chloride filled rubbers it was observed that the specimens filled with coarse particles desintegrated during the first period of (rather rapid) swelling. This difficulty could be solved by two means:

(i) use of specimens with smaller cross-sections, e.g. 2 x 7 mm.
(ii) "pre-swell" of the specimens in solvent vapour.

For practical reasons, method (ii) was used throughout. The "pre-swollen" specimens could be immersed in the swelling liquid without damage.

The experimental accuracy of the determination of the degree of swelling, which could be realized was well between ± 5 % of S_v. A comparison between the results of the method described above and the method of weighing the swollen specimen, showed complete agreement for unfilled rubbers.

An example of the relationship between volume swelling vs the sqaure root of swelling time is shown in Figure B 1. It is seen that after a certain time a well-defined maximum degree of swelling is reached. This was the case with all rubbers, filled or unfilled, prepared at T.N.O. during this investigation proving that we deal with well crosslinked systems. The equilibrium value of swelling found, was given in all cases.

From a considerable number of unfilled rubbers the volume swelling in chloroform and in trichloro-ethylene was determined. The results of these measurements are listed in Table B 1, together with composition and Shore A hardness. So far no simple correlation could be found between composition and swelling properties. Results of the swelling of filled rubbers in chloroform and trichloro-ethylene are listed in Table 2.

APPENDIX B (continued)

Table B 1 Composition, hardness and swelling of unfilled urethane rubbers prepared.

Exp. no.	composition per 100 g Desmophen 3600			Shore A hardness	volume swelling % vol. increase at 23° C in	
	T.D.I.	T.M.P.	D.B.		chloroform	trichloro-ethylene
3600/5	20.1	4.0	-	43	434	344
3600/8	16.9	1.9	1.0	50	425	335
3600/10	15.7	2.1	-	44	491	400
3600/11	17.8	2.9	-	41	480	370
3600/12	19.8	3.7	-	47	438	327
3600/14	18.6	3.0	1.1	46	463	355
3600/14 B	-	-	-	45	450	346 *)
3600/15	17.8	3.1	2.2	44	453	350
3600/16	19.8	4.1	2.2	51	396	315
3600/17	16.4	3.1	1.9	41	533	411
3600/18	16.5	2.8	1.9	47	461	355
3600/19	16.7	3.0	2.0	47	458	360
3600/23	18.0	3.0	2.0	52	388	310
3600/24	17.9	3.0	2.0	52	395	320
3600/25	18.5	3.9	0.95	44	424	334
3600/26	18.3	3.9	1.0	45	428	334
3600/27	20.3	3.9	1.0	56	347	278
3600/28	20.3	3.9	0.9	56	359	272
3600/29	20.4	4.1	-	50	370	294
3600/31	20.1	4.0	-	46	442	328
3600/41	20.5	4.0	1.5	54	370	280
3600/56	20.1	3.9	1.5	48	410	315
3600/57	20.1	4.1	1.5	48½	422	319
3600/73	20.4	4.0	4.0	48½	402	305
3600/74	20.4	4.0	1.5	49½	420	312

*) After-curing 1½ h 130° C

APPENDIX B (continued)

The swelling behaviour of Model Substance A was quite different from the swelling of the rubbers prepared at T.N.O. As is seen from Figure B 2, there are at least two different mechanisms of swelling, a rapid and a slow one. Even after very long swelling times no real equilibrium value of swelling was reached. The values of swelling listed for this substance in Table 3 were the swelling values read (interpolated) after 24 hours.

In butanone, Model Substance A even dissolved completely after 1,600 hours swelling time.

APPENDIX C NUMERICAL DATA OF DYNAMIC MECHANICAL MEASUREMENTS OF SHEAR MODULI

In the undermentioned tables, numerical data are given of the results of dynamic mechanical measurements presented in Figures 20 to 29.

Results of measurements are given in 3 figures. In several cases the meaning of the last figure given may be uncertain.

In some cases, data in the tables are given in parentheses. Those data seem to be unrealistic due to the unsuitability of the technique. Generally, they were omitted in plotting the results.

APPENDIX C (continued)

Table C 1   Shear modulus G and damping tan δ of unfilled polyurethane rubbers.

temp. °C	G 10^7 N/m^2			tan δ 10^{-3}		
	free torsional vibration 1c/s		non-resonance vibration 1 c/s	free torsional vibration 1 c/s		non-resonance vibration 1 c/s
	3600/29	3600/41	3600/29	3600/29	3600/41	3600/29
- 140	192	-		(26)	-	
- 130	186	-		(21)	-	
- 120	179	-		(17)	-	
- 110	177	-		(16)	-	
- 100	172	-	151	(17)	-	-
- 90	164	-	151	(18)	-	-
- 80	157	158	151	(18)	(14)	-
- 70	150	-	129	(20)	-	-
- 60	149	148	122	(21)	(17)	-
- 50	123	132	93.7	79	58	70
- 45	98.0	100	51.3	160	185	305
- 40	30.9	38.0	16.7	580	540	645
- 35	10.5	10.0	3.41	730	770	915
- 30	-	2.97	1.13	-	950	885
- 25	-	0.782	0.533	-	800	725
- 20	0.285	-	0.296	-	-	565
- 19	-	0.335	-	-	500	-
- 15	0.178	-	-	385	-	-
- 10	0.157	0.200	0.189	280	260	280
0	0.144	0.145	0.166	166	150	185
10	0.127	-	0.148	120	-	115
20	0.121	0.126	0.142	98	(51)	(83)
30	0.121	-	-	(59)	-	-
40	0.116	0.128	0.143	(40)	(41)	(42)
50	0.120	-	0.145	(30)	-	(33)
60	0.122	0.132	0.142	-	-	(25)
70	0.127	-	0.146	-	-	(21)
80	-	-	0.146	-	-	(17)
90	-	-	0.144	-	-	(13)
100	-	-	0.149	-	-	(8)

APPENDIX C (continued)

Table C 2 Shear modulus G and damping tan δ at 10-100 c/s of unfilled polyurethane rubber 3600/29

temp. °C	frequency c/s	G 10^7 N/m²	tan δ 10^{-3}
- 140	70.1	176	13
	27.3	176	11
	13.8	176	13
- 130	70.1	176	15
	27.0	172	14
	13.7	171	15
- 120	69.2	172	15
	26.7	169	16
	13.6	167	16
- 110	68.4	168	17
	26.3	163	18
	13.3	162	18
- 100	67.6	164	19
	26.0	161	18
	13.3	160	18
- 90	66.6	159	21
	25.7	156	20
	13.1	155	22
- 80	66.0	156	31
	25.4	153	35
	13.0	152	38
- 70	63.4	144	40
	24.2	139	76
	12.3	137	59
- 60	69.0	132	79
	26.4	132	94
	13.5	132	170
- 60	64.2	126	210
-	23.9	113	140
	12.0	108	200

APPENDIX C (continued)

Table C 2 (continued)

temp. °C	frequency c/s	G 10^7 N/m^2	tan δ 10^{-3}
- 50	55.3 19.4 9.4	84.3 61.6 51.7	300 535 400
- 50	50.4 18.5 8.9	63.6 52.8 42.0	315 530 480
- 40	43.1 15.9 7.4	36.7 28.9 17.4	480 430 470
- 40	25.7	39.3	410
- 30	46.8 11.1	6.26 6.57	320 680
- 20	26.4	1.03	100
- 20 - 10 0 10 20 30 40	16.7 11.7 9.9 9.7 9.6 9.6 9.6	0.789 0.256 0.110 0.0909 0.0883 0.0883 0.0883	915 375 240 145 89 58 41
50 60 70 80 90 100	9.8 9.8 9.9 9.9 10.0 9.9	0.0977 0.103 0.108 0.112 0.114 0.108	35 33 21 20 17 15

APPENDIX C (continued)

Table C 3 Shear modulus G and damping tan δ (1 c/s) for polyurethane rubbers filled with 300-480 μ NaCl.

temp. °C	G 10^7 N/m^2			tan δ 10^{-3}		
	3600/44 52 vol. %	3600/47 42 vol. %	3600/52 32 vol. %	3600/44 52 vol. %	3600/47 42 vol. %	3600/52 32 vol. %
- 140	462	-	-	14	-	-
- 130	451	-	-	13	-	-
- 120	446	-	-	14	-	-
- 110	441	-	-	14	-	-
- 100	462	-	-	12	-	-
- 90	452	-	-	13	-	-
- 80	449	337	260	13	10	11
- 70	432	-	-	13	-	-
- 60	424	312	246	17	18	14
- 50	391	280	216	36	61	49
- 45	-	218	174		165	150
- 40	278	101	82.7	170	490	470
- 35	-	50.0	21.5		600	1,140
- 30	49.0	20.6	15.5	385	670	850
- 25	27.1	-	4.62	595	-	-
- 20	12.7	5.80	1.20	595	615	640
- 15	8.3	3.01	0.920	435	-	400
- 10	4.28	1.50	0.740		345	315
- 5	3.31	-	-	280	-	-
0	2.70	0.980	0.480	201	220	185
10	2.04	-	-	140	-	-
20	1.85	0.720	-	105	62	-
22	-	-	0.383	-	-	100
30	1.44	-	-	66	-	-
40	1.38	0.620	0.342	44	41	51
50	1.32	-	-	38	-	-
60	1.29	0.560	0.340	28	-	30
70	1.03	-	-	41	-	-
80	1.00	0.525	-	25	24	-

APPENDIX C (continued)

Table C 4 Shear modulus G and damping tan δ (1 c/s) of polyurethane rubbers filled with 210-300 μ NaCl.

temp. °C	G 10^7 N/m²				tan δ 10^{-3}			
	3600/48 52 vol.%	3600/49 42 vol.%	3600/53 32 vol.%	3600/55 21 vol.%	3600/48 52 vol.%	3600/49 42 vol.%	3600/53 32 vol.%	3600/55 21 vol.%
- 80	438	344	273	209	12	14	12	14
- 60	409	324	255	191	21	17	21	22
- 50	386	298	233	-	41	44	46	-
- 48	-	-	-	157	-	-	-	88
- 45	341	261	199	-	87	85	110	-
- 43	-	-	-	116	-	-	-	185
- 40	224	160	90	87.4	250	295	425	320
- 35	114	64.5	35.4	26.1	420	600	695	610
- 30	47.7	30.8	11.0	10.6	700	875	870	940
- 25	19.2	14.0	-	-	780	750	-	-
- 20	7.92	5.67	1.66	1.19	-	585	635	795
- 15	5.51	3.18	0.964	0.759	520	-	485	570
- 10	2.87	1.77	0.670	0.505	365	330	352	395
0	2.12	1.07	0.440	0.294	240	180	160	180
20	1.25	0.840	0.372	0.214	82	78	71	64
40	1.10	0.740	0.360	0.220	36	62	36	49
60	1.09	0.720	0.350	0.224	32	36	-	23
80	-	0.625	-	-	-	23	-	-

APPENDIX C (continued)

Table C 5 Shear modulus G and damping tan δ (1 c/s) of polyurethane rubbers filled with NaCl 125-150 μ.

temp. °C	G 10^7 N/m^2				tan δ 10^{-3}			
	3600/78 47 vol.%	3600/59 37 vol.%	3600/61 26 vol.%	3600/63 16 vol.%	3600/78 47 vol.%	3600/59 37 vol.%	3600/61 26 vol.%	3600/63 16 vol.%
- 80	372	311	235	202	12	13	14	14
- 60	354	290	220	187	12	16	20	22
- 50	331	271	202	167	29	36	50	56
- 45	315	246	180	142	48	80	99	119
- 40	229	153	113	84.0	175	255	280	320
- 35	132	72.3	43.3	26.2	335	455	570	670
- 30	62.4	34.7	21.0	10.0	520	600	800	895
- 25	27.2	9.95	4.0	1.73	680	755	-	770
- 20	8.40	-	1.38	0.790	795	-	-	645
- 15	-	1.96	0.755	0.502	-	540	545	470
- 14	4.80	-	-	-	525	-	-	-
- 10	2.32	1.17	0.539	0.321	340	360	390	280
0	1.48	0.731	0.357	0.235	190	215	184	220
20	0.940	0.576	0.286	0.191	75	95	81	74
40	0.870	0.510	0.270	0.190	36	37	54	23
60	0.846	0.485	0.277	0.190	-	24	-	-

APPENDIX C (continued)

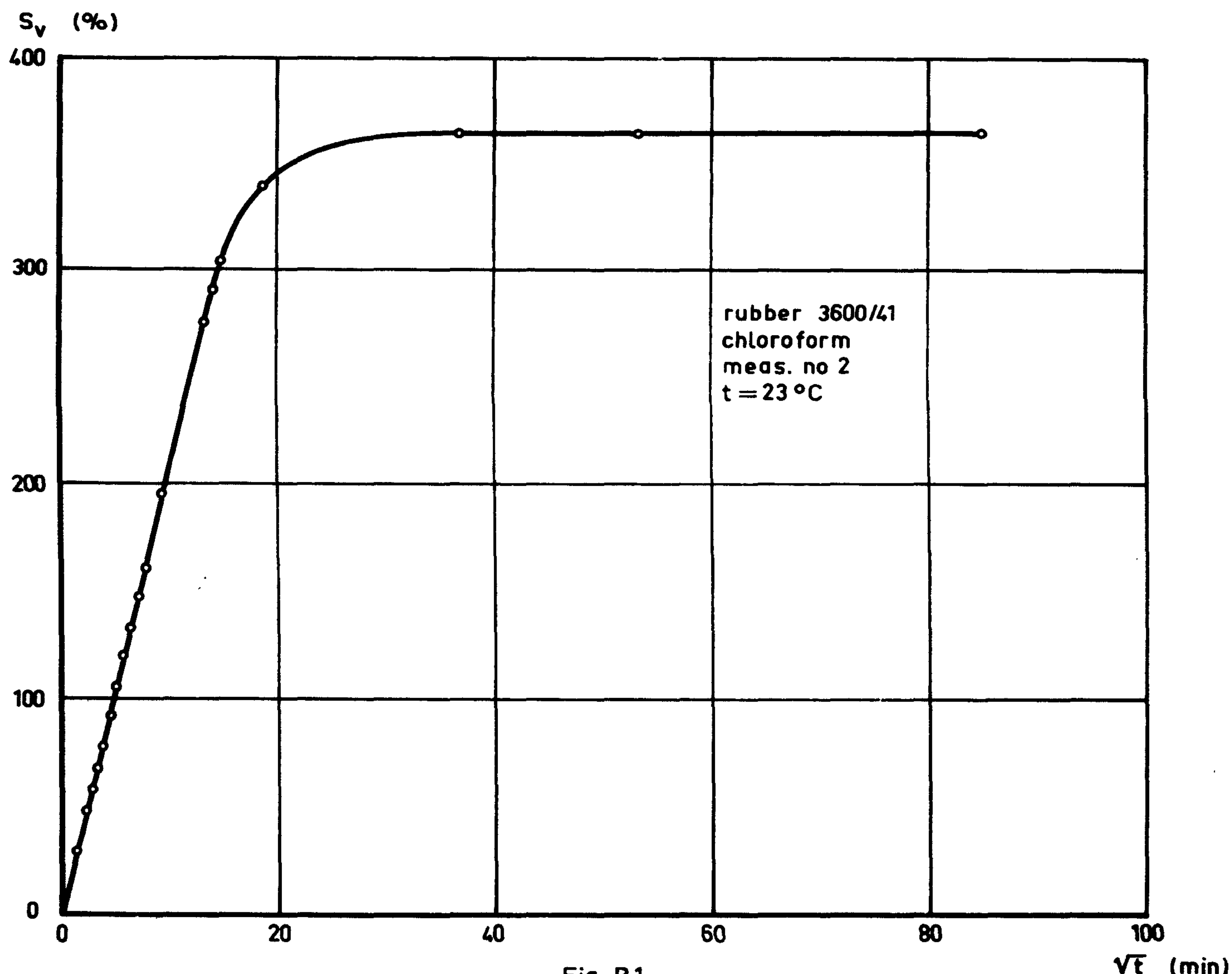
Table C 6 Shear modulus G and damping tan δ (1 c/s) of polyurethane rubbers filled with NaCl 90-105 μ.

temp. °C	G 10^7 N/m²				tan δ 10^{-3}			
	3600/60 42 vol.%	3600/62 31 vol.%	3600/64 21 vol.%	3600/65 10 vol.%	3600/60 42 vol.%	3600/62 31 vol.%	3600/64 21 vol.%	3600/65 10 vol.%
- 82	-	294	-	180	-	8	-	14
- 80	362	-	221	-	13	-	11	-
- 60	340	273	211	166	19	15	15	22
- 50	315	239	165	152	42	52	92	45
- 45	280	202	102	124	84	120	275	115
- 40	189	110	40.0	78.9	220	320	535	295
- 35	89.6	44.9	11.0	27.7	415	535	820	585
- 30	45.2	19.0	5.00	11.0	545	685	1,090	845
- 25	16.8	7.07	1.95	-	810	850	640	-
- 20	7.00	2.90	0.725	0.721	715	555	500	680
- 15	3.04	1.43	0.492	0.389	525	460	375	495
- 10	1.85	0.970	0.358	0.279	370	360	295	355
0	1.08	0.637	0.262	0.190	205	200	170	150
20	0.766	0.509	0.220	0.162	52	76	54	66
40	0.677	0.398	0.215	0.163	-	38	42	-
60	0.677	0.387	0.225	0.157	10	25	26	-

APPENDIX C (continued)

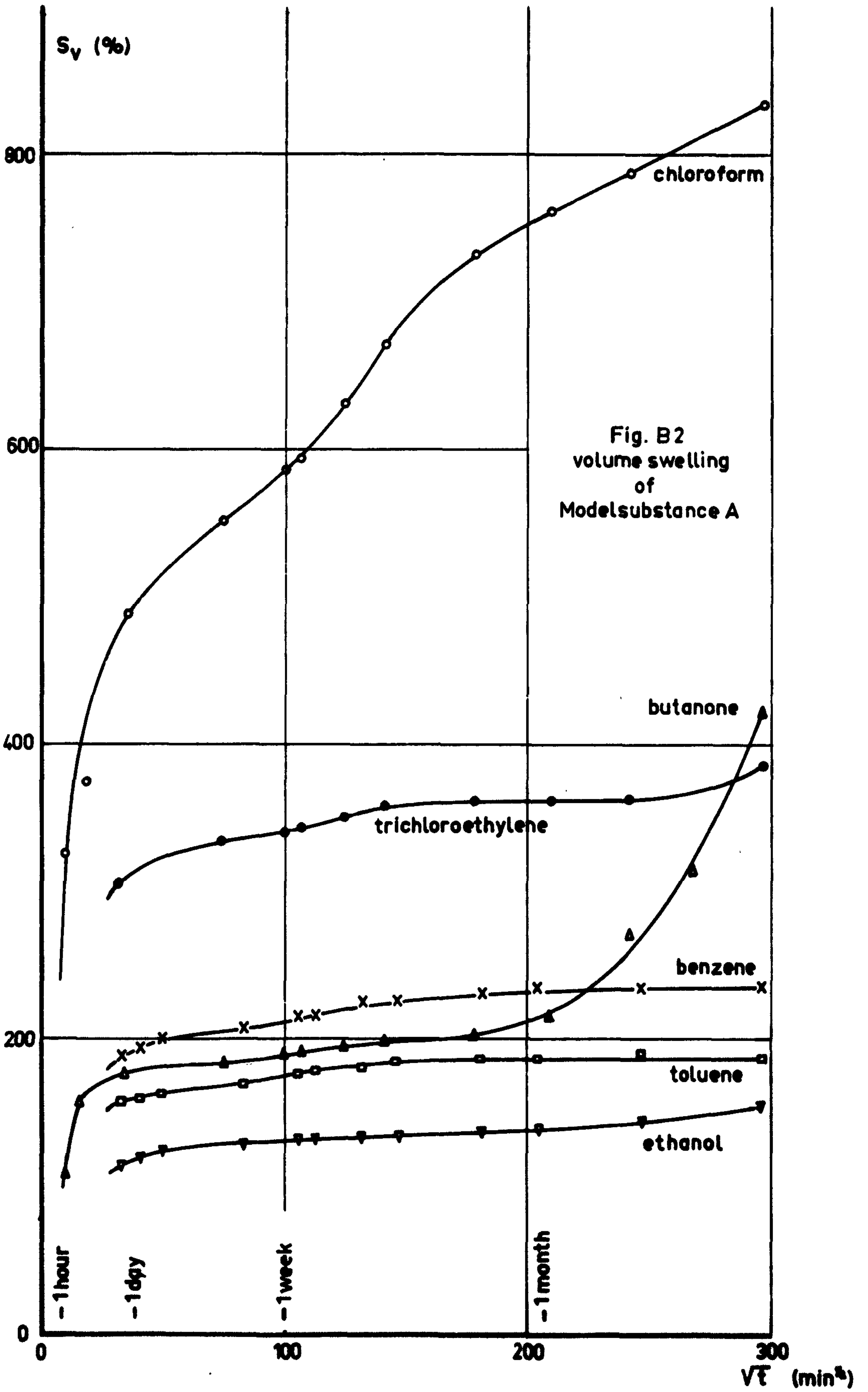
Table C 7 Shear modulus G and damping tan δ (1 c/s) of polyurethane rubbers filled with 33 - 40 μ NaCl.

temp. °C	G 10^7 N/m^2				tan δ 10^{-3}			
	3600/70 41 vol.%	3600/71 31 vol.%	3600/76 21 vol.%	3600/77 10 vol.%	3600/70 41 vol.%	3600/71 31 vol.%	3600/76 21 vol.%	3600/77 10 vol.%
- 80	360	290	214	182	10	12	13	10
- 60	339	276	200	168	15	12	20	16
- 50	317	261	177	155	34	43	48	34
- 45	285	233	159	134	77	74	105	100
- 40	216	160	97.0	78.2	175	265	290	300
- 35	102	80.5	38.2	30.2	375	425	550	540
- 30	61.2	29.2	17.5	14.0	500	610	760	650
- 25	23.0	11.0	3.55	-	625	-	1,060	-
- 20	8.25	4.37	1.06	1.04	800	635	-	610
- 15	3.80	2.10	0.708	0.503	620	480	630	512
- 10	2.32	1.60	0.480	0.282	446	390	380	390
0	1.17	0.790	0.326	0.205	251	230	210	112
20	0.790	0.575	0.220	0.155	82	97	56	56
40	0.728	0.450	0.226	0.154	-	45	40	36
60	0.690	0.411	0.232	0.159	38	-	34	-



Sv (%)
400
300
200
100
0
0
20
40
60
80
100
√t (min)
rubber 3600/41
chloroform
meas. no 2
t = 23 °C

Fig. B1



S_V (%)
800
600
400
200
0
100
200
300
$\sqrt{t}$ (min½)
chloroform
Fig. B2
volume swelling
of
Modelsubstance A
butanone
trichloroethylene
benzene
toluene
ethanol
1 hour
1 day
1 week
1 month