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236

ADIPRENE®
VIBRATHANE®
polyurethane elastomers

A COMPARISON OF RUBBER WITH CAST POLYURETHANE ELASTOMERS: PROPERTIES FOR TYPICAL APPLICATIONS

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INTRODUCTION:

It is estimated that the total world market for rubber elastomers (other than for tires, tubes, foam, and coated fabric is about thirty times that of cast polyurethanes. If this 3 percent share for cast polyurethanes could be increased to 3 1/2 percent by finding new niche markets where previously rubber was only considered, it would represent an additional eleven million pound of business for our industry. Obviously not all rubber applications can be replaced with cast polyurethanes at a cost penalty of 2 to 3 times that of rubber. There may be applications where cast polyurethane brings sufficient value to justify this price. But to find them we need to have information about how the two types of elastomers compare. That's the purpose of this paper - to define cast polyurethane's assets and liabilities relative to rubber.

The paper examines a limited number of rubber and polyurethane materials. It attempts to explore some generic differences between the two categories of elastomers. It should be treated as a reference point. Obviously there are hundreds of rubber material formulations that could have been tested. Literally thousands of polyurethane materials could have been included.

CONCLUSIONS:

(1) "Letting down", or softening polyurethane with polyol curatives can lead to poor flex fatigue relative to rubber materials especially at high strains (35% to 55%).

(2) Not all polyurethanes are poor for fatigue even at 35% or more A 90A caprolactone MDI ester cured with 1-4 BD tested recently had better fatigue results than all the rubber materials tested - including the natural rubber materials.

(3) Polyurethane is best at a hardness of 80 Shore A or higher. In Competing for rubber applications polyurethane processors would do better to use a material in this hardness range and rely on design changes to remove material and achieve the same performance as the rubber part.

(4) If this industry needs to compete directly with rubber on a volume - for - volume basis, prepolymers need to be designed for the 60 to 75 Shore A range with specific performance requirements. The 72A ester polyurethane in this study is a good example of this.

(5) Surprisingly, the polyurethane materials tested here are defensive for NBS abrasion. This is a failry aggressive abrasion test with somewhat elevated contact pressure (5psi). The tread rubber - not suprisingly did best here. Past experience with aggressive dry abrasion applications indicates that the addition of 1.5 pphr of Dow Q2-3238 reactive silicone can reduce wear in this type of test by as much as 25 to 1.

(6) Friction on a clean, dry, smooth surface is generally the same for rubber and polyurethane.

(7) Polyurethanes, other than those that are not "let down" with polyol cures, are less hysteretic than rubber at high temperature.

(8) Polyurethanes tend to retain modulus better at temperatures up to 130°C.

(9) Even ether polyurethanes are equal to, or better than nitrile rubber in hydrocarbon liquids.

DETAILS:

The materials that were tested are listed in Table 1. A more detailed description of the specific ingredients and process conditions are given in the appendix.

COMPRESSION SET:

There doesn't seem to be any particular trend in the compression set results. Some urethane material are low and some high. The same is the case for rubber. Nitrile seems to be quite good. Figure 1 shows these results.

NBS ABRASION:

Normally polyurethanes do extremely well in abrasive applications . But there are many types of abrasion. In this case, with an aggressive sliding media at 5 psi contact pressure the rubber materials - particularly the tread rubber- have a distinct advantage. Figure 2 demonstrates these results.

FRICTION:

Coefficient of friction for elastomers is not a constant material property. It is a function of contact pressure and surface conditions. Friction measurements are reported at 50 and 200 psi on a smooth, dry, clean steel surface. They were obtained from a thrust washer tester as opposed to the standard ASTM sled apparatus. This uses a very low contact pressure and was considered impractical.

TABLE 1

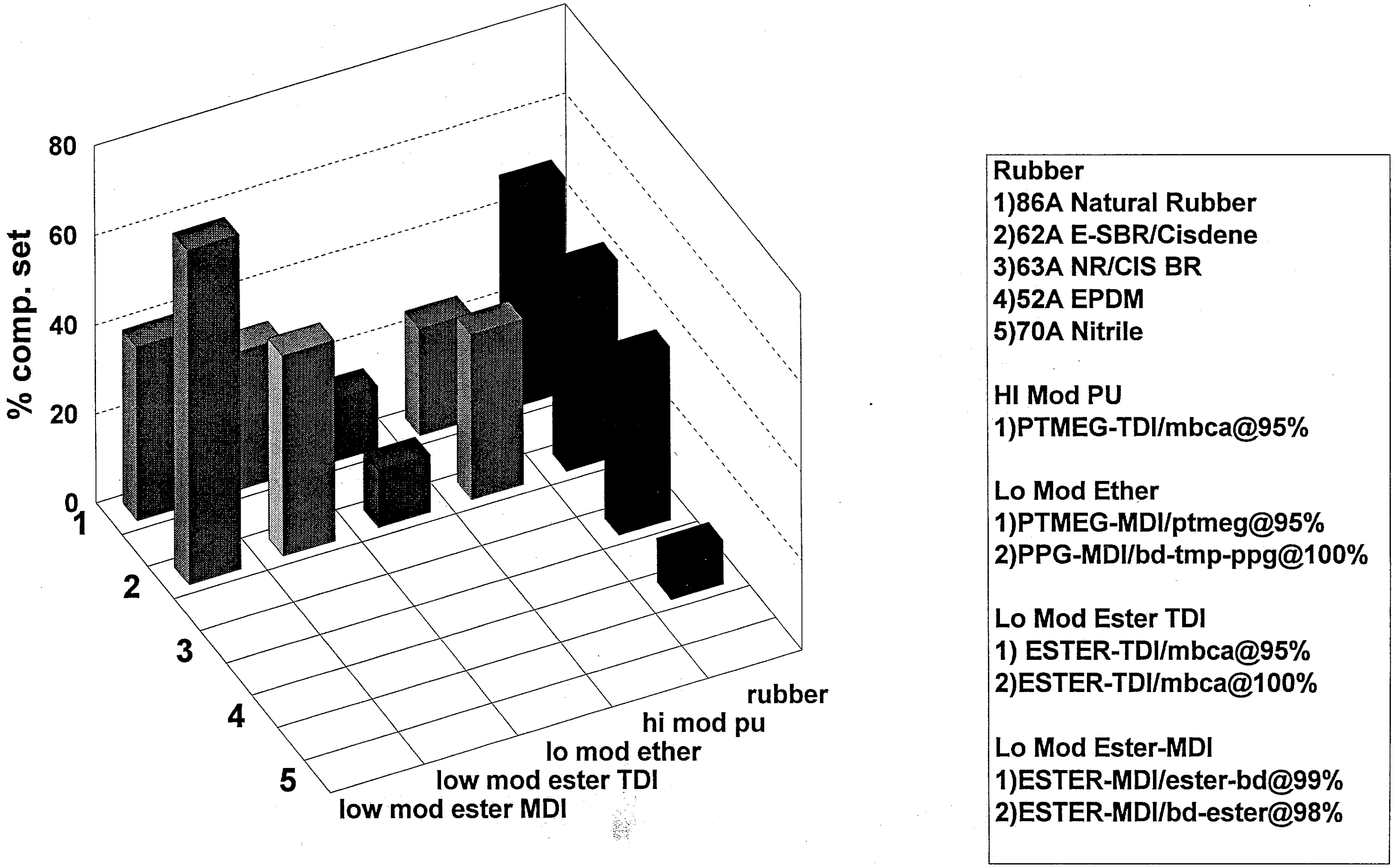
LIST of MATERIALS TESTED

Material number	Description
1	86A natural rubber used for tire rim flange stock
2	62A E-SBR/Cisdene used for tire tread stock
3	63A NR/CIS BR used for tire sidewall stock
4	52A EPDM used for engine mounts
5	70A nitrile used in wheels, belts, and rolls
6	89A low free monomer PTMEG-TDI cured with mbca @95%
7	93A low free monomer ESTER-TDI cured with mbca @97%
8	62A PTMEG-MDI cured with ptmeg polyol @95%
9	66A PPG-MDI cured with a blend of 1-4 bd, tmp, and ppg polyol
10	72A ESTER-TDI cured with mbca @95%
11	72A ESTER-TDI cured with mbca @100%
12	65A ESTER-MDI cured with 70 molar% ester polyol and 30 molar% 1-4bd @99%
13	76A ESTER-MDI cured with 70 molar% 1-4bd and 30 molar% ester polyol @98%
14	91A Caprolactone-MDI cured with 1-4bd

Compression Set by Method B

@70C, 20%

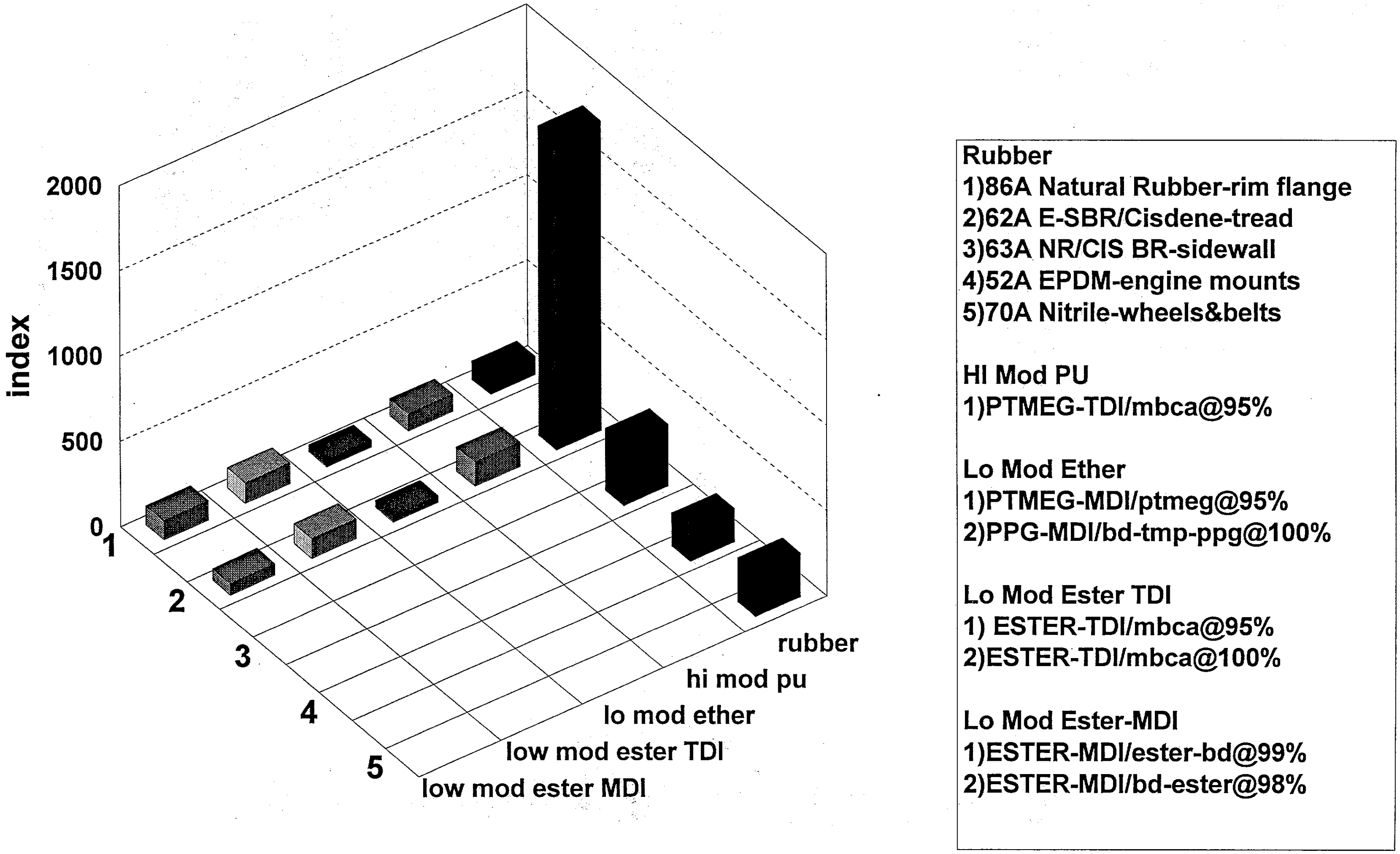
FIGURE 1



NBS Abrasion Index Measurements

larger is better

FIGURE 2



Results indicate that, contrary to popular impression, the polyurethanes tested here have somewhat higher coefficient of friction than the rubber materials tested at both 50 and 200 psi. See Figures 3 and 4. We didn't test wet friction for this paper and here the results may be different. Further testing will be needed for this.

MOONEY CONSTANTS:

There seems to be an increased call for hyperelastic constants used in non-linear F.E.A. The first two Mooney constants were measured for these materials. They were obtained from uniaxial stress-strain curves where the stress was cycled twenty times to some maximum value which produced about 25% max strain. The constants were determined by a curve fitting process in MATHCAD 5.0 (Appendix 2 has a typical result). They were also measured for 75% maximum strain cycle. Table 2 gives these results. Interestingly, these constants are strain-cycle dependent for all but a few of the elastomers.

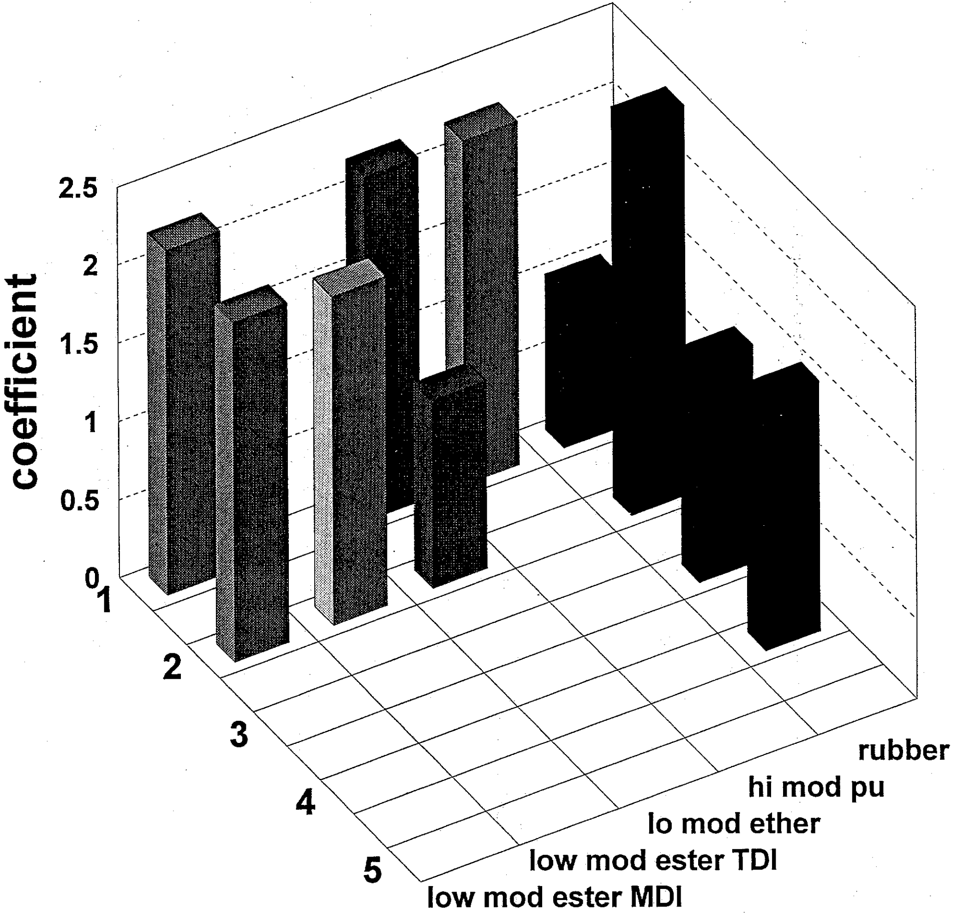
FLEX FATIGUE:

Fatigue resistance was measured on all the materials used in the previous sections plus a 91A caprolactone - MDI cure with 104 BD. The data was obtained from a Texus Flex tester at 35%, 45%, and 55%. Fatigue life was predicted for 10% - a more practical strain for most applications. This was done by the method described in the SAE recommended guidelines for fatigue testing of elastomeric materials and components - SAE J 1183. Fatigue life at the higher strains was measured because much more accurate results can be obtained at higher strains.

FRICTION COEFFICIENTS

@ 50psi contact pressure

FIGURE 3



Rubber
1)86A NR-rim flange
2)62A E-SBR/Cisdene-tread
3)63A NR/CIS BR-sidewall
4)52A EPDM-engine mounts
5)70A NITRILE-wheels&belts

Hi Mod PU
1)89A PTMEG-TDI/mbca@95%
2)93A ESTER-TDI/mbca@100%

Lo Mod Ether
1)62A PTMEG-MDI/ptmeg@95%
2)66A PPG-MDI/bd-tmp-ppg@100%

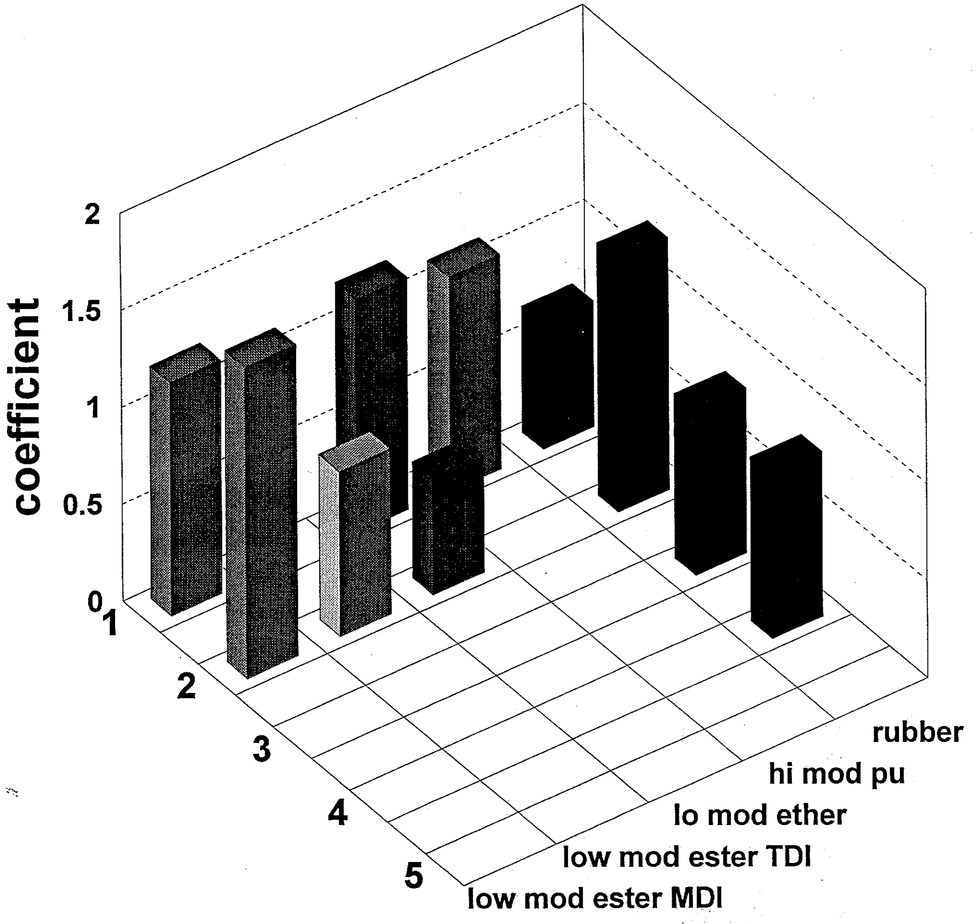
Lo Mod Ester-TDI
1)72A ESTER-TDI/mbca@95%
2)72A ESTER-TDI/mbca@100%

Lo Mod Ester-MDI
1)65A ESTER-MDI/ester-bd@99%
2)76A ESTER-MDI/bd-ester@98%

FRICTION COEFFICIENTS

@ 200psi contact pressure

FIGURE 4



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2)72A ESTER-TDI/mbca@100%

Lo Mod Ester-MDI
1)65A ESTER-MDI/ester-bd@99%
2)76A ESTER-MDI/bd-ester@98%

TABLE 2

Mooney Constants

	C1	C2	C1	C2	C1	C2
	@~25%		@~75%		@~150%	
Natural Rubber (rim flange stock)	-105	386	-104	375		
E-SBR/Cisdene(tread stock)	62	44	4	79		
NR/CIS BR(sidewall stock)	-5	129	18	81		
EPDM(for engine mounts)	12	56			15	40
Nitrile(for wheels and belts)	24	131	13	111		
PTMEG-TDI/Mbca@95%	-309	929				
ESTER-TDI/Mbca@97%						
PTMEG-MDI/Ptmeg@95%	48	41			17	47
PPG-MDI/BD-TMP-PPG@100%	32	89			47	25
ESTER-TDI/Mbca@95%	393	-148	40	73		
ESTER-TDI/Mbca@100%	239	72	49	84		
ESTER-MDI/Bd-ESTER@98%	190	74	34	146		
Capralactone-MDI/BD@99%	-2942	4172				

The extrapolation was done in MATHCAD by a log-log fit. The 10% fatigue values were calculated from the resulting equation for cycles to failure vs strain energy density. Appendix 3 shows a typical derivation. Figure 5 shows the results of the fatigue testing at 35%, 45% and 55% strain. The first five materials shown are the rubber materials. The last material (#16) is the 91A caprolactone - MDI. It is clear that the "let-down" polyurethanes are very defensive relative to rubber at high strains. However at 35% the 91A caprolactone ester material - without even considering higher strain energy - is very comparable to the rubber materials.

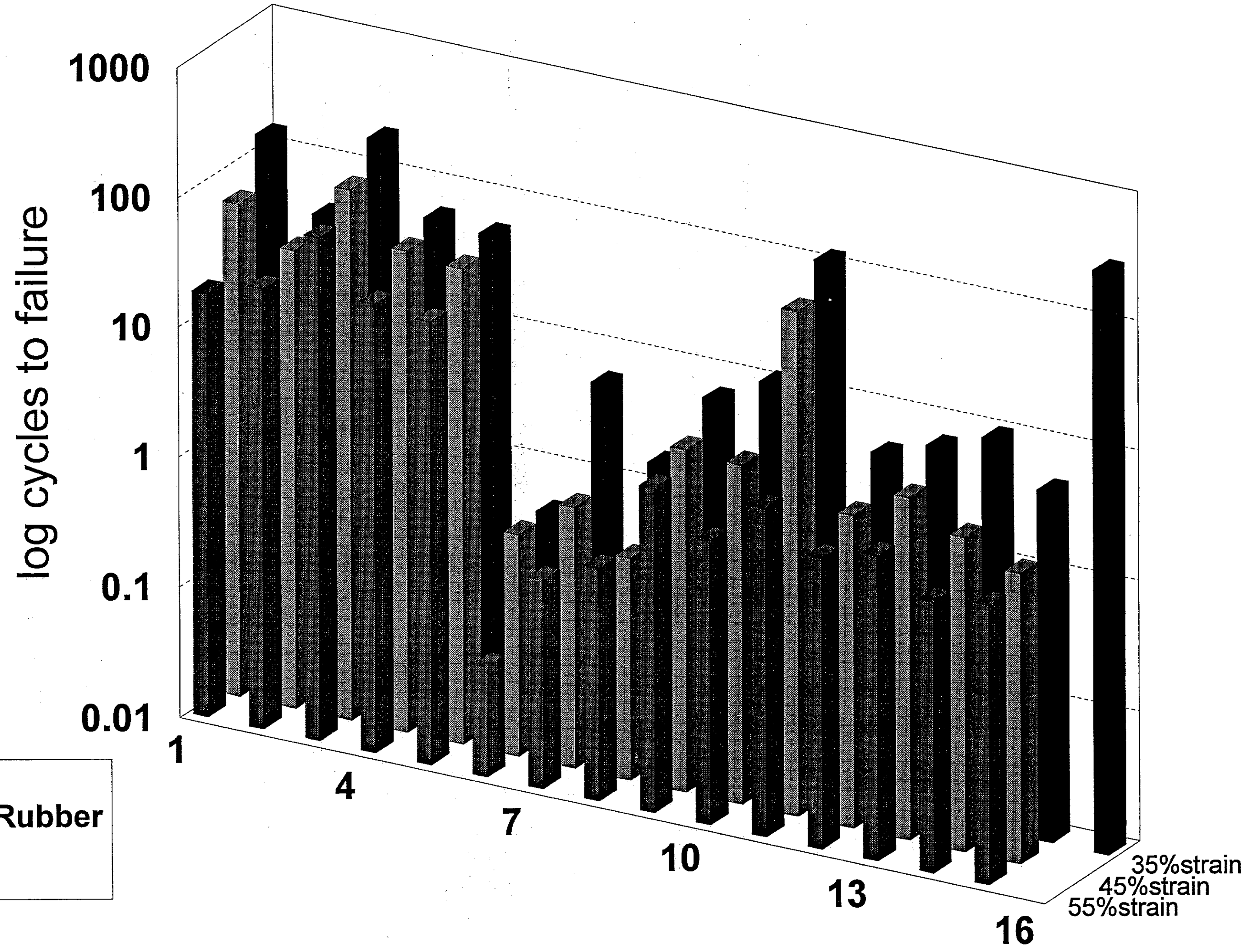
The rubber materials in this study have a lower sensitivity to high strains. In order to compare materials with a range of modulus, as is the case here, a fatigue resistance index was calculated. This is given by the following:

INDEX=(CYCLES to FAILURE)X(STRAIN ENERGY DENSITY)/1000

Figure 7 is a plot of this index for 10% strain. The ester-TDI at 100% stoichiometry compares quite well with the various rubber materials. The same index was calculated for 35% strain (Figure 8). The ester-TDI @ 100% still looks good at 35%. The 91A caprolactone - MDI proves that polyurethanes <u>can</u> have superior fatigue properties. The 72A ester-TDI demonstrates the advantage of a prepolymer that is designed to be a low modulus material.

Texus Flex Fatigue

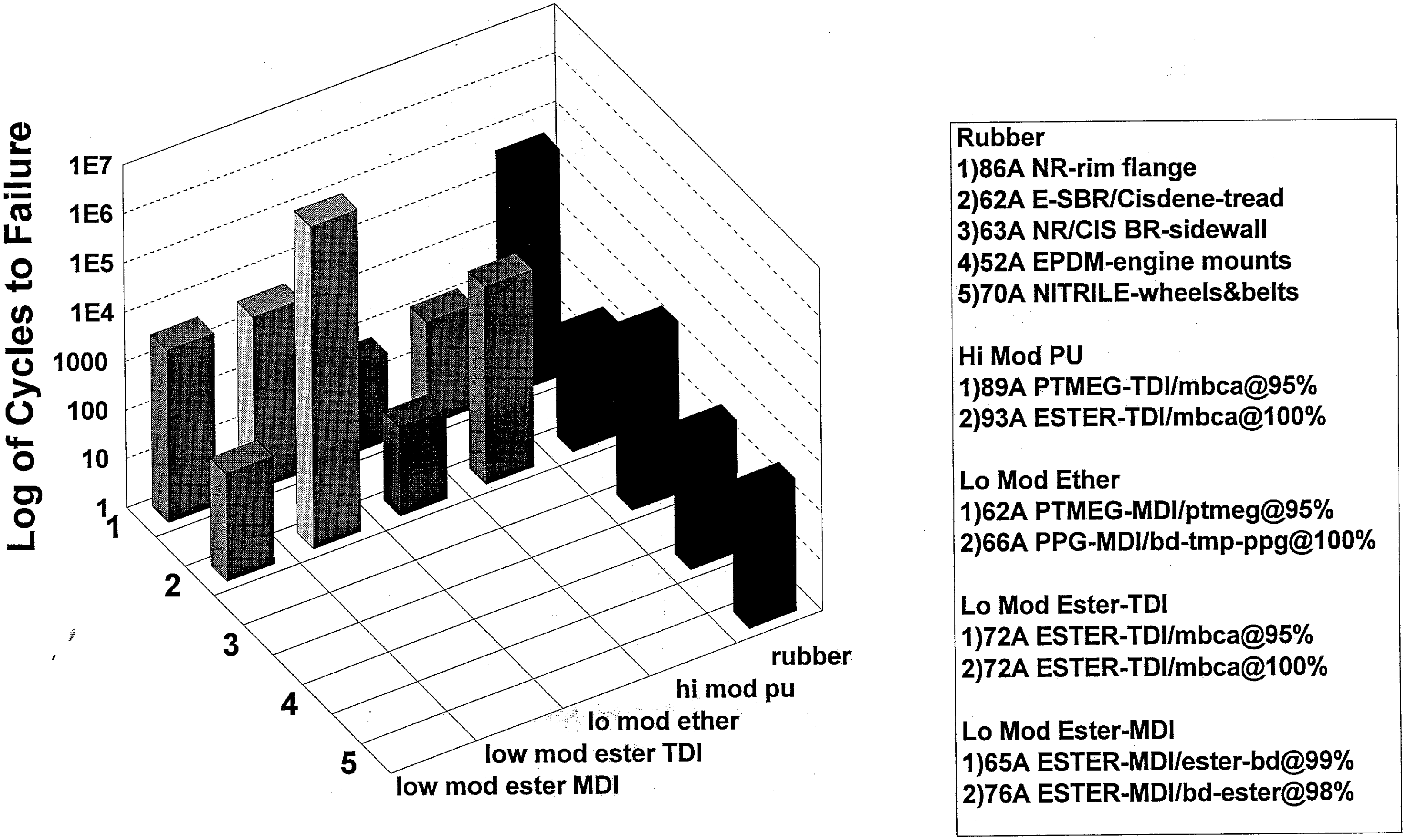
FIGURE 5



The First Five Materials Are Rubber Materials

TEXUS FLEX FATIGUE
Projected Cycles to Failure @10%

FIGURE 6

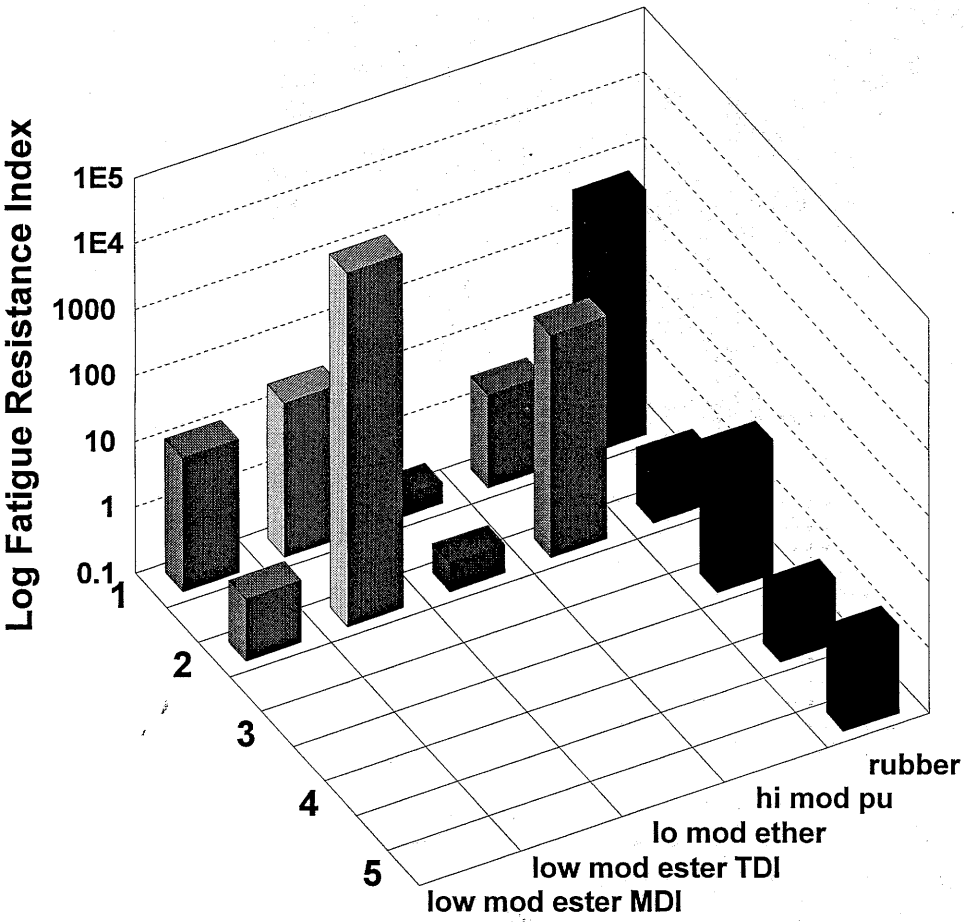


TEXUS FLEX FATIGUE

Projected Fatigue Resistance Index-10%

Index=cyclesXstrain energy density/1000

FIGURE 7



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Lo Mod Ester-TDI
1)72A ESTER-TDI/mbca@95%
2)72A ESTER-TDI/mbca@100%

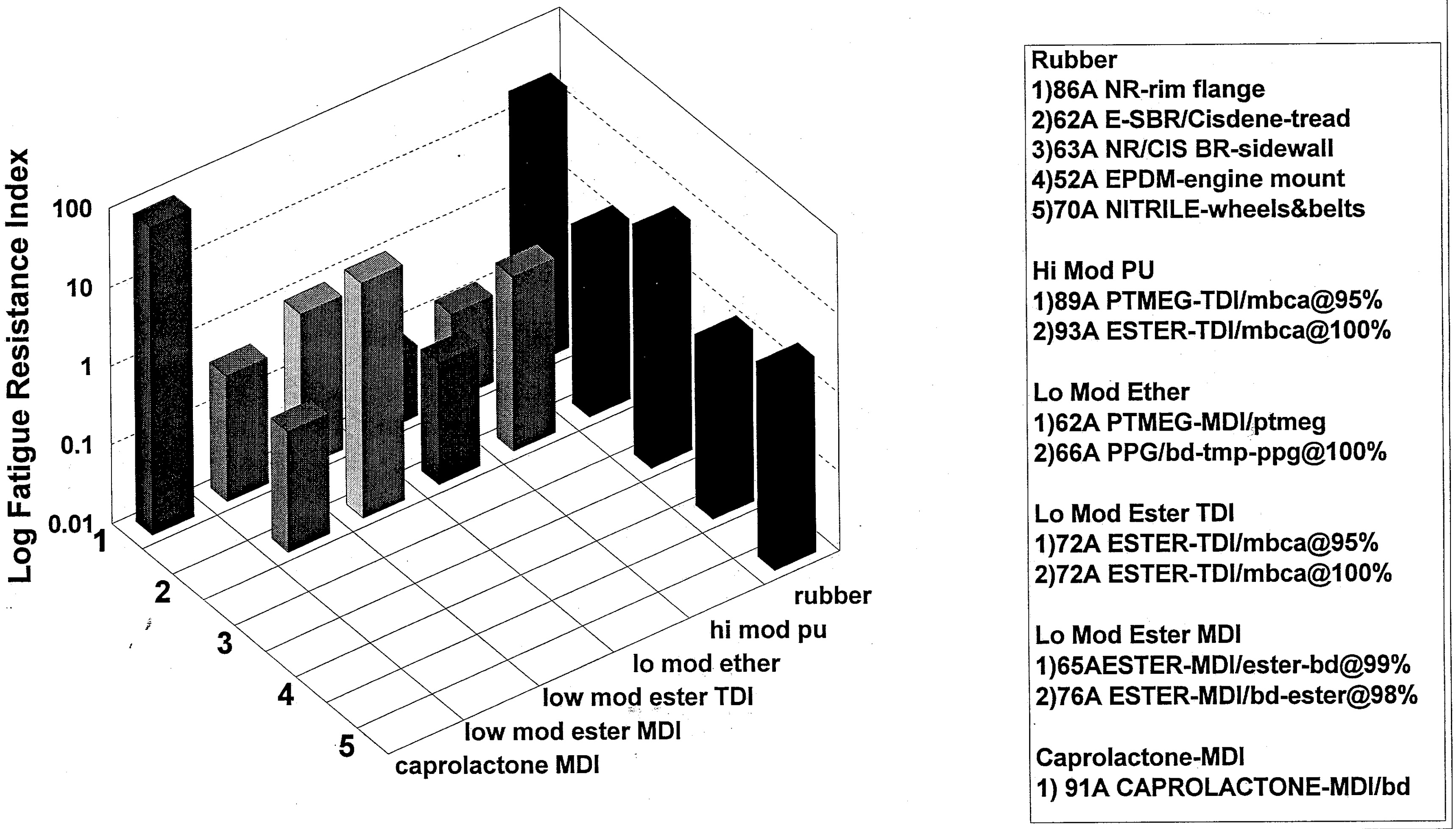
Lo Mod Ester-MDI
1)65A ESTER-MDI/ester-bd@99%
2)76A ESTER-MDI/bd-ester@98%

TEXUS FLEX FATIGUE

Fatigue Resistance Index @35%

Index=cyclesXstrain energy density/1000

FIGURE 8



DYNAMIC MODULUS AND TANδ VS TEMPERATURE:

Dynamic modulus and tanδ were measured on a Rheometrics tester for temperatures from - 50°C to 200°C. For many applications - for example, solid wheels and die springs, - heat build-up due to repeated cycling of strain is important design consideration.

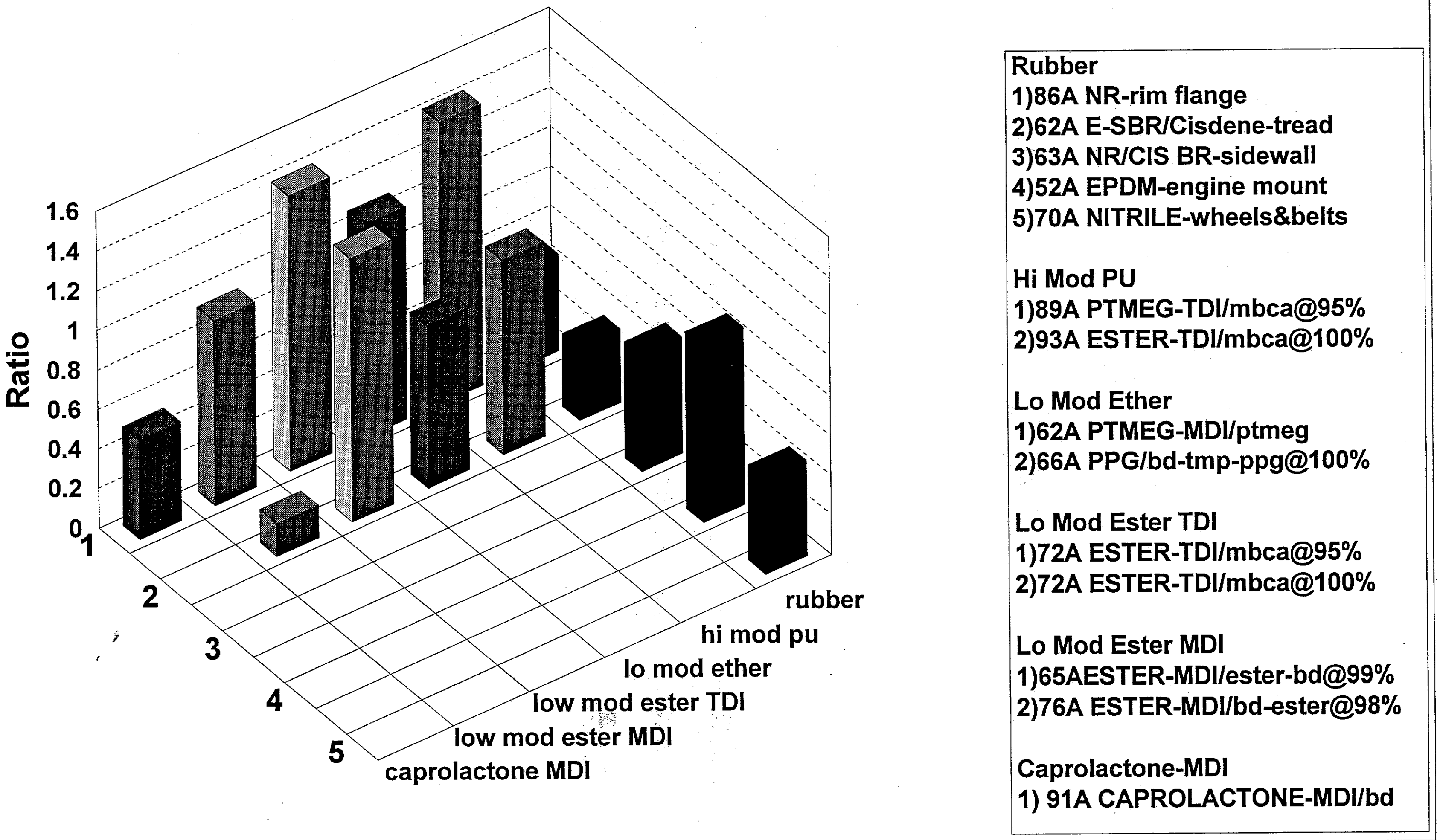
In this case, it is important to know how the material maintains modulus as it heats up. Figure 9 is a graph of the ratio of modulus at 130°C to the modulus at 30°C. A ratio of one or more is desirable since many applications are load determined or require a well defined load at a given deflection. Here the polyurethane materials generally do well relative to rubber - particularly the materials not softened by polyol cures. Low temperature modulus retention is also important for many applications not only where cold temperatures are involved, but also where very high strain cycle frequencies are encountered. Figure 10 is a graph of the ratio of the modulus at - 30°C to the modulus at 30°C. (A ratio of one is desirable.)

The ether, the caprolactone and four of the rubber materials (nitrile excepted) are best for this property. Many parts that are cycled - particularly ride wheels - will get so hot internally due to hysteresis that they either lose bond or melt at their geometric center. In this case hysteretic properties as well as modulus retention is important. Figure 11 shows the tanδ values for the test materials. High tanδ usually leads to increased heat build-up. Here the polyurethanes, with the exception of the "let-down" ester - MDI materials, are generally better than the rubber materials.

Dynamic Modulus/Temperature Ratio
@130C/30C- one or more is better

G'(130C)/G'(30C)

FIGURE 9

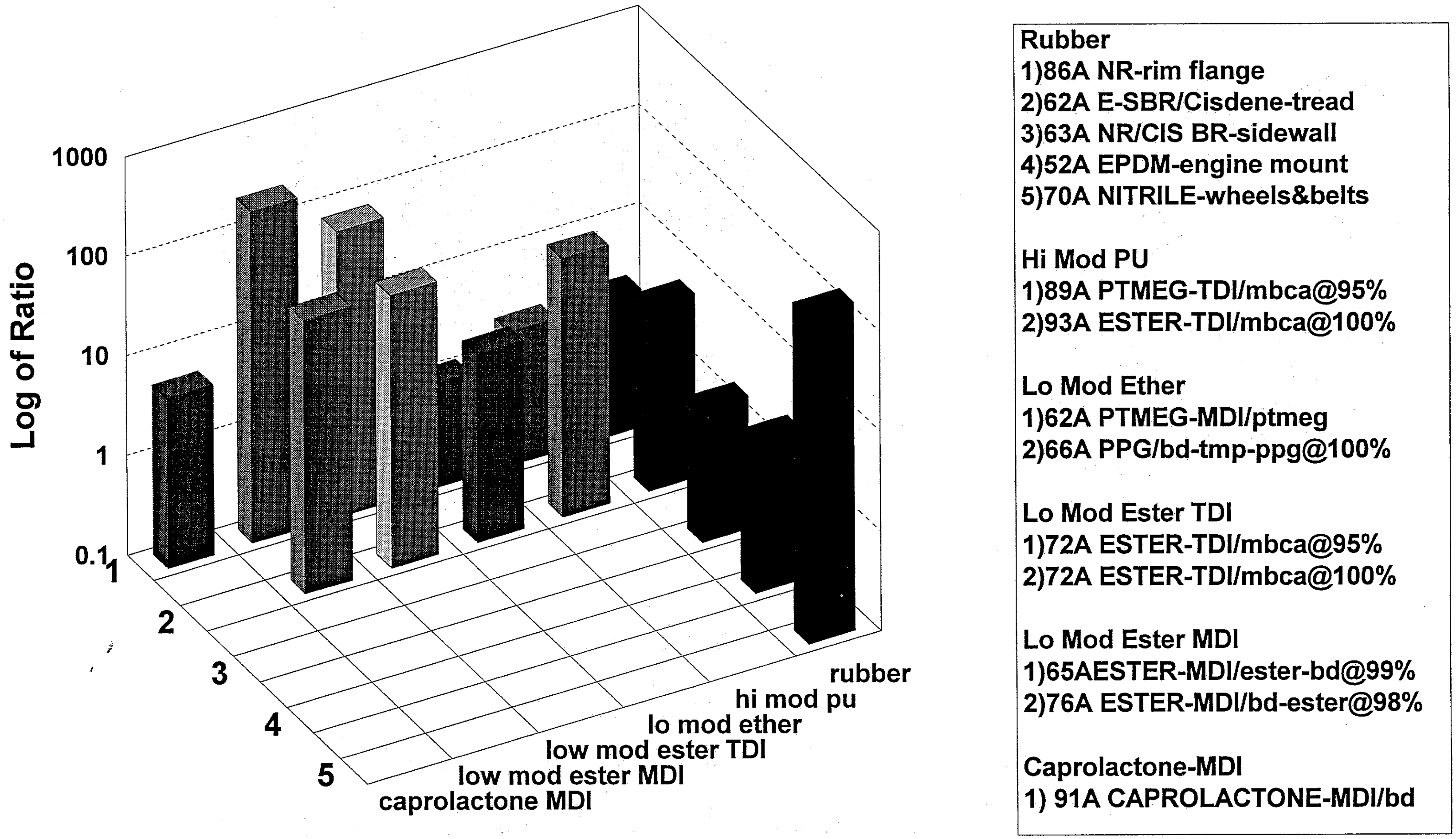


Dynamic Modulus/Temperature Ratio

@-30C/30C

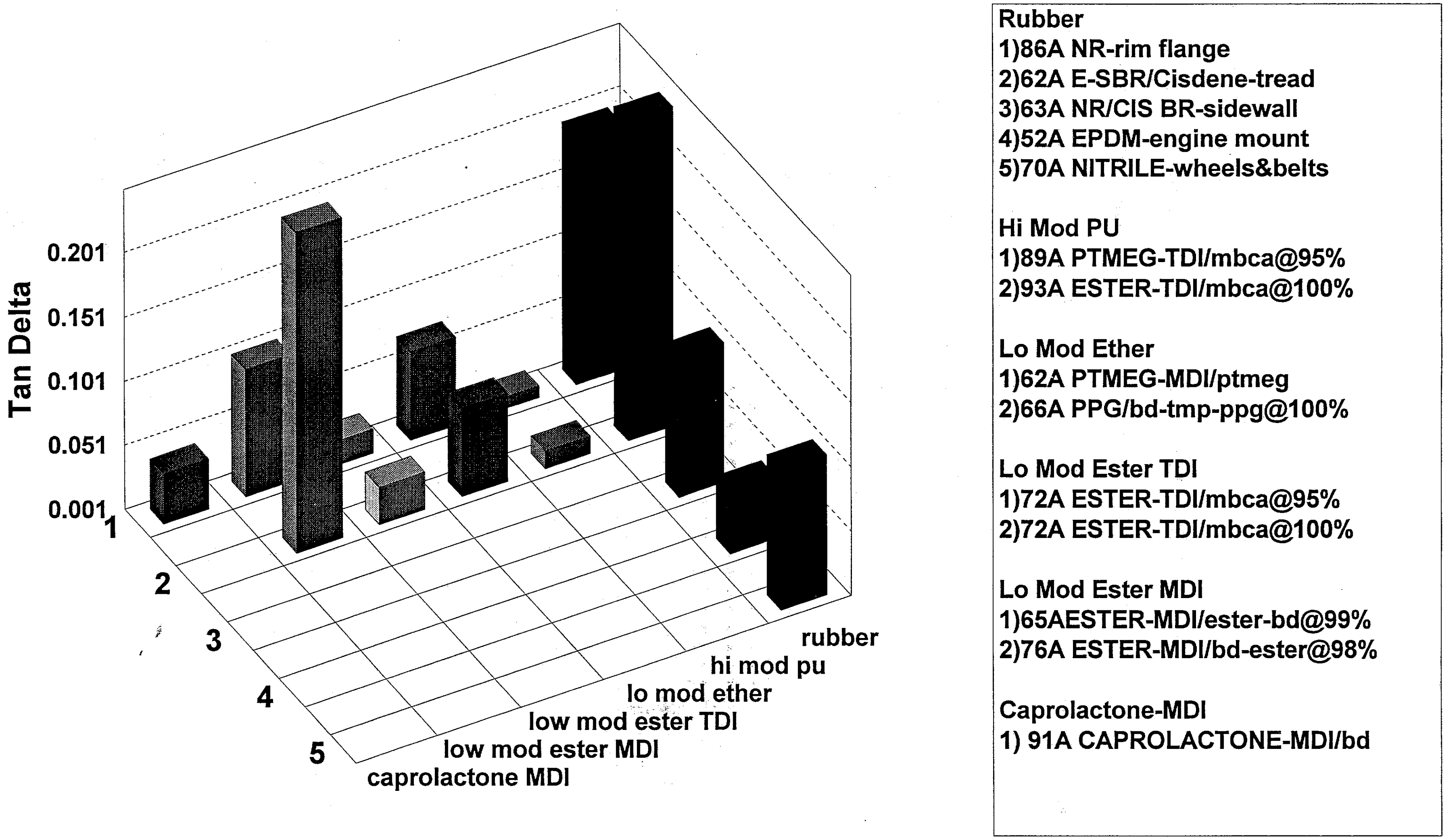
G'(-30C)/G'(30C)

FIGURE 10



Tan Delta
@130C

FIGURE 11



THERMAL CONDUCTIVITY:

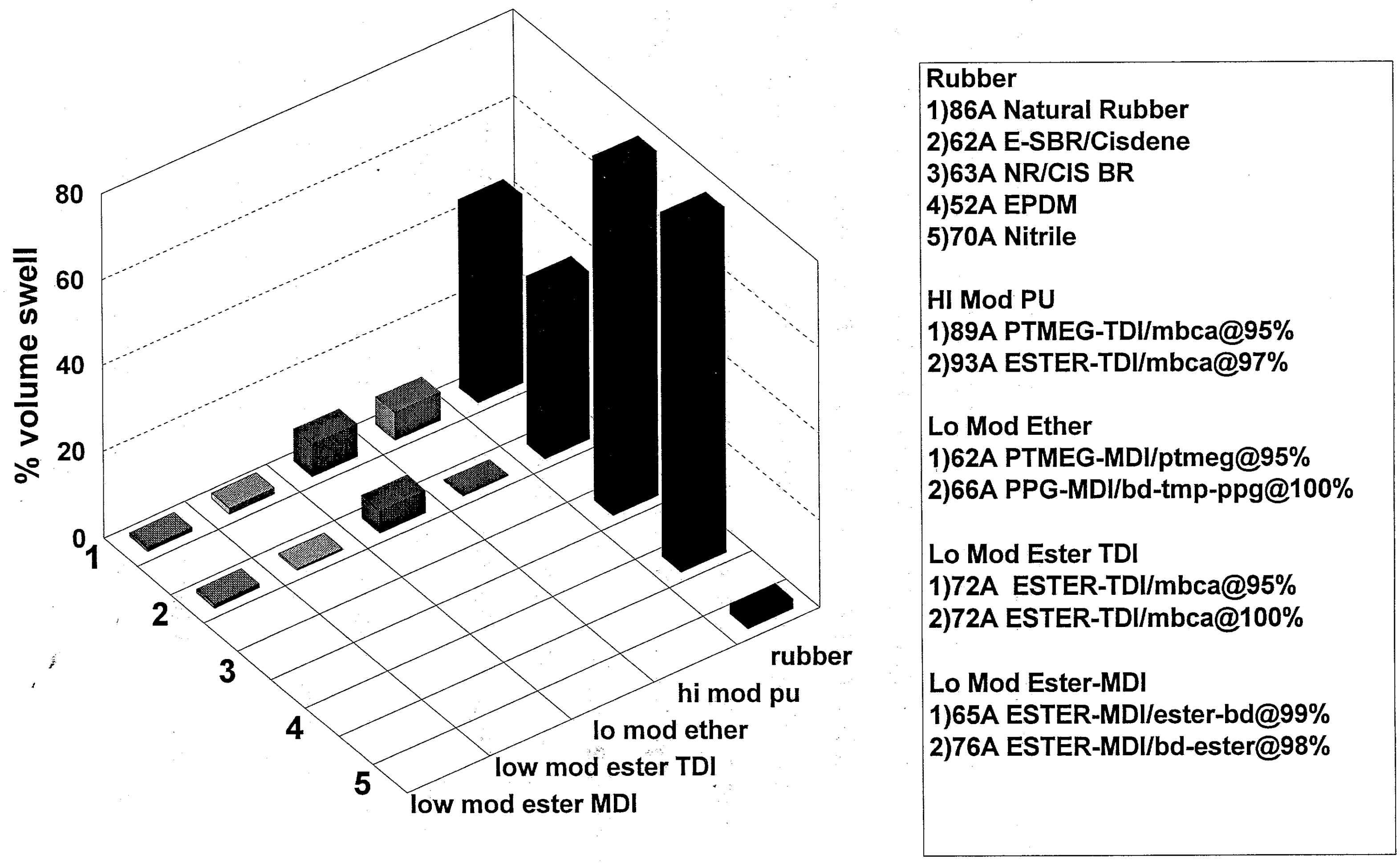
In dealing with heat build-up there are three design options: (1) tolerate more; (2)generate less: or (3) get rid of it better. Thermal conductivity addresses the third option. It was anticipated that the high carbon black loading of the rubber material would result in higher thermal conductivity. Figure 12 demonstrates that this expectation was correct. It's possible that higher thermal conductivity could off set higher hysteretic properties. To examine the relative importance of these properties, a comparison was made between the predicted performance of the 70A nitrile rubber and the 72A ester-TDI polyurethane in a 12x6x7.5 solid wheel. Both materials are used in solid industrial tires. A computer tire model was used. It requires modulus, tanδ and thermal conductivity to predict heat related failures in solid wheels. Figure 13 shows the result of this analysis and demonstrates the importance of low hysteresis. The 72A ester-TDI carries twice the load of the nitrile. Of course one might question what effect the higher modulus retention of the ester-TDI had on the final result. In figure 14 the lower modulus of the nitrile rubber was imposed on the ester polyurethane.

Even here the polyurethane is predicted to carry more load. Figure 15 is a graph of predicted rolling resistance near the failure load. The polyurethane develops significantly lower power consumption. For electric vehicles this could be an important consideration.

Volume Swell after Oil/Fuel Aging@70C

% volume swell after 24 hours

FIGURE 16



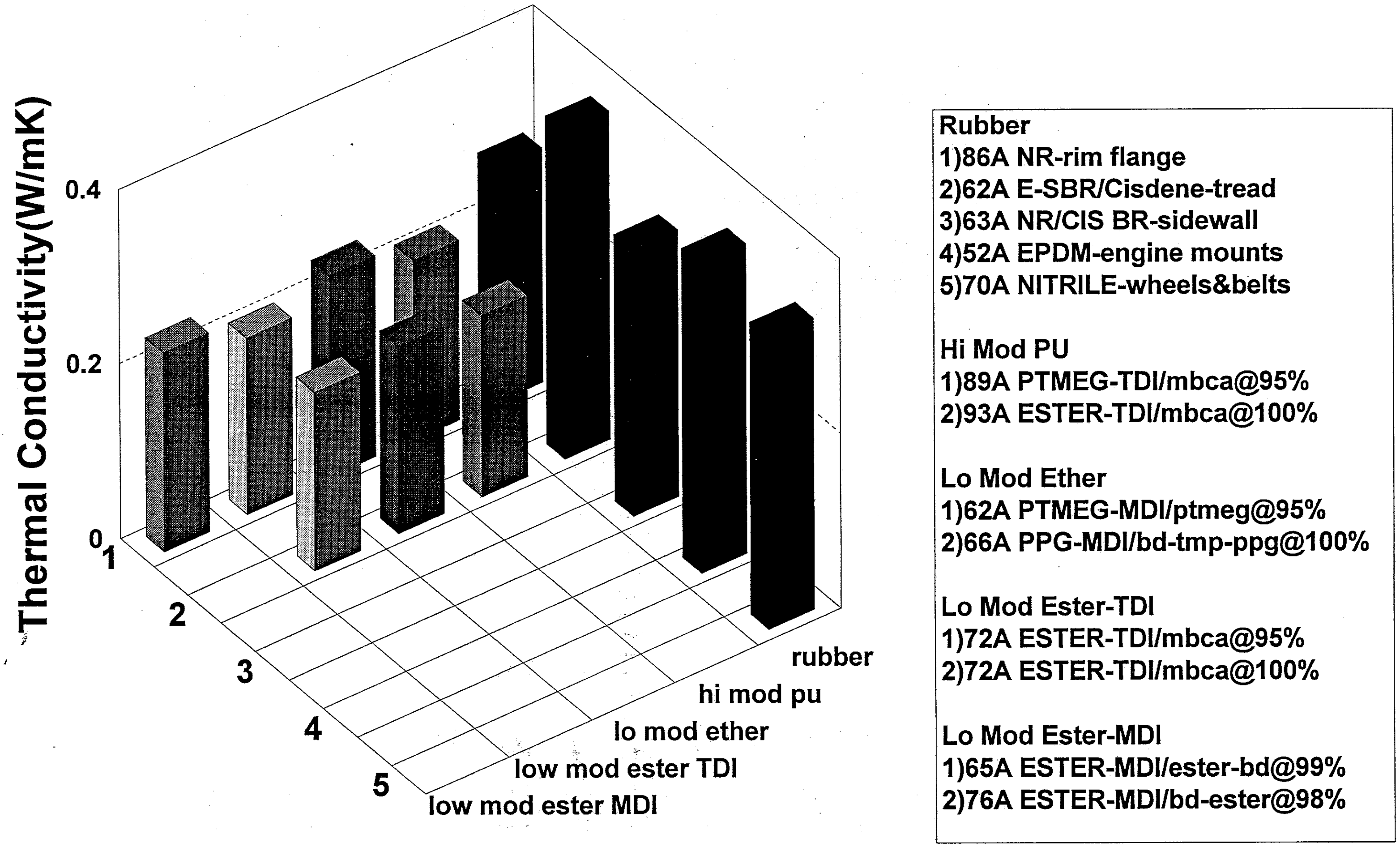
HYDROCARBON FLUIDS AGING:

The effects of various environmental conditions on rubber and polyurethane is fairly well known. For example, polyurethane is virtually immune to ozone while rubber generally is attached by ozone and must be protected by anti-ozonates. Ester-TDI polyurethane is slowly attached in hot, humid environments. But many applications like engine mounts involve exposure to hydrocarbon fluids. Here the differences are not well known. In the rubber industry it is known that nitrile rubber is superior to other rubber materials in hydrocarbon fluids. But it was not clear how the two classes of elastomer compared to one another in hydrocarbons. To do this comparison parts were tested before and after immersion in a 70°C mixture of 80/20 oil-diesel fuel. Previous testing indicated that most damage was done in 24 hours. Figure 16 shows the effect of 24 hours aging on volume swell. Figure 17 gives the effect on Shore A hardness. Finally Figures 18 and 19 are plots of D 1938 tear before aging and % change after aging respectively. Interestingly, nitrile rubber compares favorably with cast polyurethane until this comparison of tear resistance is made. Also, the ether materials, while not as good as the esters, are very comparable to the nitrile rubber.

FIGURE 12

THERMAL CONDUCTIVITY

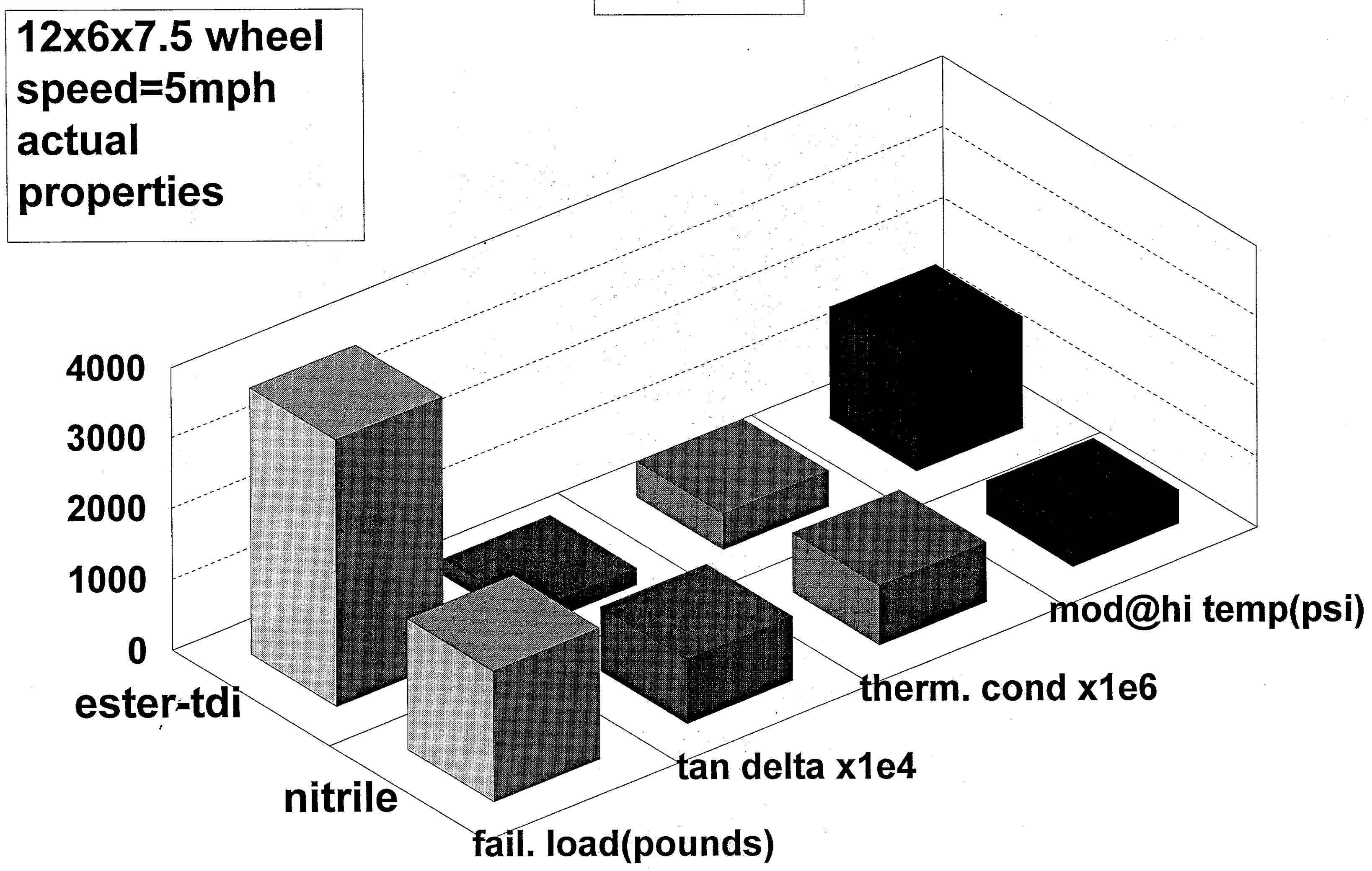
(Watts per Meter Degree Kelvin)



SOLID WHEEL MAXIMUM LOAD

Comparison of ester-tdi & nitrile

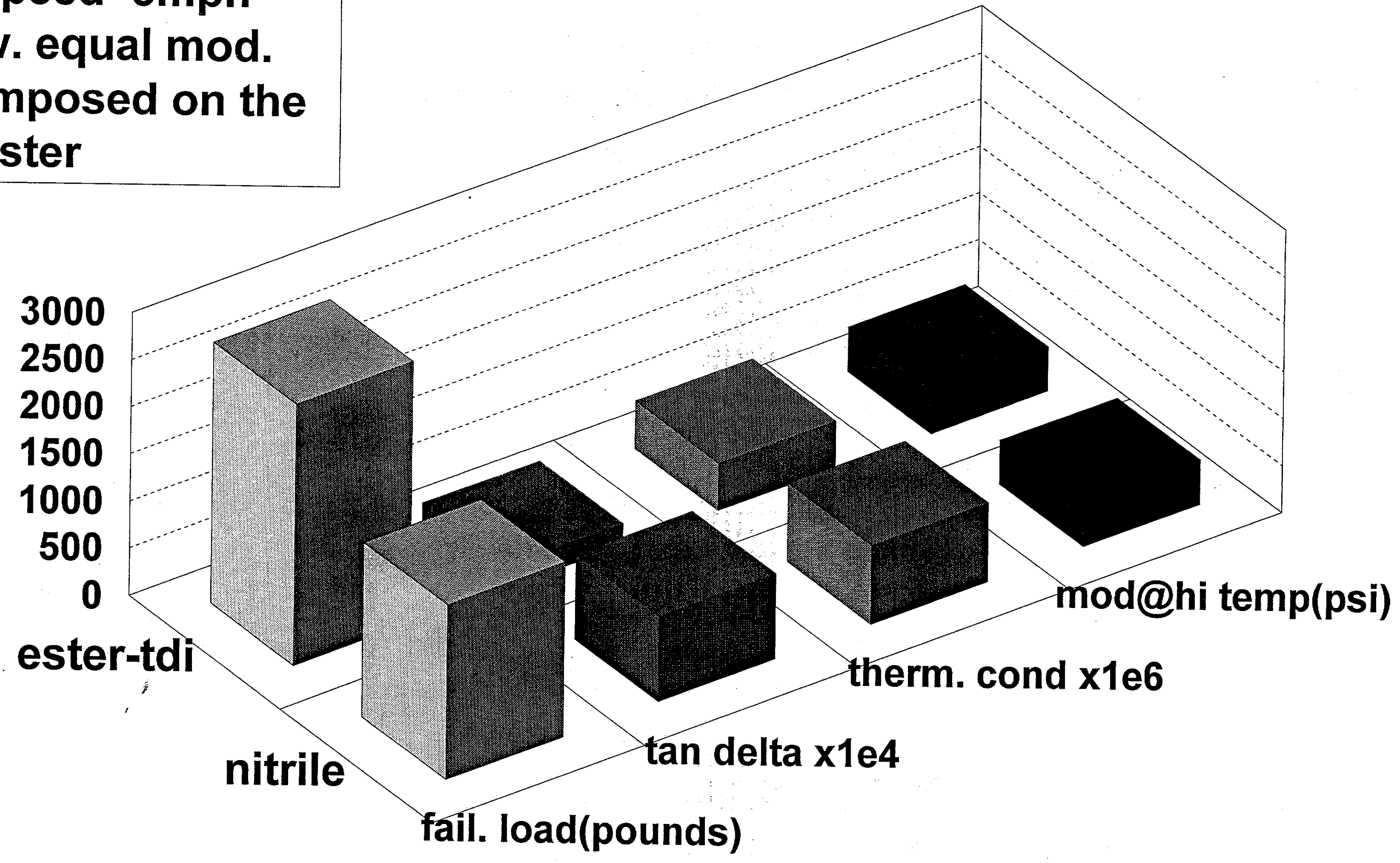
FIGURE 13



SOLID WHEEL MAXIMUM LOAD

Comparison of ester-tdi & nitrile

FIGURE 14

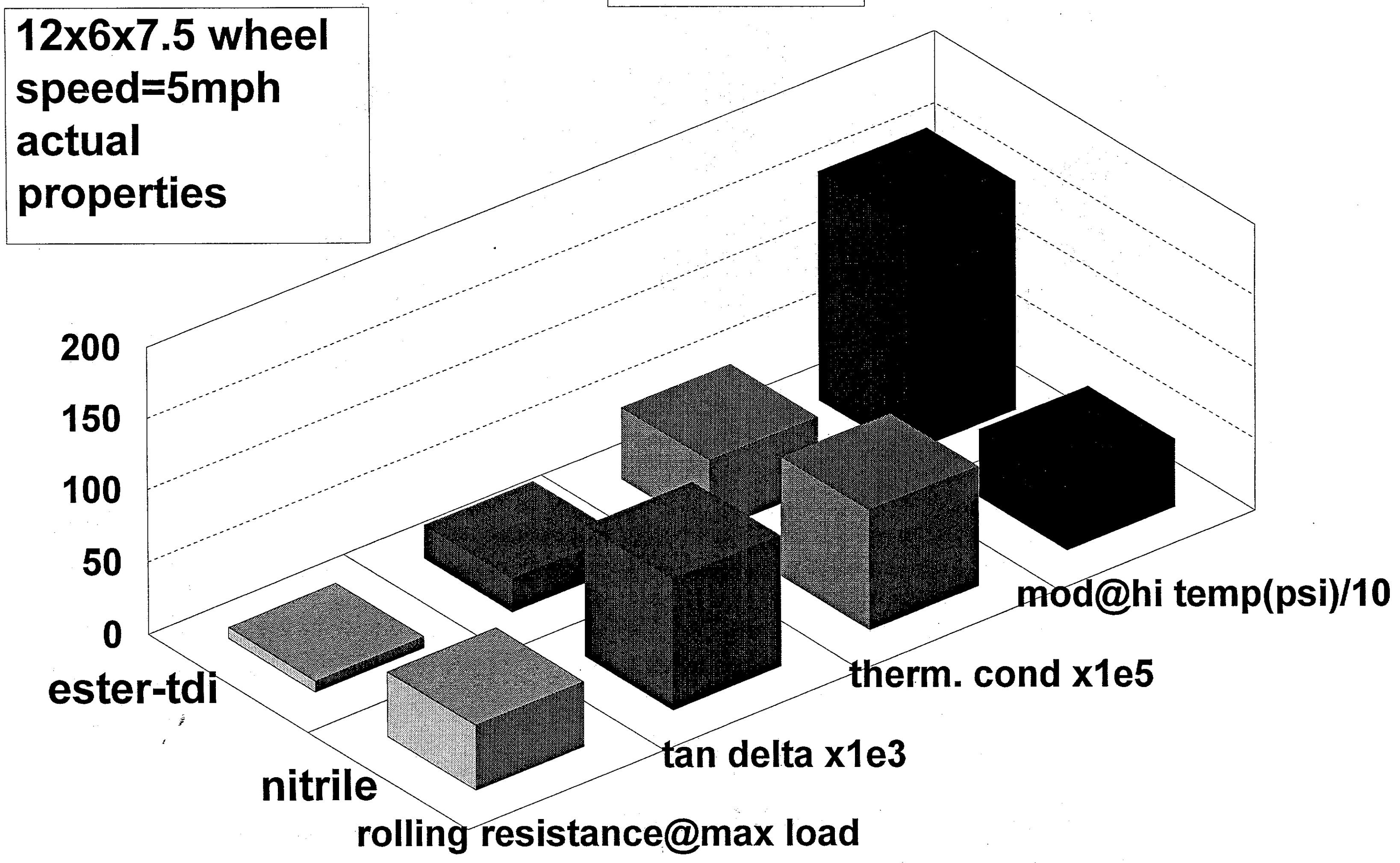


12x6x7.5 wheel
speed=5mph
w. equal mod.
imposed on the
ester

ROLLING RESISTANCE COMPARISON

RR(lbs.) values at max loads

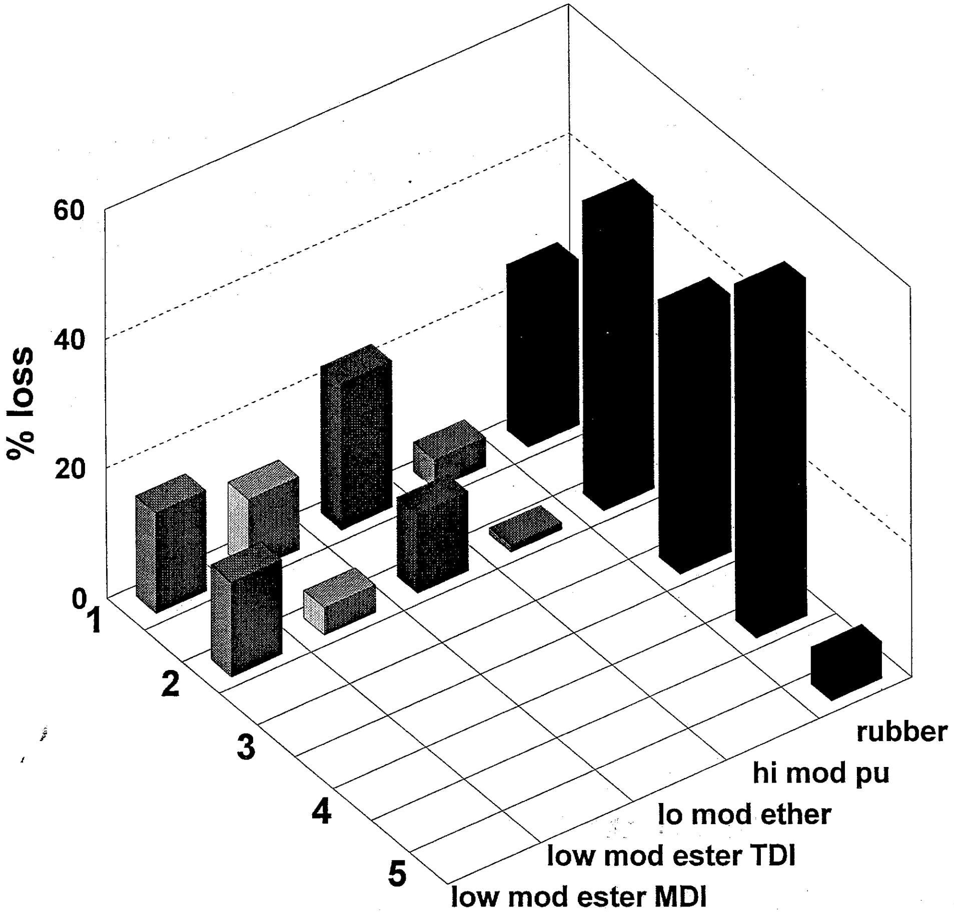
FIGURE 15



Shore A Change with Oil/Fuel Aging@70C

% Shore A loss after 24 hours

FIGURE 17



Rubber
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2)62A E-SBR/Cisdene
3)63A NR/CIS BR
4)52A EPDM
5)70A Nitrile

HI Mod PU
1)PTMEG-TDI/mbca@95%

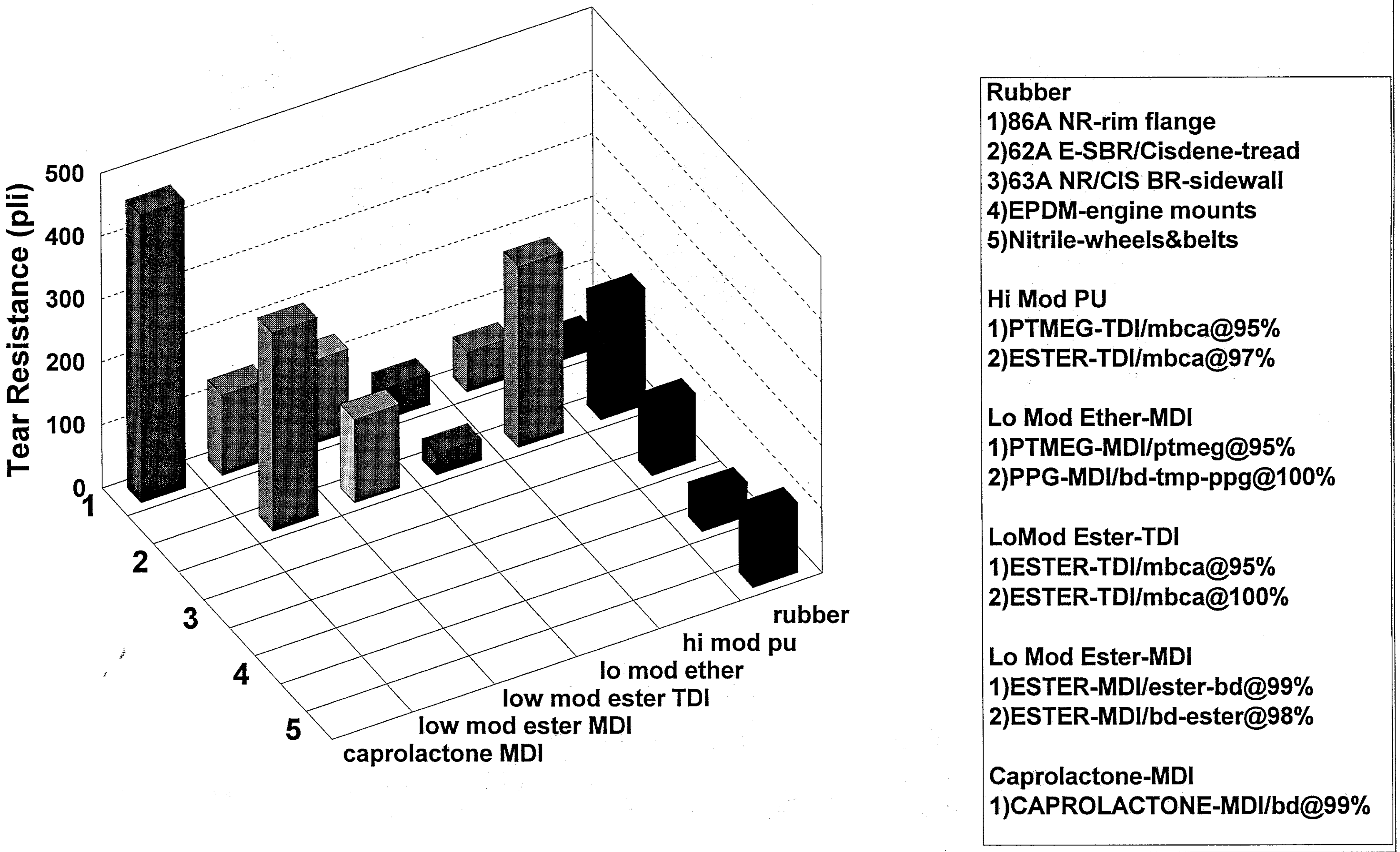
Lo Mod Ether
1)PTMEG-MDI/ptmeg@95%
2)PPG-MDI/bd-tmp-ppg@100%

Lo Mod Ester TDI
1) ESTER-TDI/mbca@95%
2)ESTER-TDI/mbca@100%

Lo Mod Ester-MDI
1)ESTER-MDI/ester-bd@99%
2)ESTER-MDI/bd-ester@98%

D1938 Trousers Tear

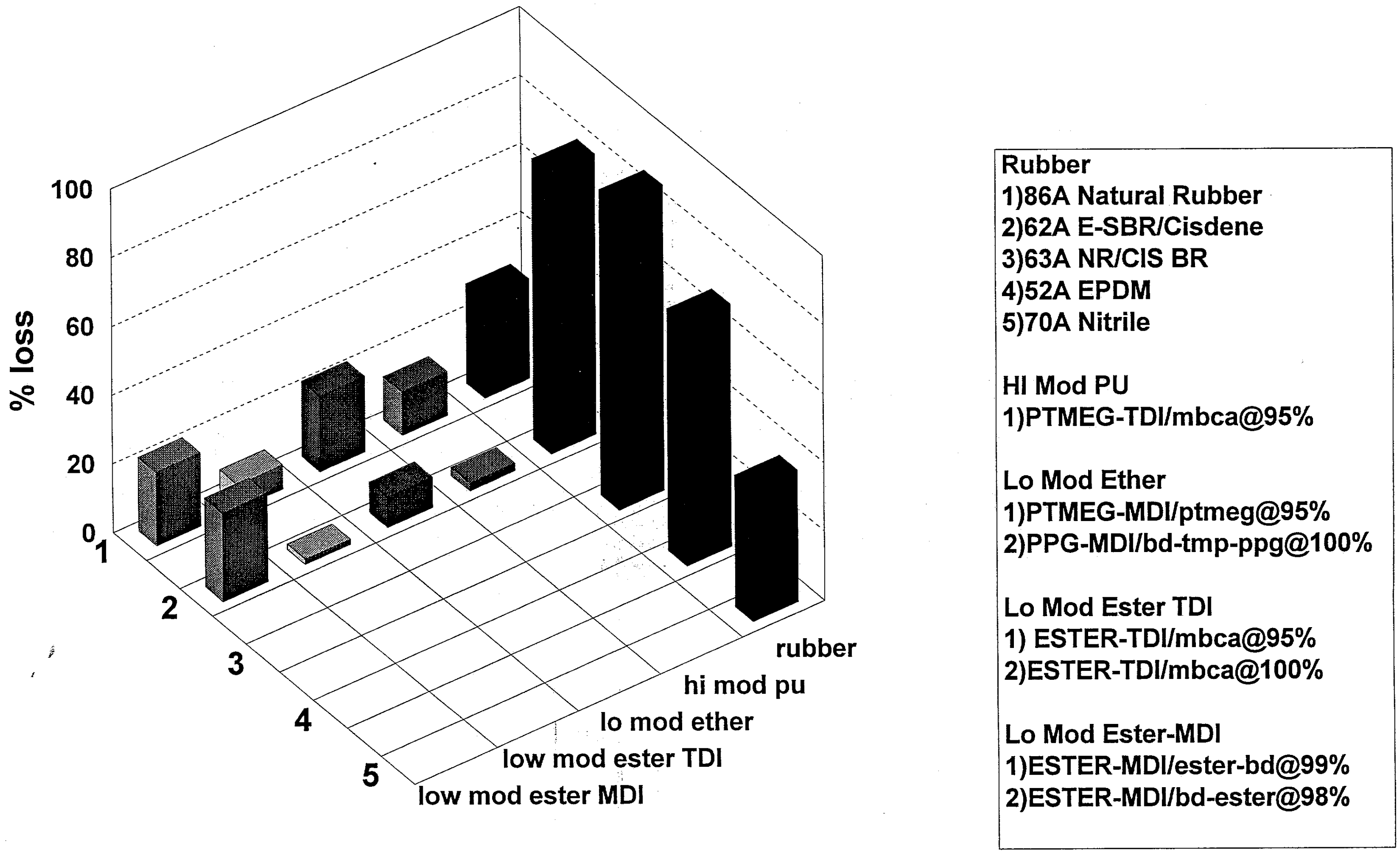
FIGURE 18



Aged D1938 Trousers Tear Results

% loss after aging in oil/desil fuel

FIGURE19



APPENDIX 1a
MATERIAL FORMULATIONS and PROCESS CONDITIONS

Material #1(rim flange rubber)

Ingredients	MB-1
1 SIR	100
2 SP-6700	10
3 N-351 BLACK	55
4 SUNDEX 790	5
5 ZINC OXIDE (KADOX 911)	10
6 STEARIC ACID	2
7 DYPHENE RESIN 8330	2
8 NAUGARD Q	2
MB-1	186
9 BONDING AGENT M3P	2
10 DELAC NS	0.6
11 BENZYL TUEX	0.25
12 SANTOGARD PVI	0.25
13 CRYSTEX SULFUR-80%	5

Material #2(tread rubber)

Ingredients	MB-1
1 E-SBR 1712	82.4
2 E-SBR 1500	20
3 Cisdene 1203	20
4 N-339 Carbon Black	85
5 Sundex 790	27.3
6 Kaddox 911C	3
7 Stearic Acid	1
8 Flexone 7P	1
9 Sunproof Wax Jr.	0.5
MB-1	
10 BONDING AGENT M3P	
11 DELAC NS	
12 BENZYL TUEX	
13 SANTOGARD PVI	
14 CRYSTEX SULFUR-80%	

Material #3(sidewall rubber)

Ingredients	
1 SIR 20 NATURAL RUBBER	60
2 CIS-BR	40
3 N-330 CARBON BLACK	50
4 NAPTHENIC OIL	7
5 FLEXONE 7P	2
6 DURAZONE 37	2
7 ZINC OXIDE	4
8 STEARIC ACID	2
9 WAX	2
10 DELAC NS	1
11 SULFUR	2

Material #4(EPDM)

Ingredients	
1 ROYALENE x3832	170
2 N-650 Black	65
3 Calsol 8240 Oil	8
4 TE 88XL	2
5 Zinc Oxide	5
6 Stearic Acid	1.5
7 Delac NS	1
8 DiCip 40KE	1.5
9 Crystex Sulfur 80%	1

Material #5(Nitrile)

1 PARACRIL X4012	100
2 IRB #6	40
3 KADOX 911C	3
4 Stearic Acid	1
5 DELAC NS	0.7
6 SPIDER SULFUR	1.5

$$F(x) := \begin{bmatrix} 2\cdot\left(x - \dfrac{1}{x^2}\right) \\ 2\cdot\left(1 - \dfrac{1}{x^3}\right) \end{bmatrix} \qquad vx := \begin{bmatrix} 1 \\ 1.08 \\ 1.17 \\ 1.25 \\ 1.33 \\ 1.5 \\ 1.58 \end{bmatrix} \qquad vy := \begin{bmatrix} 0 \\ 51 \\ 90 \\ 119 \\ 145 \\ 186 \\ 205 \end{bmatrix}$$

$W := \mathrm{linfit}(vx, vy, F)$

$$W = \begin{pmatrix} 40.075 \\ 73.021 \end{pmatrix} \quad \begin{matrix} =c1(psi) \\ =c2(psi) \end{matrix}$$

$r := 1, 1.125 .. 2.0$

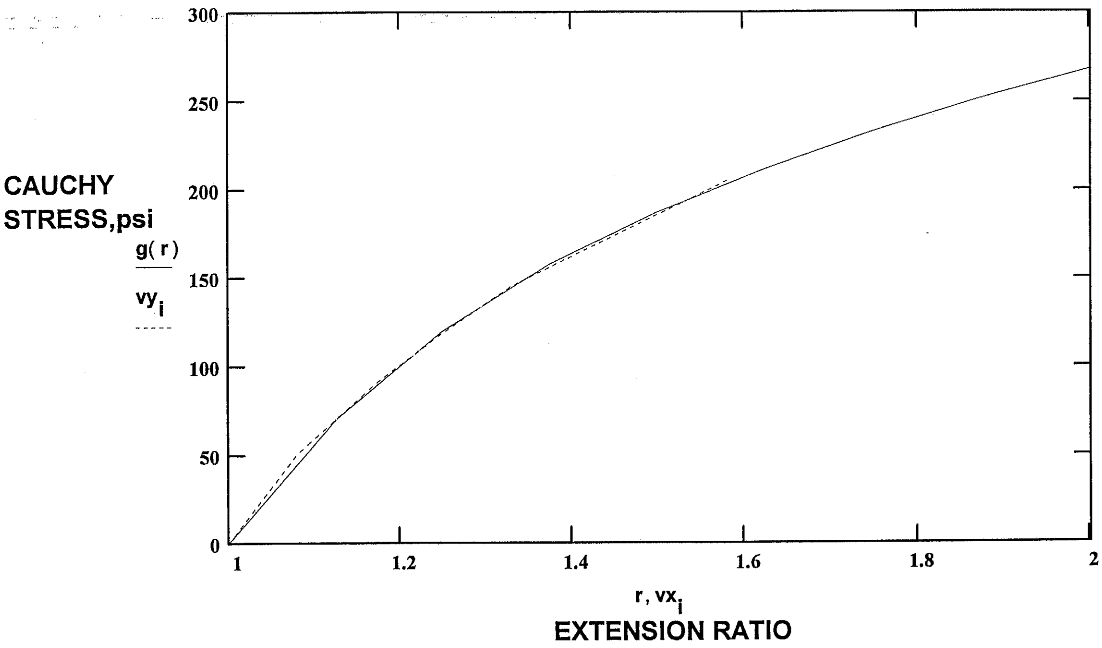
$g(t) := F(t)\cdot W$

APPENDIX 2

MOONEY-RIVLIN MATERIAL MODEL

uniaxial tension

Material 9(LF1700/M/95)
first 100%



Mooney constants: C_1=491kN/m^2
C_2=885kN/m^2

----- =emperical data
___ =Mooney calculated

APPENDIX 1b
MATERIAL FORMULATIONS and PROCESS CONDITIONS

MATERIAL	CURATIVE			RATIO %		CATYLIST			CURE TEMP.(F)
						type	pphr		
#6 LF900A	MBCA			95					212
#7 LF1900A	MBCA			97					212
#8 B625	A120			95		teda L33	0.15		240
#9 B895	1-4 BD	TMP	PPG	100					212
(+0.1pphr Naugard	75%MW	4%MW	21%MW						
#10 LF1700A	MBCA			95					212
#11 LF1700A	MBCA			100					212
#12 8523	A125	1-4BD		99		teda L33	0.05		240
	70%MW	30%MW							
#13 8523	1-4BD	A125		98					240
#14 8045/8030	1-4BD			100					240
80/20									

APPENDIX 3

TEXUS FLEX FATIGUE

vx_j=log strain energy density (psi)
vy_j=log cycles to failure (thousands)
E_o=modulus of elasticity
ε=strain
$w(\varepsilon)$=strain energy density
C_y=cycles to failure(thousands)

material=EPDM (52A)

$$vx := \begin{pmatrix} \ln(25) \\ \ln(42) \\ \ln(62) \end{pmatrix} \qquad vy := \begin{pmatrix} \ln(60) \\ \ln(50) \\ \ln(28) \end{pmatrix} \qquad F(x) := \begin{pmatrix} 1 \\ x \end{pmatrix} \qquad E_o := 410$$

$$j := 0 .. 2 \qquad S := \text{linfit}((vx),(vy),F)$$

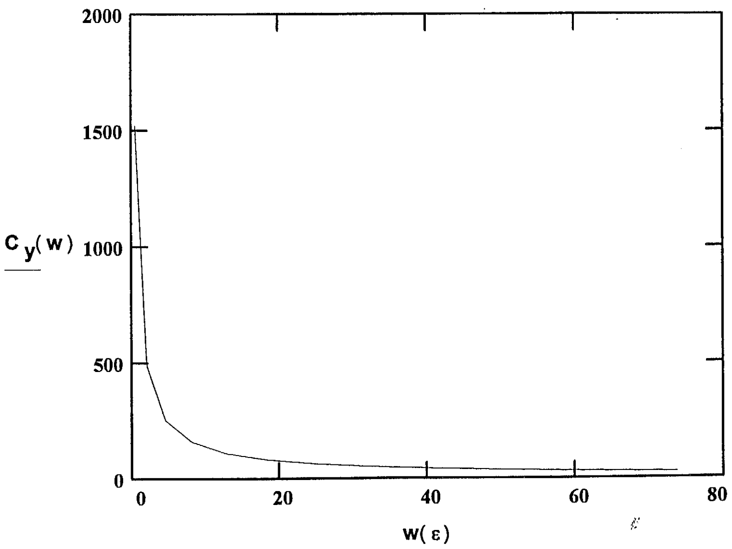
$$\varepsilon := .05, .10 .. .60 \qquad w(\varepsilon) := \frac{E_o \cdot \varepsilon^2}{2}$$

$$g(t) := F(t) \cdot S$$

$$S = \begin{pmatrix} 6.783 \\ -0.813 \end{pmatrix} \qquad C_y(w) := 883 \cdot w(\varepsilon)^{(-.813)}$$

$C_y(w)$=cycles to failure(thousands)

ε	$w(\varepsilon)$	$C_y(w)$
0.05	0.513	$1.52 \cdot 10^3$
0.1	2.05	492.612
0.15	4.613	254.789
0.2	8.2	159.599
0.25	12.813	111.034
0.3	18.45	82.548
0.35	25.112	64.247
0.4	32.8	51.708
0.45	41.512	42.695
0.5	51.25	35.973
0.55	62.012	30.809
0.6	73.8	26.744



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