NG-Migration into Double-Base Inhibitors. I. Sorption

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SYNOPSIS

Double-base propellants are inhibited with polymeric material to restrict the burning surface. The energetic plasticizer may migrate out of the propellant into the inhibitor. This may then cause the inhibitor to deteriorate. Thus, the measurement of the amount of energetic plasticizer that migrates into the inhibitors is important.

Sorption measurements are done using a "sandwich" test. The data obtained are used in an empirical formula to calculate the maximum amount of energetic plasticizer that will be absorbed by a particular polymer. The validity of the formula is confirmed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Double-base propellants are inhibited with polymeric material to restrict the burning surface of the material. A regulated, predictable, and lengthened burning time is thus achieved. The problem with double-base propellants is, however, that the energetic plasticizer (nitroglycerine), used in the propellants, migrates out of the propellant into the polymeric coating. This may cause the polymeric material to degrade and debond with time. The inhibitor must thus have as low as possible sorption and diffusion characteristics.

Sorption Measurements

The measurement of sorption can be achieved by liquid absorption methods[1] or by a "sandwich"[1,2] method. The liquid absorption method is performed by the immersion of the polymeric material in liquid nitroglycerine (NG). The increase in mass with time is then measured. This method requires that measurements be done with liquid nitroglycerine, which is a dangerous procedure. The "sandwich" method makes use of propellant blocks, in which the poly-

meric material is placed between two propellant blocks to form a "sandwich." The "sandwich" is then stored at elevated temperatures and the mass increase of the polymeric material is noted. This experiment was conducted by the "sandwich" method.

Commercial Raw Materials

The polymeric materials, used for this test, are subdivided into commercial raw materials and synthesized raw materials. The commercial raw materials were obtained from various companies represented in the Republic of South Africa, and the raw materials for synthesis were based on polypropylene oxide (PPO) and polyepichlorohydrin (PECH) copolymers. The commercial raw materials used are presented in Table I.

The various polymers used were compatable with double-base propellants. The main chemical industries are represented in Table I and only the "best" polymeric candidate was taken for tests.

Raw Materials for Synthesis of Copolymers

The use of chloropolyurethanes as inhibitors has not been discussed in the literature and, based on the experience of chloropolyesters,[3-8] a polyurethane with chloro-groups in the backbone structure was

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Table I Commercial Raw Materials

Raw Material Code	Type of Polymer	Reason for Use	Company Name
D3644 (37.02%) Cl	Chloropolyester	For lower NG-migration	NCS
N7200MV	Isophthalic Polyester	To mix with Chloropolyester to produce higher elongation	NCS
EE170	PPG Based Polyol	Low T_g	Urethane Industries
Duthane 30	MDI Adduct	Crosslinker for EE170	Urethane Industries
C6610 A	Polyester Polyol	Polyester Polyol	BASF
C6610 B	Polymeric MDI	Crosslinker for C6610 A	BASF
E840 A	PTMG Polyol	Low T_g	NUI
E840 B	MDI Adduct	Crosslinker for E840 A	NUI
FR976 A	PPG Based Polyol	Low T_g	Elite
FR976 B	IPDI	Crosslinker for FR976 A	Elite

Abbreviations: (NCS) NCS Plastics, (NUI) National Urethane Industries, (ELITE) Elite Chemicals, (PPG) Polypropylene Glycol, (MDI) 4,4-Diphenylmethane Diisocyanate, (PTMG) Polytetramethylene Glycol, and (IPDI) 3—Isocyanatomethyl—3,5,5—Trimethyl-cyclohexyl-Isocyanate (Isophorone Diisocyanate).

selected. An ideal candidate seemed to be epichlorohydrin, which could be polymerized to poliepichlorohydrin (PECH). A 99.5% pure sample of epichlorohydrin was used as monomer.

To be able to compare the influence of the chlorine atom on NG-absorption, polypropylene oxide (PPO) was chosen for use in the copolymer. The increased or decreased concentration of chlorine content in the random copolymer would then be correlated to NG-content. A 99.5% pure propylene oxide monomer was used.

The difference between random copolymers of PECH and PPO, as well as blended copolymers of PPO and PECH, were also examined. It was assumed at this stage that random copolymers would yield "better" performance characteristics with respect to NG-migration and T_gs, due to the more homogeneous character.

EXPERIMENTAL

Crosslinking of Commercial Polymers

The commercial polyols were crosslinked with the respective isocyanates at room temperature and were left overnight. The samples were released from the molds the next day and were placed in an oven for 24 h at 60°C to ensure that the samples were fully cured. All the samples, that is, the commercial as well as the synthesized, were cured by using a com-

mercial catalyst THORCAT 535 (a mercury based catalyst) and an antifoaming agent, BAYSILONE (Bayer). The ratios of polyol to isocyanate are presented in Table II.

The chloropolyester (CP) and isophthalic polyester (IP) were crosslinked with 1% MEKP (Methylethylketone peroxide) and 1% Co-octoate (6% solution). The two polyesters were crosslinked alone, and in combinations, in order to compare the NG-migration results with those obtained for the synthesized copolymers. The crosslinking ratios are presented in Table III.

Synthesis of Polymers

Low molecular mass hydroxy-terminated polyethers are obtained by using a $BF_3O(C_2H_5)_2$ catalyst in the presence of a polyol such as glycerol. Other Lewis

Table II Crosslinking Ratios of Polyols and Isocyanates

Polyol	% (w/w)	Isocyanate	% (w/w)
E840A[a]	59.2	E840B	35.2
C6610A	74.1	C6610B	25.9
EE170	65.5	Duthane 30	34.5
FR976A	73.5	FR976B	26.5

[a] 5.6% 1,4 Butanediol was added to this formulation.

Table III Crosslinking Ratios of Polyesters

	Percentage Component			
New Name	D3644	N7200MV	MEKP	Co-Octoate
C1	98		1	1
C2	74	24	1	1
C3	49	49	1	1
C4	24	74	1	1
C5		98	1	1

acids can be used as catalysts, but give rise to higher molecular mass. The low viscosity polymers obtained were crosslinked with isocyanates to form urethane polymers.

Crosslinking of Synthesized Polymers

The synthesized polymers were crosslinked using HMDI (1,6-hexamethylene diisocyanate, 168.22 g/mol) and MDI (250.27 g/mol). Both are diisocyan-

ates, but differ in molecular mass and stiffness of backbone. The net result is thus more stiff or less stiff crosslinked products. The crosslinking ratios are presented in Table IV.

Preparation of Samples

The samples discussed above are free-flowing resins, when mixed in the ratios shown. These resins were processed in the different ways discussed below.

Dogbones

The samples are mixed in the right ratios, then placed under vacuum until the foam produced "falls flat." Vacuum is still drawn for another minute and the dogbone mold is filled by gravitational casting, ensuring that no air is trapped in the resins. The dogbone samples (60 mm × 5 mm × 3.5 mm, Lo = 38.8 mm) were used, after curing, to determine the samples maximum tensile strength, maximum

Table IV Crosslinking Ratios of Synthesized Polymers

	Percentage Component						
New Name	91/35[a]	91/26[a]	91/17[a]	91/08[a]	91/00[a]	HMDI	MDI
H1	82.9					17.1	
H2[b]	62.1				20.7	17.2	
H3[b]	41.3				41.3	17.4	
H4[b]	20.6				61.8	17.6	
H5					82.3	17.7	
M1	55.8						44.2
M2[b]	41.7				13.8		44.5
M3[b]	27.6				27.6		44.7
M4[b]	13.8				41.3		44.9
M5					54.8		45.2
1H	82.9					17.1	
2H		79.8				20.2	
3H			77.5			22.5	
4H				76.0		24.0	
5H					82.3	17.7	
1M	55.8						44.2
2M		70.2					29.8
3M			68.2				31.8
4M				66.8			33.7
5M					54.8		45.2

[a] The second part of the synthesized polymers code (e.g., 35 of 91/35) gives an indication of the calculated chlorine mass percentage. The 91 refers to the year that the polymer was synthesized.
[b] Mixed blends to produce "block" copolymers.

Table V   Mechanical and Physical Tests

Type of Test	Method	ASTM or DIN Test Number
M_n	GPC, VPO	D 3593-80, D 3592-77
OH-number	Wet analysis	D 1957-63
Cl-content	Wet analysis	D 1726-73
Tensile strength	Instron	D 6384M-84
Elongation	Instron	D 6384M-84
T_g	DMTA	Refs. 9 and 10
NG-migration	Sandwich	Refs. 3 and 11

elongation, Young's modulus, and toughness, for relative comparison.

T_gs

The mold for DMTA samples (sample size was ca. 80 mm × 10 mm × 3 mm; samples were cut to a length of ca. 50 mm to fit in the machine grips) were filled by gravitational casting and the cured samples were used to determine the T_g of the sample.

NG-Absorption Molds

The molds for the preparation of NG-migration samples (block dimensions were 25 mm × 25 mm × 2.5 mm) were filled by gravitational casting. The cured samples were prepared into "sandwiches." The "sandwich" would then consist of a propellant block (25 mm × 25 mm × 5 mm), a polymer block, and a propellant block.

Mechanical and Physical Tests

The mechanical and physical tests, performed on the raw materials and crosslinked polymers, are shown in Table V. The modulus is calculated by computer, as the Young's modulus. The toughness

Table VI   Synthesized Polyol Results

Sample No.	Tests			Theoretical Calculated % Cl
	OH-Value (mEq/g)	M_n (g/mol)	Cl-Content (%)	
91/35	2.25	1060	31.32	35.01
91/26	3.00	870	25.00	26.02
91/17	3.44	871	16.75	17.15
91/08	3.75	790	12.20	8.47
91/00	2.66	1170	0	0

is also calculated by computer and represents the area under the stress vs. strain curve. The toughness thus provides a relative indication of how much energy is needed to break a polymer sample.

The NG-migration values are determined by measuring the mass increase of a polymer in a "sandwich," with time[3,11] (the test was done at 70°C). The mass increase of the polymer is divided by the original sample mass in order to obtain the percentage mass increase $[M(t)]$. The various polymers were also placed in the oven on their own to assess the amount of volatiles lost. The loss of volatiles were added to the sample masses to give the absolute sorption values.

RESULTS

Synthesis Results

The analysis of the results for the raw synthesized polyols are shown in Table VI.

The commercially obtained polymers were analyzed for M_n, but the OH-values were done by the respective companies (Table VII).

Mechanical and Physical Results

The mechanical and physical results for the crosslinked polymers are presented in Table VIII.

The amount of nitroglycerine, absorbed by the polymers, is depicted in Table IX. Table IX depicts the average values for duplicate analysis, except for C6610, which was done in triplicate.

Table VII   Commercial Raw Material Results

Sample Name	OH-Number (mEq/g)	NCO Percentage	M_n (g/mol)
C6610A	3.45		736
C6610B		31	
E840A	1.38		3211
E840B		22.4	
FR976A	2.67		760
FR976B		36.19	
EE170	3.58		1380
Duthane 30		28.6	
D3644			1450
N7200MV			3660

The data in Table IX was used and Margolin's[12] formula was applied in order to determine the constants a and b,

$$M(t) = \frac{t}{a + bt} + c \qquad (1)$$

and

$$M(\infty) = 1/b \qquad (2)$$

where (t) time in seconds, (c) % plasticizer originally in polymeric material = 0, $[M(\infty)]$ amount of the NG absorbed at time infinity).

The values for a, b, and $M(\infty)$ are presented in Table X.

DISCUSSION

Mechanical and Physical Properties Discussion

The results in Table VIII show a decrease in T_g with an increase in PPO (see 5H, H5, 5M, and M5). This is to be expected, since PPO has a lower T_g than PECH. Table VIII shows the general trend of decreasing tensile strength with increasing PPO concentration. This can be attributed to the fact that intermolecular bond strength is enhanced by the dipole that is caused by the chlorine atoms.

Generally, there is a decrease in toughness with increasing PPO concentration. This indicates that more energy is required to break a sample with increasing PECH concentration. The polyester samples (C1 to C5) show a slight increase in toughness

Table VIII   Mechanical and Physical Results

Sample No.	Max. Tensile Strength (MPa)	Max. Elongation (%)	Young's Modulus (MPa)	Toughness (MPa)	T_g (°C)	Cl (%)
C6610	13.8	75.6	102.9	7.24	5	0
E840	12.4	472.6	9.8	35.93	−55	0
EE170	8.1	162.4	7.0	6.84	−6	0
FR976D	9.0	156.5	7.4	7.36	−3	0
C1	51.7	9.8	91.7	1.74	84	24.80
C2	21.9	16.3	53.5	0.37	68	18.60
C3	17.5	25.6	61.9	0.50	44	12.40
C4	14.2	34.0	49.2	3.20	15	6.20
C5	11.1	45.5	24.2	3.00	7	0
H1	3.3	161.8	2.2	1.39	3	29.02
H2	1.0	158.0	1.1	0.87	−6	21.74
H3	1.0	139.2	0.7	0.69	−15	14.46
H4	0.9	101.9	0.8	0.47	−23	7.21
H5	0.7	103.1	0.7	0.37	−27	0
M1	17.3	57.9	109.3	7.54	31	19.54
M2	8.9	102.6	25.7	4.83	29	14.60
M3	4.7	134.2	4.0	3.20	19	9.66
M4	3.0	123.8	2.1	1.85	8	4.83
M5	1.8	83.5	1.6	0.75	−4	0
1H	3.3	161.8	2.2	1.39	3	29.02
2H	2.0	149.8	1.8	1.61	1	20.76
3H	2.0	100.4	2.6	1.12	−6	13.29
4H	1.3	85.1	1.9	0.48	−14	9.27
5H	0.7	103.1	0.7	0.37	−27	0
1M	17.3	57.9	109.3	7.54	31	19.54
2M	32.5	13.1	592.1	1.71	36	18.27
3M	26.7	11.0	522.5	5.60	31	11.70
4M	6.5	137.2	12.0	4.42	15	8.09
5M	1.8	83.5	1.6	0.75	−4	0

Table IX   NG-Absorption vs. Days at 70°C

Days at 70°C	C1	C2	C3	C4	C5
0	0.00	0.00	0.00	0.00	0.00
1	2.19	5.92	11.29	15.57	16.53
2	2.05	7.34	15.34	21.70	21.45
3	2.64	8.17	19.78	30.24	26.09
7	2.84	13.68	27.33	38.37	28.64
9	2.21	14.87	30.93	Tacky, broke during handling	Tacky, broke during handling
11	Rigid, broke during handling	16.58	32.79		
18		19.42	Broke during handling		
25		20.85			
32		21.97			
37		22.84			
43		23.17			
44		22.98			
45		22.96			
46		23.15			

Days at 70°C	C6610	FR976D	E840	EE170	H1
0	0.00	0.00	0.00	0.00	0.00
1	12.40	18.51	13.87	11.88	11.67
2	17.41	23.79	17.21	16.98	16.49
3	20.48	25.07	19.33	21.39	20.01
7	26.78	41.93	26.25	33.67	18.05
9	28.01	45.68	26.82	35.99	22.83
11	27.90	47.93	27.95	38.04	24.10
18	28.90	55.62	32.59	45.49	27.84
25	30.22	62.55	37.17	49.41	32.52
32	30.21	64.82	39.59	52.40	36.20
37	30.42	65.27	41.77	54.41	38.10
43	30.92	65.87	43.63	55.07	39.48
44	Data levels off	Data levels off	43.55	55.15	39.42
45			43.75	55.43	39.44
46			43.63	55.53	39.45

Days at 70°C	H2	H3	H4	H5	M1
0	0.00	0.00	0.00	0.00	0.00
1	14.76	1.77	18.44	13.79	6.26
2	16.82	7.41	23.03	17.44	8.35
3	22.26	10.29	28.07	22.07	10.17
7	31.25	24.12	24.46	28.21	18.48
9	Tacky, broke during handling	Tacky, broke during handling	23.66	Tacky, broke during handling	20.01
11			21.58		21.97
18			22.51		26.53
25			22.51		30.72
32			Tacky, broke during handling		32.49
37					34.15
43					35.86
44					36.02
45					36.20
46					36.39

Table IX   (*Continued*)

Days at 70°C	M2	M3	M4	M5	2H
0	0.00	0.00	0.00	0.00	0.00
1	8.05	12.01	12.05	11.52	12.66
2	10.55	15.33	15.26	14.82	18.57
3	12.88	18.37	18.32	17.80	22.25
7	20.48	26.67	26.48	26.23	32.25
9	22.90	29.42	30.65	29.16	36.11
11	24.63	31.80	33.95	30.87	39.40
18	29.45	35.38	38.41	37.62	48.34
25	32.69	38.38	41.72	41.34	55.95
32	34.80	40.08	43.09	43.67	60.85
37	35.92	41.29	44.45	45.32	61.03
43	37.89	43.17	45.11	46.47	59.59
44	37.88	43.11	45.17	46.50	Data levels off
45	38.10	43.47	45.29	46.66	
46	38.36	43.48	45.40	46.73	

Days at 70°C	3H	4H	2M	3M	4M
0	0.00	0.00	0.00	0.00	0.00
1	18.09	17.20	3.75	8.94	9.41
2	26.16	21.47	4.65	11.61	10.15
3	30.90	28.04	5.28	14.79	12.40
7	41.08	40.01	8.85	22.51	20.64
9	46.01	43.35	9.96	24.68	22.50
11	50.50	47.93	11.02	26.62	24.79
18	60.59	54.18	14.97	29.91	29.60
25	64.79	Broke during handling	18.55	31.87	32.37
32	Broke during handling		21.74	33.46	34.74
37			23.91	34.78	36.13
43			26.46	36.75	37.48
44			26.70	37.10	37.63
45			27.24	37.45	38.05
46			27.53	37.44	38.44

with decreasing chlorine content. This is due possibly to the increase in crosslink density with increasing isophthalic concentration.

It is interesting to note that the "blends" (H1 to H5 and M1 to M5) have lower T_gs than the corresponding random copolymers. The "blends" are, on average, 8°C lower in their T_gs than the random copolymers. This average proves that the backbone of the random copolymers are truly random and that the influence of PPO in a copolymer is more pronounced when it is in a block form. Second, the random copolymers are relatively stronger than the "block" copolymers, due to either a more homogeneous nature (closer packing) or due to the more pronounced PECH character.

Sorption Discussion

The data in Table IX conform to the formula suggested by Margolin (see Appendix 1 for examples of graphs). The value for $M(\infty)$ can thus be calculated and indicates the maximum amount of NG that the inhibitor will absorb, without performing the experiment, until $t = \infty$. Using this formula thus avoids the trouble and time of obtaining $M(\infty)$ at $t = \infty$. This parameter is necessary if the diffusion coefficient is to be determined.

Figures 1 and 2 depict the maximum NG that is absorbed by the specific polymeric materials. The error bars in the figures correspond to a confidence level of 95.5% or ± two standard deviations.
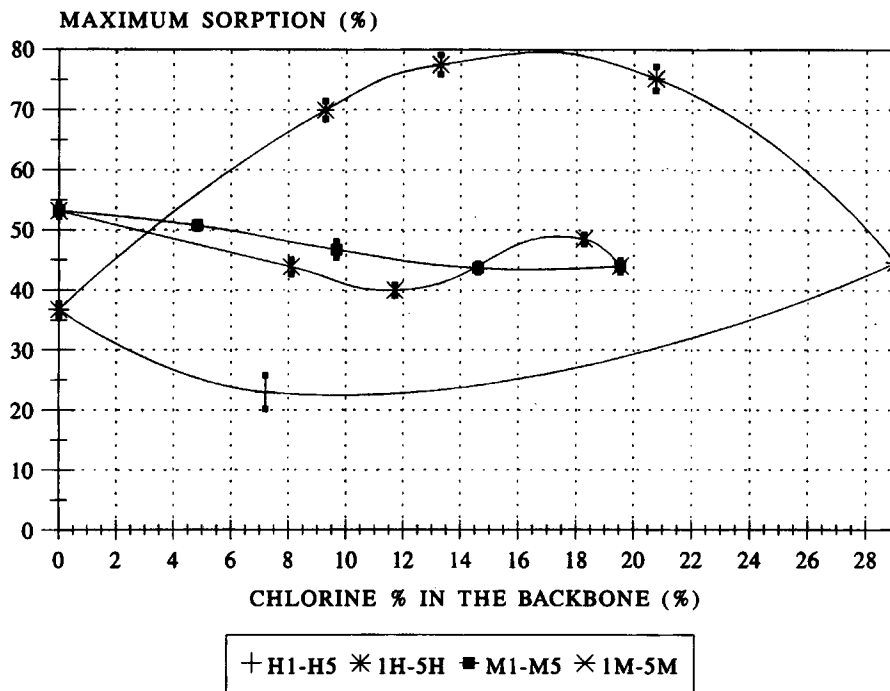
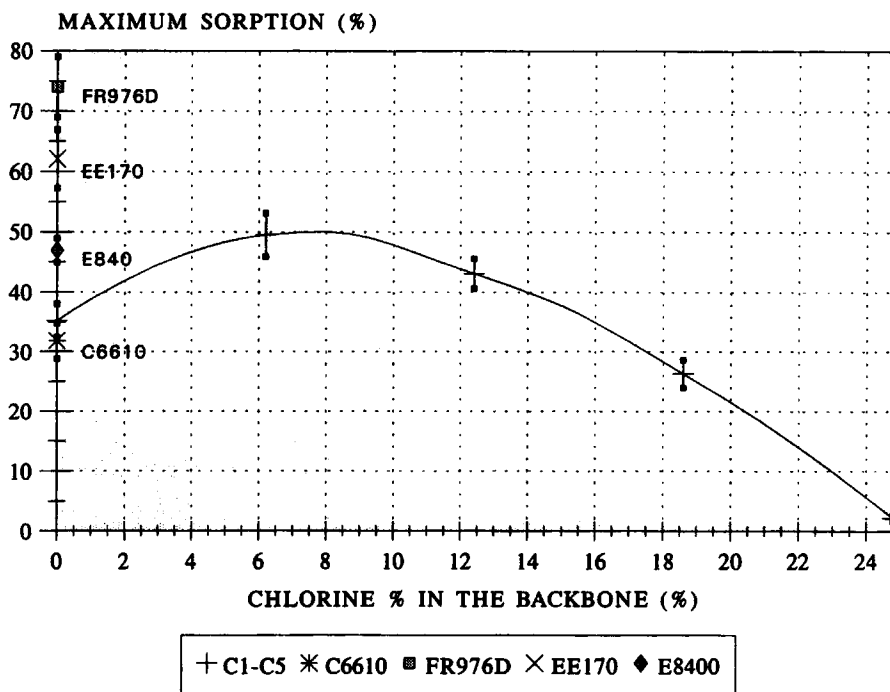**Figure 1**   Maximum sorption (%) vs. chlorine % in the backbone.

Figure 2   Maximum sorption (%) vs. chlorine % in the backbone.

Table X **Values for the Constants (Sorption Curves) According to Margolin's Formula**

Sample No.	Constant a	Constant b	$M(\infty) = 1/b$
C6610	0.0498	0.0314	31.84
FR976D	0.0713	0.0135	74.07
EE170	0.1022	0.0159	62.89
E840	0.1255	0.0213	46.95
C1	0.0089	0.4590	2.18
C2	0.2400	0.0380	26.32
C3	0.0827	0.0232	43.10
C4	0.0458	0.0202	49.50
C5	0.0314	0.0284	35.21
H1	0.1799	0.0224	44.64
H2	—	—	—
H3	—	—	—
H4	0.0074	0.0435	22.98
H5	0.0496	0.0272	36.76
M1	0.2478	0.0227	44.05
M2	0.1828	0.0229	43.68
M3	0.1074	0.0214	46.73
M4	0.1081	0.0197	50.76
M5	0.1322	0.0188	53.19
1H	0.1799	0.0224	44.64
2H	0.1192	0.0133	75.19
3H	0.0671	0.0129	77.51
4H	0.0684	0.0143	69.93
5H	0.0496	0.0272	36.76
1M	0.2478	0.0227	44.05
2M	0.7842	0.0206	48.54
3M	0.1370	0.0250	40.00
4M	0.1864	0.0228	43.86
5M	0.1322	0.0188	53.19

The initial assumption, that the chlorine content in the polymer backbone reduces NG-sorption, is not necessarily true. The MDI-crosslinked PECH/PPO (M1–M5 and 1M–5M) polymers show a decrease in NG-sorption with chlorine content. The HMDI-crosslinked PECH/PPO (1H–5H), however, do not show the same decrease as the MDI-crosslinked series. Presumably, this is due to a disruption in the normal packing of the polymer backbone by the bulkier chlorine atoms. There is too little data for the H1 to H5 series to form any conclusion.

The C1 to C5 series show the same trend as the 1H to 5H series, which supports the theory of the disruption of the backbone, since both are "blends" and thus form "block" copolymers. The random copolymers do not show the same tendency.

CONCLUSIONS

Margolin's formula can be applied to thermoset polymers that are absorbing plasticizer. The value for $M(\infty)$ can be calculated using this formula, although the constant a has no significance at this stage.

The chlorine content in the backbone is not directly related to a lowering in plasticizer absorption, and steric packing of the backbone must also be taken into account.

The "best" inhibiting material seems to be C6610 and the H1–H5 series, if $M(\infty)$, elongation (> 100%), and the T_g (< −5°C) are taken as criteria. The diffusion coefficient must, however, still be considered in order to provide a complete picture.

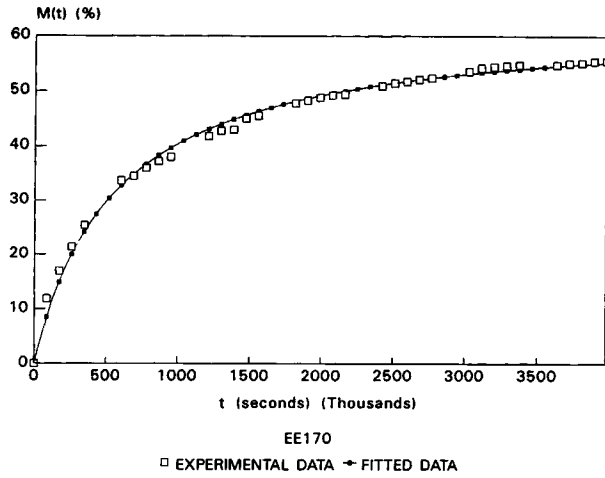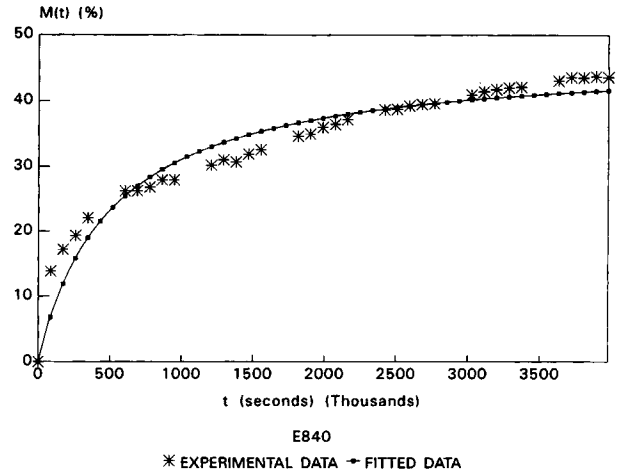# APPENDIX 1

Graphs of $M(t)$ vs. time (s)
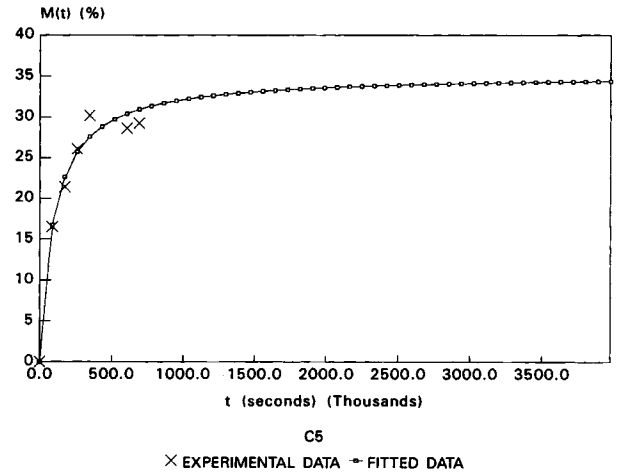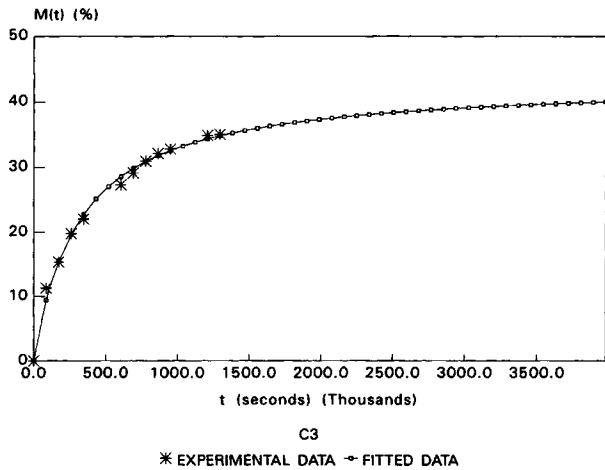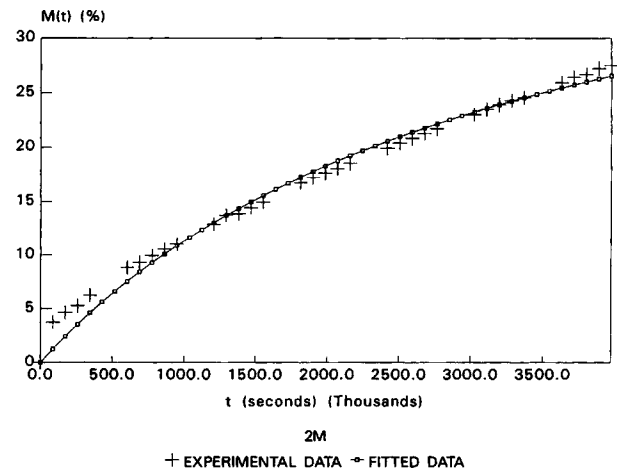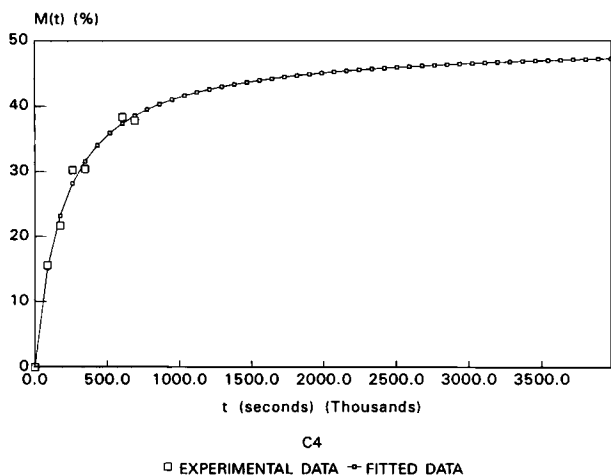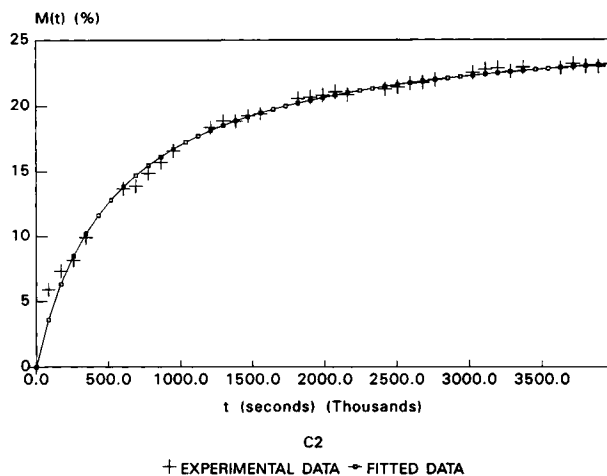
M(t) (%)

EE170
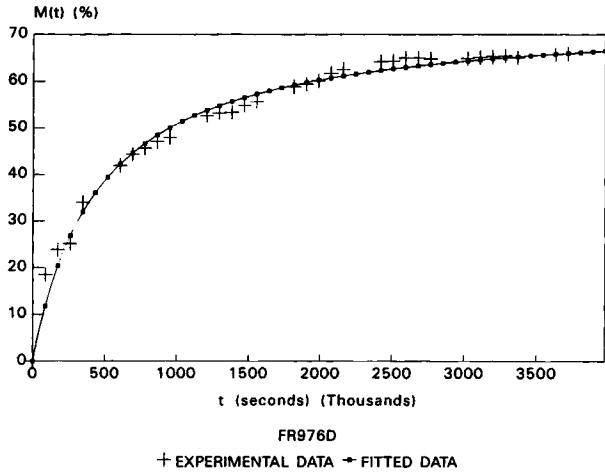□ EXPERIMENTAL DATA ✦ FITTED DATA

Figure A.1

M(t) (%)

E840
✳ EXPERIMENTAL DATA ✦ FITTED DATA

Figure A.2

M(t) (%)

FR976D
+ EXPERIMENTAL DATA ✦ FITTED DATA

Figure A.3

M(t) (%)

C5
✕ EXPERIMENTAL DATA ✦ FITTED DATA

Figure A.4

M(t) (%)

C3
✳ EXPERIMENTAL DATA ✦ FITTED DATA

Figure A.5

M(t) (%)

2M
+ EXPERIMENTAL DATA ✦ FITTED DATA

Figure A.6

C4

□ EXPERIMENTAL DATA ⊸ FITTED DATA

Figure A.7

C2

+ EXPERIMENTAL DATA ⊸ FITTED DATA

Figure A.8

C6610

+ EXPERIMENTAL DATA ⊸ FITTED DATA

Figure A.9

4H

□ EXPERIMENTAL DATA ⊸ FITTED DATA

Figure A.10

1M

+ EXPERIMENTAL DATA ⊸ FITTED DATA

Figure A.11

H1

+ EXPERIMENTAL DATA ⊸ FITTED DATA
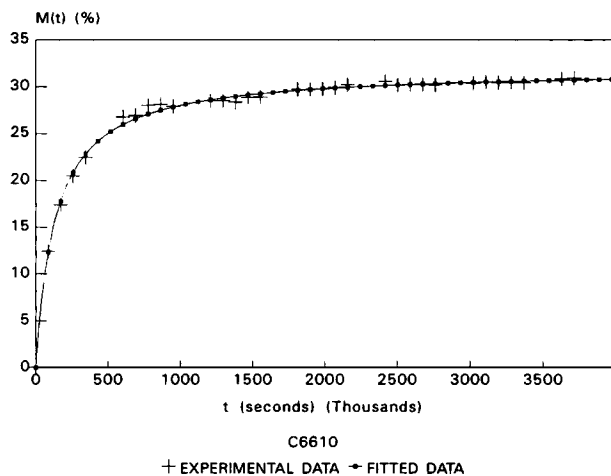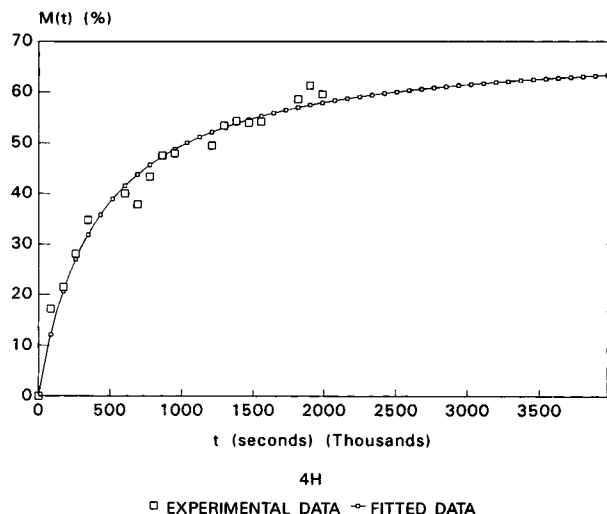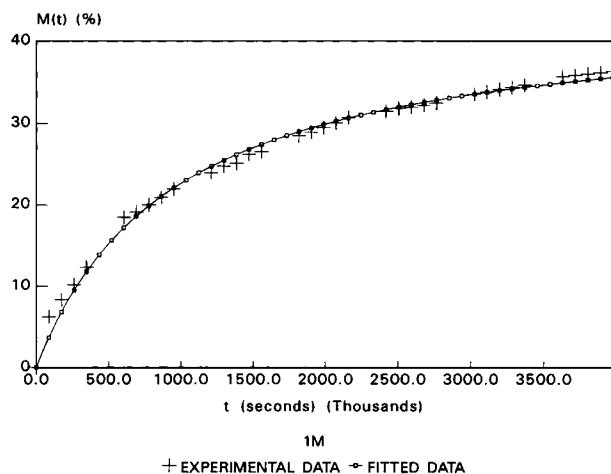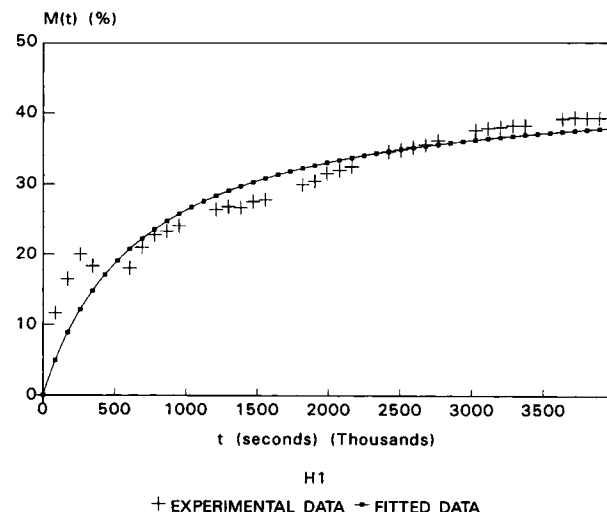
Figure A.12

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