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(71) **Demandeur/Applicant:**
BAYER INC., CA

(72) **Inventeur/Inventor:**
VON HELLENS, CARL WALTER, CA

(74) **Agent:** DE GAGNE, JACQUELINE A.

(54) **Titre :** COMPOSITION AMELIOREE DE CAOUTCHOUC
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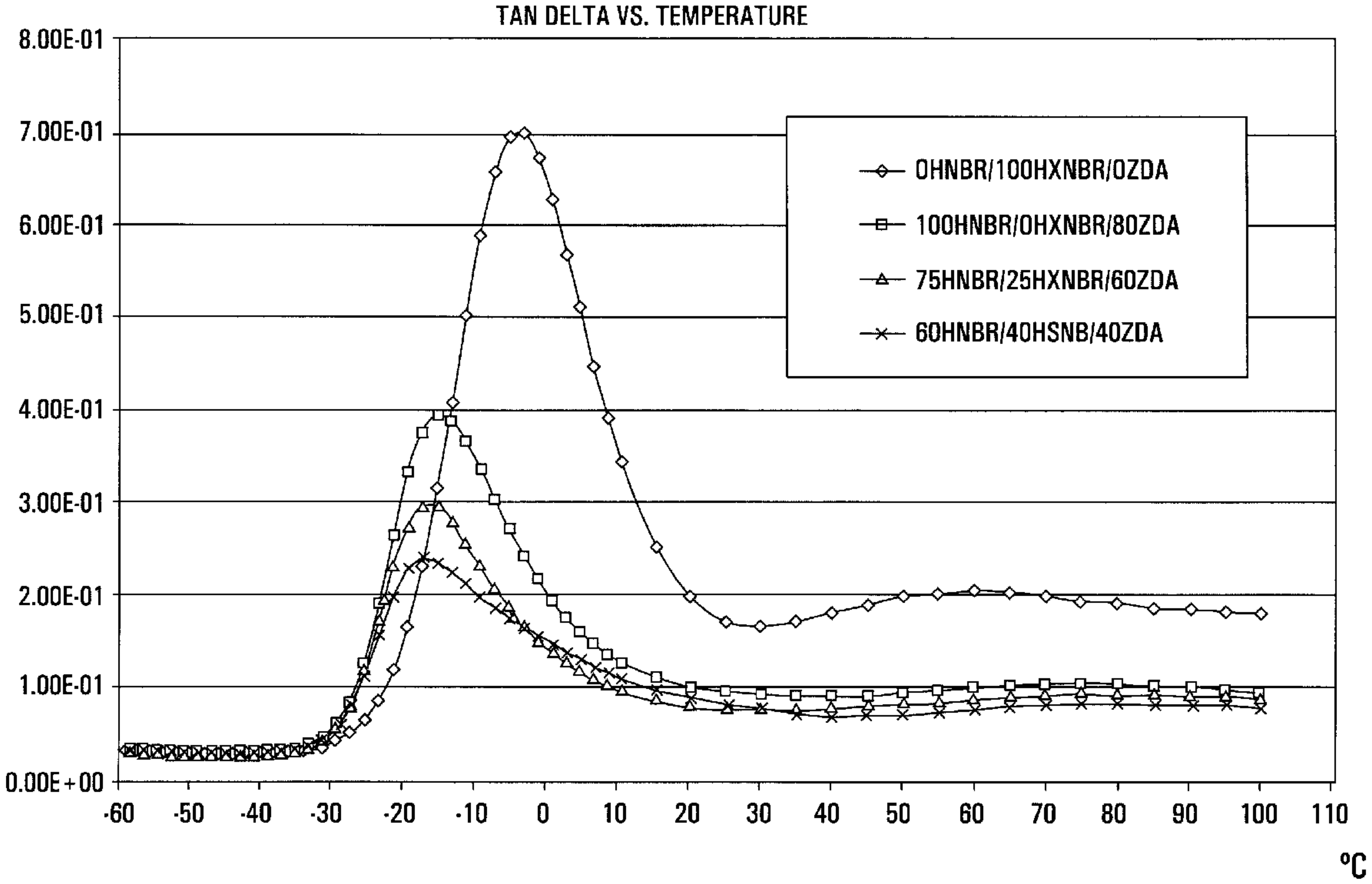


(57) **Abrégé/Abstract:**

The invention relates to novel crosslinkable carboxylated nitrile rubber compositions that also comprise a multivalent salt of an organic acid and a peroxide crosslinking agent. The compositions may also contain nitrile rubber in admixture with the carboxylated nitrile rubber. The rubber may be hydrogenated. Cured compositions made from the crosslinkable compositions display improved properties, particularly an unexpectedly high modulus.

ABSTRACT

The invention relates to novel crosslinkable carboxylated nitrile rubber compositions that also comprise a multivalent salt of an organic acid and a peroxide crosslinking agent. The compositions may also contain nitrile rubber in admixture with the carboxylated nitrile rubber. The rubber may be hydrogenated. Cured compositions made from the crosslinkable compositions display improved properties, particularly an unexpectedly high modulus.

The present invention relates to novel crosslinkable carboxylated nitrile rubber compositions having improved properties.

Background of the Invention

An important characteristic of a rubber composition is its elastic modulus, or stiffness. To determine this characteristic of a rubber composition, a sample of the composition is subjected to testing and there is obtained a graph of the stress applied to the sample versus the strain observed. A commonly quoted parameter for a rubber composition is the stress at 100% elongation, i.e., the stress needed to double the length of the sample. For some purposes it is desired that this stress should be as high as possible. Other characteristics of importance are the elongation at break, and the stress required to cause the break. Again, for some purposes, especially dynamic purposes, it is desired that these shall be as high as possible.

Summary of the Invention

One aspect of the present invention is a process for improving the properties, especially the properties of importance for dynamic applications, of a carboxylated nitrile rubber, especially hydrogenated carboxylated nitrile rubber. Another aspect is a carboxylated nitrile rubber, especially a hydrogenated carboxylated nitrile rubber, having improved properties.

Accordingly, the present invention provides a crosslinkable rubber composition that comprises a carboxylated nitrile rubber (XNBR) or a hydrogenated carboxylated nitrile rubber (HXNBR), a peroxide curing agent and a multivalent salt of an organic acid.

The invention also provides a process for preparing a crosslinkable rubber composition, which comprises blending a carboxylated nitrile rubber or a hydrogenated carboxylated nitrile rubber, a peroxide curing agent and a multivalent salt of an organic acid.

Description of the Preferred Embodiments

Many conjugated dienes are used in nitrile rubbers and these may all be used in the present invention. Mention is made of 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene and piperylene, of which 1,3-butadiene is preferred.

The nitrile is normally acrylonitrile or methacrylonitrile or α-chloroacrylonitrile, of which acrylonitrile is preferred.

The α,β-unsaturated acid can be, for example, acrylic, methacrylic, ethacrylic, crotonic, maleic (possibly in the form of its anhydride), fumaric or itaconic acid, of which acrylic and methacrylic are preferred.

The conjugated diene usually constitutes about 50 to about 85% of the copolymer, the nitrile usually constitutes about 15 to 50% of the copolymer and the acid about 0.1 to about 10%, these percentages being by weight. The polymer may also contain an amount, usually not exceeding about 10%, of another copolymerisable monomer, for example, an ester of an unsaturated acid, say ethyl, propyl or butyl acrylate or methacrylate, or a vinyl compound, for example, styrene, α-methylstyrene or a corresponding compound bearing an alkyl substituent on the phenyl ring, for instance, a p-alkylstyrene such as p-methylstyrene.

The composition of the invention can contain other polymers in addition to the XNBR or HXNBR and mention is made particularly of nitrile rubber (NBR) and hydrogenated nitrile rubber (HNBR). Hydrogenation of nitrile rubber is well known, and both nitrile rubber and hydrogenated nitrile rubber are available commercially. As examples of hydrogenated nitrile rubber there are mentioned the products available from Bayer under the trademark Therban. Another polymer that can be present is EPDM, a terpolymer of ethylene, propylene and a non-conjugated diene, for example a cyclic or aliphatic diene such as hexadiene, dicyclopentadiene or, preferably, ethylidene-norbornene. Preferred blends contain from 20 to 80 parts by weight of XNBR or HXNBR and from 20 to 80 parts of EPDM, more preferably from 25 to 40 parts of XNBR and HXNBR or from 75 to 60 parts of EPDM.

Carboxylated nitrile rubbers are also available commercially, and there are mentioned rubbers available from Bayer under the trade mark Krynac.

Nitrile rubbers and carboxylated nitrile rubbers that are not hydrogenated contain ethylenic carbon-carbon double bonds. Hydrogenation of these polymers enhances certain properties of these polymers but, of course, the hydrogenation process adds cost. It is found that if hydrogenated polymer is blended with unhydrogenated polymer the properties of the blend approximate much more closely to the properties of the unhydrogenated polymer than the hydrogenated polymer. No advantage is seen in blending hydrogenated and non-hydrogenated polymers. Hence, preferred embodiments of the invention include compositions containing blends of XNBR and NBR and blends of HXNBR and HNBR, but blends of XNBR and HNBR, or blends of NBR and HXNBR are not preferred. As preferred blends there are mentioned blends of HXNBR and HNBR containing from 20 to 80 wt%, especially 25 to 75 wt % of HNBR, based on the total weight of HXNBR and HNBR, and similar blends of XNBR and NBR.

Hydrogenated carboxylated nitrile rubbers (HXNBR) have been proposed, as have proposals for making these compounds by catalytic hydrogenation of carboxylated nitrile rubbers. No commercial HXNBR product is available. It is believed that difficulty has been encountered in achieving selective hydrogenation whereby carbon-carbon double bonds are hydrogenated but carboxyl groups are not. An attempt to get around this problem was made by hydrogenating a nitrile rubber and subsequently carboxylating by adding an unsaturated acid to the hydrogenated nitrile rubber. This process is expensive and difficult to control. A product made in this manner was commercially available but was then withdrawn, possibly because production problems prevented the obtaining of a product with consistent properties.

The present applicant has now found a process for selectively hydrogenating carbon-carbon double bonds of a carboxylated nitrile rubber without concomitant hydrogenation of carboxyl and nitrile groups. This process, and the product that is a hydrogenated carboxylated nitrile rubber free of hydrogenated carboxyl and nitrile groups, are the subject of Canadian Patent Application Serial No (Agents reference 76533-14), filed April 10, 2000, and a copy of the specification of that application is appended hereto and incorporated by reference. Preferred hydrogenated carboxylated nitrile rubbers for use in this invention are the products of this selective hydrogenation process.

The carboxylated nitrile rubber or hydrogenated carboxylated nitrile rubber, is admixed with a salt of a multivalent cation and an organic acid. Suitable multivalent cations are derived from metals, of which zinc, magnesium, calcium and aluminum are mentioned. As organic acids, there are mentioned aliphatic saturated and unsaturated acids having up to 8 carbon atoms, preferably up to 6 carbon atoms. The preferred organic acids are acrylic and methacrylic acids and the preferred salts are zinc di-acrylate and zinc di-methacrylate. It is possible to form the salt in situ, but this is not normally preferred.

The amount of the salt should be at least about 2 parts preferably at least about 5 parts by weight, per 100 parts by weight (phr) of rubber. The more of the salt that is added the greater the effect in enhancing the modulus of the cured composition, as demonstrated in the examples below. The upper limit on the amount of the salt is not particularly critical. There can be used up to about 100 parts by weight of salt, per 100 parts by weight of rubber.

The carboxylated nitrile rubber or hydrogenated carboxylated nitrile rubber is admixed with the salt and a peroxide crosslinking agent and crosslinked in known manner. Suitable organic peroxide crosslinking agents include dicumyl peroxide, di-t-butyl peroxide, benzoyl peroxide 2,5-dimethyl-2,5-di(t-butylperoxy)-hexyne-3 and 2,5-dimethyl-2,5-di(benzoylperoxy)hexane and the like. They are suitably used in amounts of about 0.2 to 20 parts by weight, preferably 1 to 10 parts by weight, per 100 parts of rubber.

The compositions of the invention may also include usual compounding ingredients such as reinforcing fillers, for example carbon black, calcium carbonate, silica, clay, talc, plasticizers, antioxidants, ultra violet absorbers, co-agents and the like.

As demonstrated in the examples below, the compositions of the invention have lower maximum values of tan δ, and those maximum values occur at the same, or lower, temperatures than with compositions that in accordance with the invention. The compositions of the invention also display steeper gradients, i.e. higher modulus, on the usual stress/strain curve and, in many cases, increased elongation at break. This renders them particularly suitable for dynamic applications such as, for example, in hard rolls used in paper-making machinery, in automotive timing belts and in belts for use in automative continuously variable transmissions.

The invention is further illustrated in the following examples and the accompanying drawings, of which:

Figure 1 is a graph of tan delta versus temperature for various compositions;

Figure 2 is a graph of elastic modulus versus temperature for the compositions of Figure 1;

Figure 3 is a graph of loss modulus versus temperature for the compositions of Figure 1;

Figure 4 is a graph of stress versus strain for various compositions;

Figure 5 is a graph of delta torque versus composition for various compositions;

Figures 6 to 13 are graphs of stress versus strain for various compositions;

Figure 14 is a graph of delta torque versus salt content; and

Figure 15 is a graph of stress versus strain for various compositions.

Examples 1

In this example there was used Therban ART VP KA 8796, a composition composed of 50% of a hydrogenated nitrile rubber having an acrylonitrile content of 34%, the balance butadiene, and a residual double bond content (RDB) of 6%, plus 40% of zinc diacrylate (ZDA) plus 10% of epoxidised soybean oil plasticizer. As HXNBR there was used a carboxylated nitrile rubber composed of 28% acrylonitrile, 7% methacrylic acid and the balance butadiene, hydrogenated to an RDB of 5%. The HXNBR was obtained by hydrogenating a carboxylated nitrile rubber in the presence of a rhodium compound as catalyst, in accordance with Applicant's Canadian Patent Application Serial No (Agent's reference 76533-14) a copy of which is appended to this specification and which is incorporated herein by reference. Also used were carbon black (N 330 VULCAN 3), a 50-50 mixture of zinc oxide and zinc peroxide (STRUKTOL ZP 1014), and a benzoyl peroxide crosslinking agent (VULCUP 40 KE).

The following compositions were blended, in accordance with the details given in Table 1

Table 1

		a	**b**	**c**	**d**
	ZDA	**80**	**60**	**48**	**0**
	HNBR	**100**	**75**	**60**	**0**
	HXNBR	**0**	**25**	**40**	**100**
THERBAN ART VP KA 8796	1A	200	150	120	0
HXNBR	1A	0	25	40	100
CARBON BLACK, N 330 VULCAN 3	1B	30	30	30	30
STRUKTOL ZP 1014	1C	7	7	7	7
VULCUP 40KE	1C	6	6	6	6
	Total	243	218	203	143
Specific Gravity		1.22	1.2	1.187	1.109

The compositions were mixed in a 6 x 12 inch mill of 1000g capacity that was supplied with cooling water at 30°C, in accordance with the following:

MIXING INSTRUCTION:

0 min - Band rubbers (1A)

2 min - Slowly add "1B"; make 3/4 cuts.

11 min - Slowly add "1C"; make 3/4 cuts

12 min - Remove and refine (6 passes).

Characteristics of the compositions are given in Table 2. All tests were carried out in accordance with ASTM procedures.

Table 2

		a	**b**	**c**	**d**
	ZDA	**80**	**60**	**48**	**0**
	HNBR	**100**	**75**	**60**	**0**
	HXNBR	**0**	**25**	**40**	**100**
COMPOUND MOONEY VISCOSITY ML 1+4' @ 100°C		31	61.6	88.7	103
COMPOUND MOONEY SCORCH Large Rotor					
t5 @ 135°C (min)		24.0	11.2	7.3	15.3
Moving Die Rheometer (MDR) CURE CHARACTERISTICS Frequency 1.7Hz; 170°C; **0.5°arc**; 60'.					
MH (max torque) (dN.m)		81.02	142.32	139.32	17.22
ML (min torque) (dN.m)		0.42	0.82	1.53	1.58
Delta MH-ML (dN.m)		80.6	141.5	137.79	15.64
STRESS STRAIN					
Cure Time at 170°C, (min)		11	10	9	26

Table 2 Continued

	Tested @ 23°C				
Stress @ 10 (MPa)		6.81	10.03	10.41	0.94
Stress @ 25 (MPa)		10.89	15.24	15.86	1.73
Stress @ 50 (MPa)		15.60	21.38	22.02	2.96
Stress @ 100 (MPa)		22.40		31.06	7.17
Stress @ 200 (MPa)					23.15
Stress @ 300 (MPa)					
Ultimate Tensile (MPa)		23.25	30.06	31.96	27.07
Ultimate Elongation (%)		106	99	105	225
Hard. Shore A2 Inst. (pts.)		90	91	93	76

It is clearly seen that the compositions with ZDA and HXNBR, i.e., compositions b and c, display higher values for Delta MH-ML and for the modulus than comparative compositions and a and d.

Example 2

In this example the HNBR used was Therban C3446, a clear polymer commercially available from Bayer. The HXNBR was the same as used in Example 1. There were also used epoxidised soybean oil (PARAPLEX G-62, and a benzoyl peroxide curing agent (VULCUP 40 KE)

Compositions were made up, whose details are given in Table 3.

Table 3

		a	b	c	d	e	f	g	h	I	j
	Polymer	**HNBR**	**HXNBR**	**HNBR**	**HXNBR**	**HNBR**	**HXNBR**	**HNBR**	**HXNBR**	**HNBR**	**HXNBR**
	ZDA Level	**0**	**0**	**5**	**5**	**10**	**10**	**20**	**20**	**40**	**40**
THERBAN C 3446	1A	100		100		100		100		100	
HXNBR	1A		100		100		100		100		100
PARAPLEX G-62	1B	5	5	5	5	5	5	5	5	5	5
SARTOMER 633 (SR633)	1B	0	0	5	5	10	10	20	20	40	40
VULCUP 40KE	1C	6	6	6	6	6	6	6	6	6	6
	Total	111	111	116	116	121	121	131	131	151	151
Specific Gravity		0.971	0.971	0.988	0.988	1.003	1.003	1.032	1.032	1.082	1.082

The mixing was carried out in a 6 x 12 inch mill of 1000g capacity supplied with water at 30°C, in accordance with the following:

MIXING INSTRUCTIONS:

0 min - Band rubber "1A"; make 3/4 cuts

1 min - Slowly add "1B"; make 3/4 cuts

7 min - Slowly add "1C"; make 3/4 cuts

10 min - Remove

Refine (6 passes)

Properties of the cured compositions are given in Table 4.

Table 4

	a	b	c	d	e	f	g	h	i	j
Polymer	**HNBR**	**HXNBR**	**HNBR**	**HXNBR**	**HNBR**	**HXNBR**	**HNBR**	**HXNBR**	**HNBR**	**HXNBR**
ZDA Level	**0**	**0**	**5**	**5**	**10**	**10**	**20**	**20**	**40**	**40**
MDR CURE CHARACTERISTICS										
Frequency: 1.7Hz; 170°C; 1/2°; 60′										
MH (dN.m)	15.00	10.99	17.87	13.35	20.59	14.28	26.44	25.70	45.74	71.58
ML (dN.m)	0.65	0.87	0.76	1.68	0.75	2.25	0.68	2.04	0.61	2.70
Delta MH-ML (dN.m)	14.36	10.12	17.10	11.67	19.85	12.03	25.76	23.66	45.13	68.88
STRESS STRAIN										
Cure Time at 170°C, (min)	15	31	16	12	16	10	16	8	14	9
Stress @ 5 (MPa)	0.15	0.15	0.18	0.20	0.22	0.28	0.31	0.55	0.71	1.87
Stress @ 10 (MPa)	0.26	0.26	0.32	0.35	0.37	0.49	0.57	0.98	1.25	3.29
Stress @ 15 (MPa)	0.35	0.35	0.43	0.47	0.51	0.69	0.77	1.38	1.71	4.57
Stress @ 20 (MPa)	0.43	0.42	0.54	0.57	0.64	0.85	0.95	1.75	2.10	5.68
Stress @ 25 (MPa)	0.50	0.49	0.62	0.67	0.75	1.00	1.12	2.16	2.47	6.60

Table 4 Continued

	a	b	c	d	e	f	g	h	i	j
Polymer	**HNBR**	**HXNBR**	**HNBR**	**HXNBR**	**HNBR**	**HXNBR**	**HNBR**	**HXNBR**	**HNBR**	**HXNBR**
ZDA Level	**0**	**0**	**5**	**5**	**10**	**10**	**20**	**20**	**40**	**40**
STRESS STRAIN CONTINUED										
Stress @ 50 (MPa)	0.76	0.71	0.97	1.05	1.16	1.77	1.81	4.68	4.41	10.84
Stress @ 100 (MPa	1.05	0.95	1.50	1.93	1.97	3.91	3.75	12.03	8.87	19.58
Stress @ 200 (MPa)	1.69	1.40	3.90	6.74	5.62		12.09		21.11	
Stress @ 300 (MPa)	3.53	2.79								
Ultimate Tensile (MPa)	4.58	5.20	5.55	10.36	7.06	*5.40*	13.38	19.95	24.36	34.20
Ultimate Elongation (%)	330	371	233	238	230	*112*	206	151	219	167
Hard. Shore A2 Inst. (pts.)	45	44	51	55	55	60	64	72	75	90

It will be seen that addition of ZDA improves the modulus of both HNBR and HXNBR but, unexpectedly, the improvement at higher levels of ZDA is much greater in HXNBR than HNBR. This is also shown in Figure 14.

Example 3

This example compares the effects of ZDA and ZDMA in blends of 75HNBR/25HXNBR. The compositions are given in Table 5. THERBAN C 3446 is a HNBR polymer commercially available from Bayer. The HXNBR is the same as that described in Example 1. NAUGARD 445 (UNIROYAL) and VULKANOX ZMB-2/C5 (BAYER) are commercially available antioxidants. PARAPLEX G-62 is an epoxidised soybean oil available from C.P.Hall. SARTOMER SR 633 and SR 634 are zinc diacrylate (ZDA) and zinc dimethacrylate (ZDMA) products commercially available from SARTOMER. The benzoyl peroxide used is VULCUP 40KE (Hercules).

Table 5

		a	b	c	d	e	f	g	h
	ZDA level	**0**	**10**	**20**	**40**	**0**	**0**	**0**	**20+A/O**
	ZDMA level	**0**	**0**	**0**	**0**	**10**	**20**	**40**	**0**
THERBAN C 3446	1A	75	75	75	75	75	75	75	75
HXNBR	1A	25	25	25	25	25	25	25	25
NAUGARD 445	1B								1.1
PARAPLEX G-62	1B	5	5	5	5	5	5	5	5
SARTOMER 633 (SR633)	1B	0	10	20	40	0	0	0	20
SARTOMER 634 (SR634)	1B	0	0	0	0	10	20	40	0
VULKANOX ZMB-2/C5 (ZMMBI)	1B								0.4
VULCUP 40KE	1C	6	6	6	6	6	6	6	6
	Total	111	121	131	151	121	131	151	132.5
Specific Gravity		0.971	1.003	1.032	1.082	1.001	1.027	1.071	1.034

The compositions were mixed in a 6 inch x 12 inch mill of 1000g capacity that was supplied with cooling water at 30°C. The mixing conditions were as given below

MIXING INSTRUCTIONS:

0 min - Band rubber "1A"; make 3/4 cuts

2 min - Slowly add "1B"; make 3/4 cuts

9 min - Slowly add "1C"; make 3/4 cuts

10 min - Remove

Refine (6 passes)

Results are given in Table 6

Table 6

	a	b	c	d	e	f	g	h
ZDA level	**0**	**10**	**20**	**40**	**0**	**0**	**0**	**20+A/O**
ZDMA Level	**0**	**0**	**0**	**0**	**10**	**20**	**40**	**0**
MDR CURE CHARACTERISTICS								
Frequency: 1.7Hz; 170°C; 0.5° arc; 60′								
MH (dN.m)	12.97	22.13	34.74	70.94	19.87	29.5	51.96	30.65
ML (dN.m)	0.74	1.03	1.07	1.09	0.96	0.99	1.13	0.98
Delta MH-ML (dN.m)	12.24	21.1	33.68	69.85	18.91	28.51	50.84	29.66
STRESS STRAIN								
Cure Time at 170°C, (min)	16	15	14	12	16	16	15	14
Stress @ 5 (MPa)	0.14	0.31	0.59	1.50	0.31	0.66	1.54	0.59
Stress @ 10 (MPa)	0.24	0.52	1.02	2.51	0.56	1.09	2.33	1.02
Stress @ 15 (MPa)	0.33	0.70	1.37	3.25	0.77	1.46	2.91	1.34
Stress @ 20 (MPa)	0.40	0.87	1.67	3.89	0.96	1.73	3.35	1.64
Stress @ 25 (MPa)	0.47	1.02	1.93	4.41	1.12	1.96	3.72	1.90
Stress @ 50 (MPa)	0.71	1.65	3.10	6.91	1.72	2.88	5.38	2.92
Stress @ 100 (MPa)	0.97	3.01	5.81	12.39	2.76	4.74	8.71	5.18
Stress @ 200 (MPa)	1.48	8.61		25.59	6.21	9.66	15.04	12.62
Stress @ 300 (MPa)	3.13					16.61	22.43	
Ultimate Tensile (MPa)	4.49	9.92	14.34	25.59	10.07	*18.02*	28.15	17.82
Ultimate Elongation (%)	342	217	198	200	273	*314*	358	259
Hard. Shore A2 Inst. (pts.)	72	62	70	75	75	70	85	69

Example 4

In this example different amounts of ZDA and ZDMA are tested in blends of 60HNBR/40HXNBR. The compositions are given in Table 7. The materials used are discussed in Example 3.

Table 7

		a	**b**	**c**	**d**	**e**	**f**	**g**	**h**
	ZDA level	**0**	**10**	**20**	**40**	**0**	**0**	**0**	**20**
	ZDMA level	**0**	**0**	**0**	**0**	**10**	**20**	**40**	**0**
THERBAN C 3446	1A	60	60	60	60	60	60	60	60
HXNBR	1A	40	40	40	40	40	40	40	40
NAUGARD 445	1B								1.1
PARAPLEX G-62	1B	5	5	5	5	5	5	5	5
SARTOMER 633 (SR633)	1B	0	10	20	40	0	0	0	20
SARTOMER 634 (SR634)	1B	0	0	0	0	10	20	40	0
VULKANOX ZMB-2/C5 (ZMMBI)	1B								0.4
VULCUP 40KE	1C	6	6	6	6	6	6	6	6
	Total	111	121	131	151	121	131	151	132.5
Specific Gravity		0.971	1.003	1.032	1.082	1.001	1.027	1.071	1.034

The mixing conditions were identical to those used in the previous example. Results are given in Table 8.

Table 8

	a	b	c	d	e	f	g	h
ZDA LEVEL	**0**	**10**	**20**	**40**	**0**	**0**	**0**	**20**
ZDMA LEVEL	**0**	**0**	**0**	**0**	**10**	**20**	**40**	**0**
MDR CURE CHARACTERISTICS								
Frequency: 1.7Hz; 170°C; 0.5° arc; 60′								
MH (dN.m)	12.38	20.99	36.10	103.62	18.16	34.65	93.72	33.04
ML (dN.m)	0.77	1.19	1.27	1.32	1.14	1.27	1.61	1.16
Delta MH-ML (dN.m)	11.60	19.80	34.83	102.30	17.02	33.38	92.11	31.88
ts 1 (min)	0.98	0.49	0.52	0.63	0.60	0.68	0.93	0.59
ts 2 (min)	1.44	0.58	0.56	0.67	0.76	0.75	1.02	0.62
t′ 10 (min)	1.05	0.58	0.61	0.75	0.71	0.83	1.20	0.70
t′ 50 (min)	3.68	2.25	1.54	1.15	3.08	2.65	2.56	1.68
t′ 90 (min)	13.96	8.96	6.91	4.89	9.87	8.98	7.75	7.18
Delta t′50-t′10 (min)	2.63	1.67	0.93	0.40	2.37	1.82	1.36	0.98
STRESS STRAIN								
Cure Time at 170°C, (min)	19	14	12	10	15	14	13	12
Stress @ 5 (MPa)	0.15	0.29	0.69	3.27	0.34	0.80	3.08	0.75
Stress @ 10 (MPa)	0.26	0.51	1.20	5.08	0.60	1.43	4.54	1.31
Stress @ 15 (MPa)	0.34	0.70	1.68	6.33	0.81	1.87	5.47	1.80
Stress @ 20 (MPa)	0.42	0.87	2.07	7.32	1.02	2.27	6.09	2.21
Stress @ 25 (MPa)	0.49	1.03	2.43	8.22	1.02	2.58	6.64	2.60
Stress @ 50 (MPa)	0.72	1.70	3.97	11.62	1.89	3.74	8.47	4.16
Stress @ 100 (MPa)	0.97	3.15	7.15	17.69	3.10	5.65	11.92	7.16
Stress @ 200 (MPa)	1.48	7.72	16.51		6.38	10.41	17.99	15.34
Stress @ 300 (MPa)	3.08					17.01	25.30	

Table 8 Continued

	a	**b**	**c**	**d**	**e**	**f**	**g**	**h**
ZDA LEVEL	**0**	**10**	**20**	**40**	**0**	**0**	**0**	**20**
ZDMA LEVEL	**0**	**0**	**0**	**0**	**10**	**20**	**40**	**0**
STRESS STRAIN CONTINUED								
Ultimate Tensile (MPa)	4.16	11.31	21.86	28.84	10.99	20.04	28.83	15.80
Ultimate Elongation (%)	339	201	243	192	286	337	343	209
Hard. Shore A2 Inst. (pts.)	48	60	76	90	62	78	89	74

Figure 1 is a graph of tan δ versus temperature for HXNBR, for HNBR blended with 80 parts of ZDA, for 75HNBR/25HXNBR/60ZDA and 60HNBR/40HXNBR/40ZDA. It is desirable that the peak value of tan δ , which correlates with the glass transition temperature, Tg, shall be as low as possible and shall appear at as low temperature as possible. It will be seen that the two latter compositions that are in accordance with the invention are both superior to the two comparative compositions. Figure 2 shows the elastic modulus versus temperature for the same compositions and again the superiority of the compositions in accordance with the invention is demonstrated. Figure 3 is a graph of loss modulus E″ versus temperature and, again, the superiority of the compositions of the invention is demonstrated.

The elastic modulus and loss modulus were determined using a Rheometrics Solid analyzer (RSA-II). In this test, a small sinusoidal tensile deformation is imposed on the specimen at a given frequency. The resulting force, as well as the phase difference between the imposed deformation and the response, are measured at various temperatures. Based on theory of linear viscoelasticity, the storage tensile modulus (E′), loss tensile modulus (E″) and tan δ can be calculated.

Figure 4 shows stress-strain curves at 23°C for five compositions, two of which are in accordance with the invention. It can be seen that these two compositions, composed of 60HNBR/40HXNBR/48ZDA and 75HNBR/25HXNBR/60ZDA, display markedly higher modulus than the other three compositions.

Figure 5 shows delta torque versus acrylate level in blends of 60HNBR/40HXNBR and 75HNBR/25HXNBR and shows that increased amount of zinc diacrylate and zinc dimethacrylate lead to increases in delta torque, with ZDA being somewhat more effective than ZDMA. The presence of antioxidant (A/O) does not markedly affect results.

Figure 6 compares the stress-strain curves of 75HNBR/25HXNBR containing no acrylate, containing 10% ZDA and 10% ZDMA. ZDA is more effective in increasing modulus but ZDMA gives greater elongation at break. Figures 7 and 8 shows similar curves but with 20% and 40%, respectively, of ZDA and ZDMA, and show similar results.

Figures 9, 10 and 11 are similar to Figures 6, 7 and 8, except that the blend is 60HNBR/40HXNBR. Results are similar to those shown in Figures 6, 7 and 8.

Figure 12 compares the stress-strain curves of 60HNBR/40HXNBR and 75HNBR/25HXNBR compositions containing 20 parts of ZDMA. The curves are similar, with the 60/40 composition showing slight superiority. Figure 13 shows somewhat similar results with 40 parts ZDMA, the superiority of the 60/40 composition being more apparent.

Figure 14 shows delta torque versus ZDA content in 100% HNBR and 100% HXNBR, and demonstrates that at higher levels of ZDA the effect is markedly greater in HXNBR than HNBR.

Figure 15 shows stress strain curves for 100% HNBR and 100% HXNBR containing no ZDA and containing 40 parts of ZDA. It is noteworthy that, in the absence of ZDA, the rubbers have very similar properties, yet with 40 parts of ZDA the modulus of HXNBR is increased markedly not only over the ZDA-free compositions but also over the HNBR composition containing 40 parts of ZDA.

CLAIMS:

1. A crosslinkable composition comprising a hydrogenated carboxylated nitrile rubber, a peroxide curing agent, and a multivalent salt of an organic acid.

2. A composition according to claim 1, wherein the multivalent ion is divalent and the organic acid is an aliphatic acid having up to 6 carbon atoms.

3. A composition according to claim 1, wherein the salt is zinc diacrylate.

4. A composition according to claim 1, wherein the salt is zinc dimethacrylate.

5. A composition according to any one of claims 1 to 4, which also contains a hydrogenated nitrile rubber.

6. A composition according to claim 5, wherein the amount of hydrogenated nitrile rubber amounts to at least 20% by weight, based on the weight of hydrogenated carboxylated nitrile rubber plus hydrogenated nitrile rubber.

7. A composition according to claim 5 or 6, wherein the amount of hydrogenated nitrile rubber is not more than 80% by weight, based on the weight of hydrogenated carboxylated nitrile rubber plus hydrogenated nitrile rubber.

8. A composition according to any one of claims 1 to 7, wherein the amount of the multivalent salt of the organic acid is at least 2 parts by weight per 100 parts by weight of rubber.

9. A composition according to any one of claims 1 to 8, which also contains ethylene-propylene-ethylidene norbornene copolymer.

10. A composition formed by crosslinking a composition according to any one of claims 1 to 9.

11. A process for preparing a crosslinkable composition which comprises admixing a hydrogenated carboxylated nitrile rubber , a peroxide curing agent and a salt of a multivalent ion and a carboxylic acid.

12. A process according to claim 11, wherein there is also admixed a hydrogenated nitrile rubber.

13. A process according to claim 12, wherein the amount of hydrogenated nitrile rubber is from about 20 to about 80% by weight, based on the weight of hydrogenated nitrile rubber plus hydrogenated carboxylated nitrile rubber.

14. A process according to claim 13, wherein the amount of hydrogenated nitrile rubber is from about 25 to about 75% by weight.

15. A process according to any one of claims 11 to 14, wherein the salt is zinc acrylate.

16. A process according to any one of claims 11 to 14, wherein the salt is zinc dimethacrylate.

17. A crosslinkable composition comprising a carboxylated nitrile rubber, a peroxide curing agent, and a multivalent salt of an organic acid.

18. A composition according to claim 17, wherein the multivalent ion is divalent and the organic acid is an aliphatic acid having up to 6 carbon atoms.

19. A composition according to claim 17, wherein the salt is zinc diacrylate.

20. A composition according to claim 17, wherein the salt is zinc dimethacrylate.

21. A composition according to any one of claims 17 to 20, which also contains a nitrile rubber.

22. A composition according to claim 21, wherein the amount of nitrile rubber amounts to at least 20% by weight, based on the weight of carboxylated nitrile rubber plus nitrile rubber.

23. A composition according to claim 21 or 22, wherein the amount of nitrile rubber is not more than 80% by weight, based on the weight of carboxylated nitrile rubber plus nitrile rubber.

24. A composition according to any one of claims 17 to 23, wherein the amount of the multivalent salt of the organic acid is at least 2 parts by weight per 100 parts by weight of rubber.

25. A composition according to any one of claims 17 to 24, which also contains ethylene-propylene-ethylidene norbornene copolymer.

26. A composition formed by crosslinking a composition according to any one of claims 17 to 25.

27. A process for preparing a crosslinkable composition which comprises admixing a carboxylated nitrile rubber, a peroxide curing agent and a salt of a multivalent ion and a carboxylic acid.

28. A process according to claim 27, wherein there is also admixed a nitrile rubber.

29. A process according to claim 28, wherein the amount of nitrile rubber is from about 20 to about 80% by weight, based on the weight of nitrile rubber plus carboxylated nitrile rubber.

30. A process according to claim 29, wherein the amount of nitrile rubber is from about 25 to about 75% by weight.

31. A process according to any one of claims 27 to 30, wherein the salt is zinc acrylate.

32. A process according to any one of claims 27 to 30, wherein the salt is zinc dimethacrylate.

SMART & BIGGAR

OTTAWA, CANADA

PATENT AGENTS

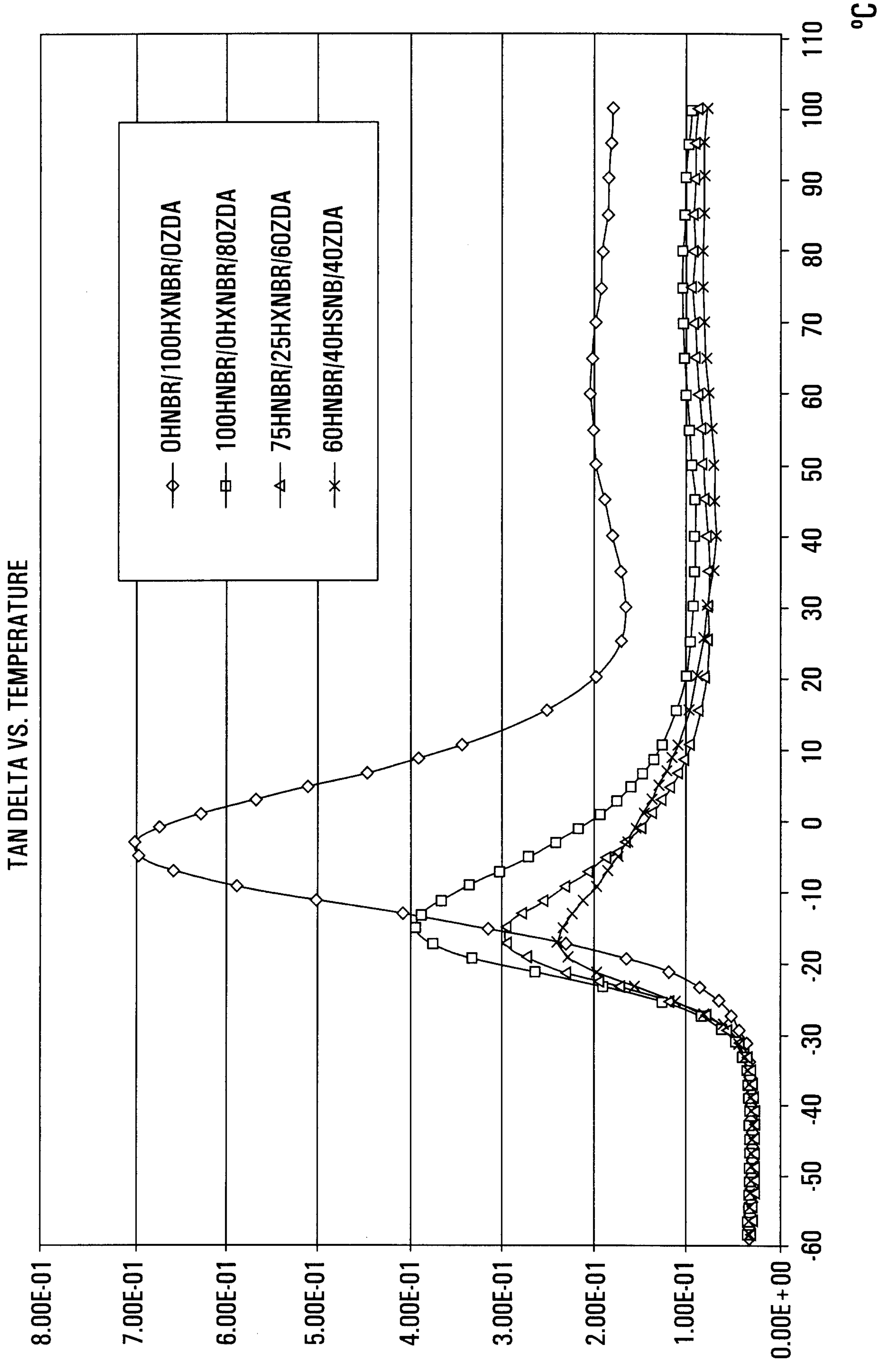

TAN DELTA VS. TEMPERATURE
0HNBR/100HXNBR/0ZDA
100HNBR/0HXNBR/80ZDA
75HNBR/25HXNBR/60ZDA
60HNBR/40HSNB/40ZDA
8.00E-01
7.00E-01
6.00E-01
5.00E-01
4.00E-01
3.00E-01
2.00E-01
1.00E-01
0.00E+00
-60
-50
-40
-30
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
°C

FIG. 1

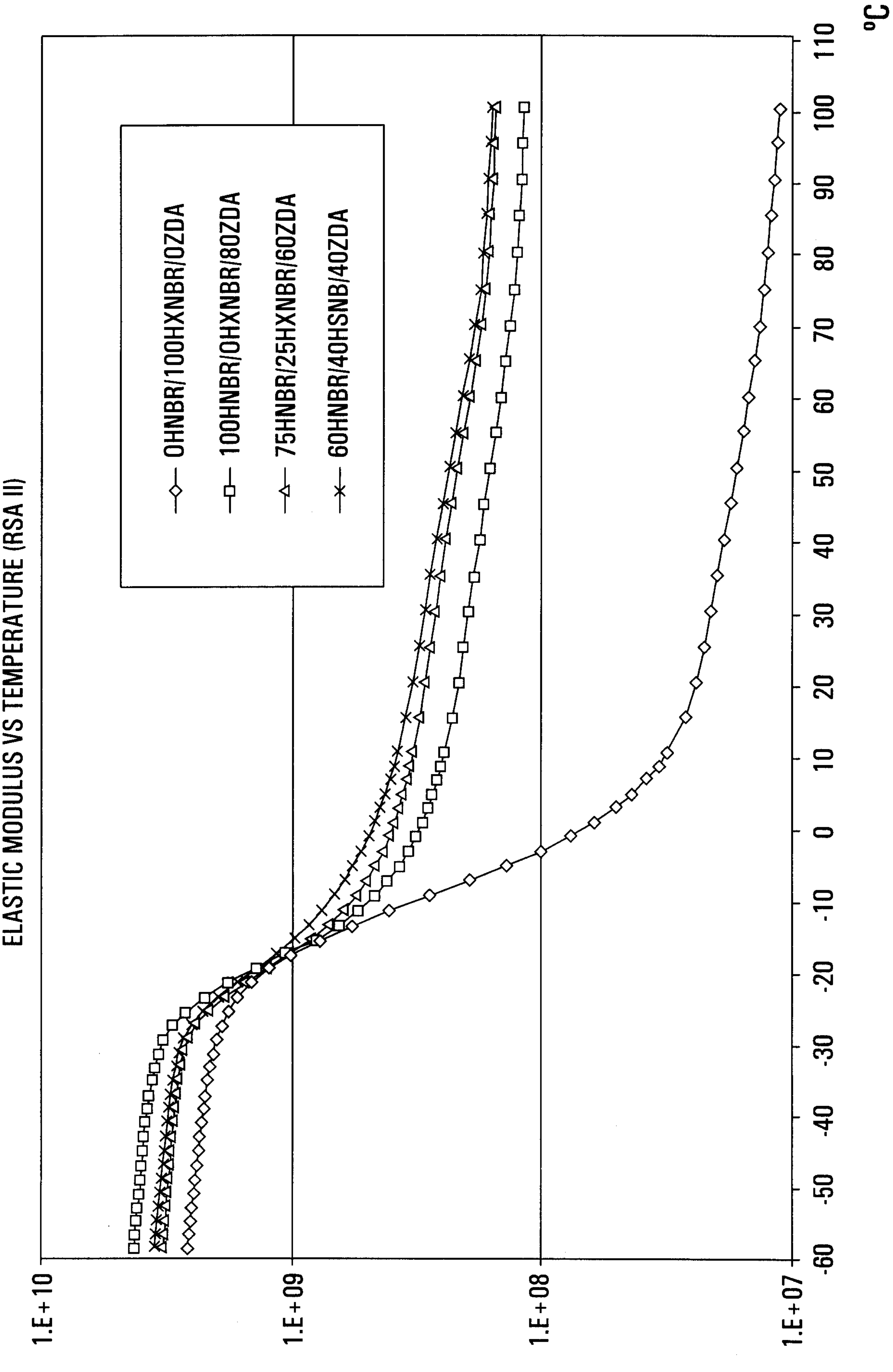

ELASTIC MODULUS VS TEMPERATURE (RSA II)
0HNBR/100HXNBR/0ZDA
100HNBR/0HXNBR/80ZDA
75HNBR/25HXNBR/60ZDA
60HNBR/40HSNB/40ZDA
1.E+10
1.E+09
1.E+08
1.E+07
-60
-50
-40
-30
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
°C

FIG. 2

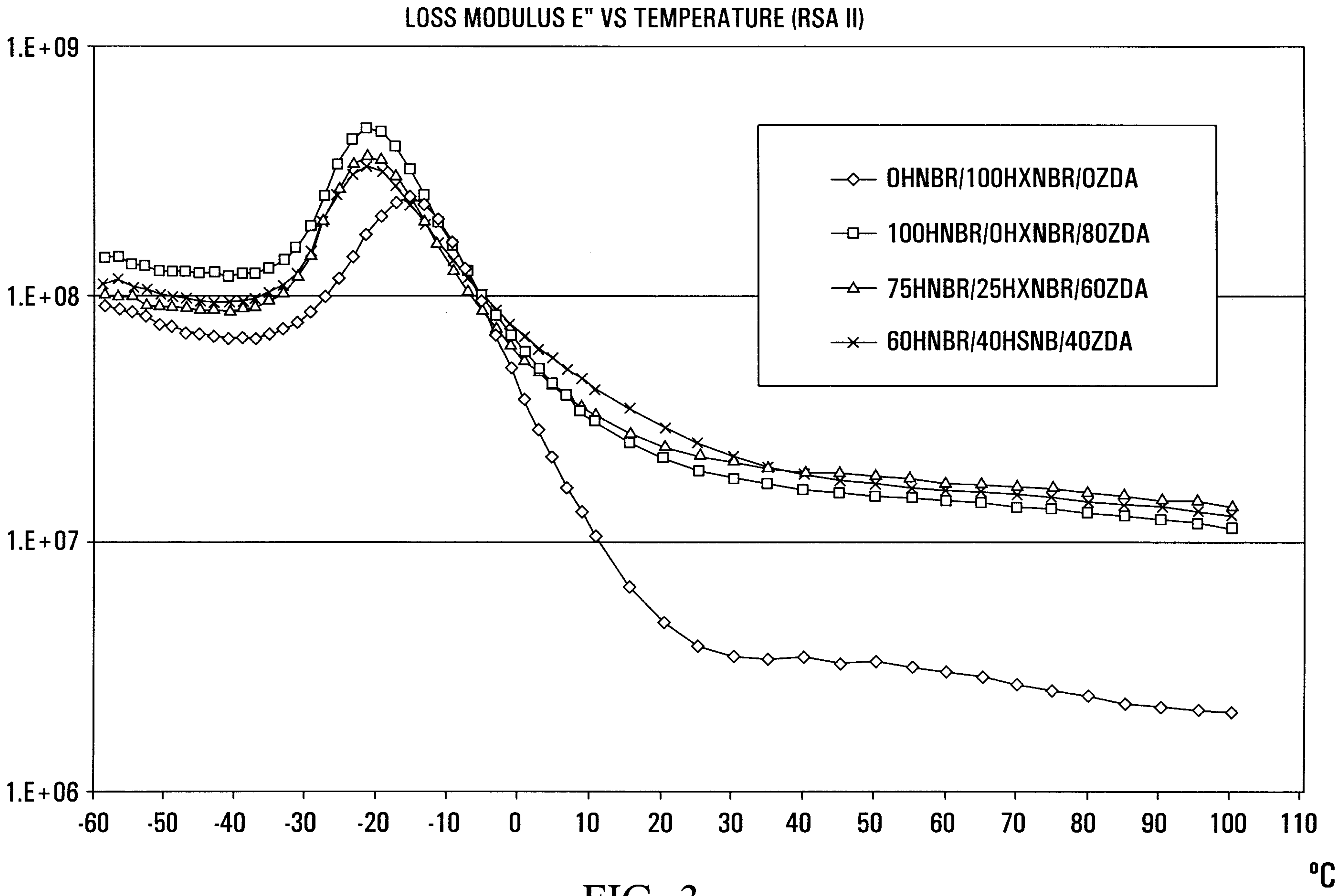

LOSS MODULUS E" VS TEMPERATURE (RSA II)
1.E+09
1.E+08
1.E+07
1.E+06
-60
-50
-40
-30
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
°C
0HNBR/100HXNBR/0ZDA
100HNBR/0HXNBR/80ZDA
75HNBR/25HXNBR/60ZDA
60HNBR/40HSNB/40ZDA

FIG. 3

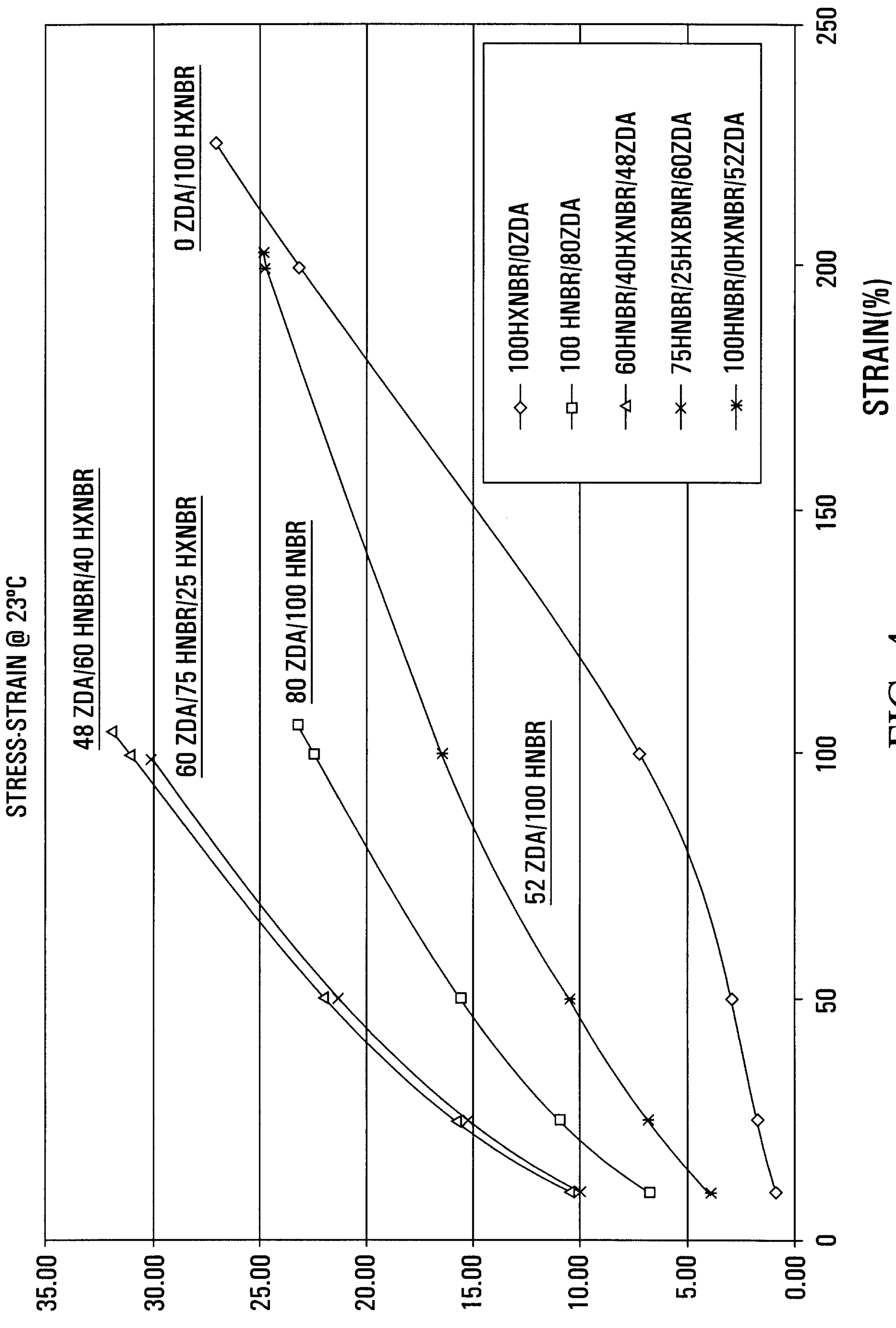

STRESS-STRAIN @ 23°C
48 ZDA/60 HNBR/40 HXNBR
60 ZDA/75 HNBR/25 HXNBR
80 ZDA/100 HNBR
52 ZDA/100 HNBR
0 ZDA/100 HXNBR
100HXNBR/0ZDA
100 HNBR/80ZDA
60HNBR/40HXNBR/48ZDA
75HNBR/25HXBNR/60ZDA
100HNBR/0HXNBR/52ZDA
35.00
30.00
25.00
20.00
15.00
10.00
5.00
0.00
0
50
100
150
200
250
STRAIN(%)

FIG. 4

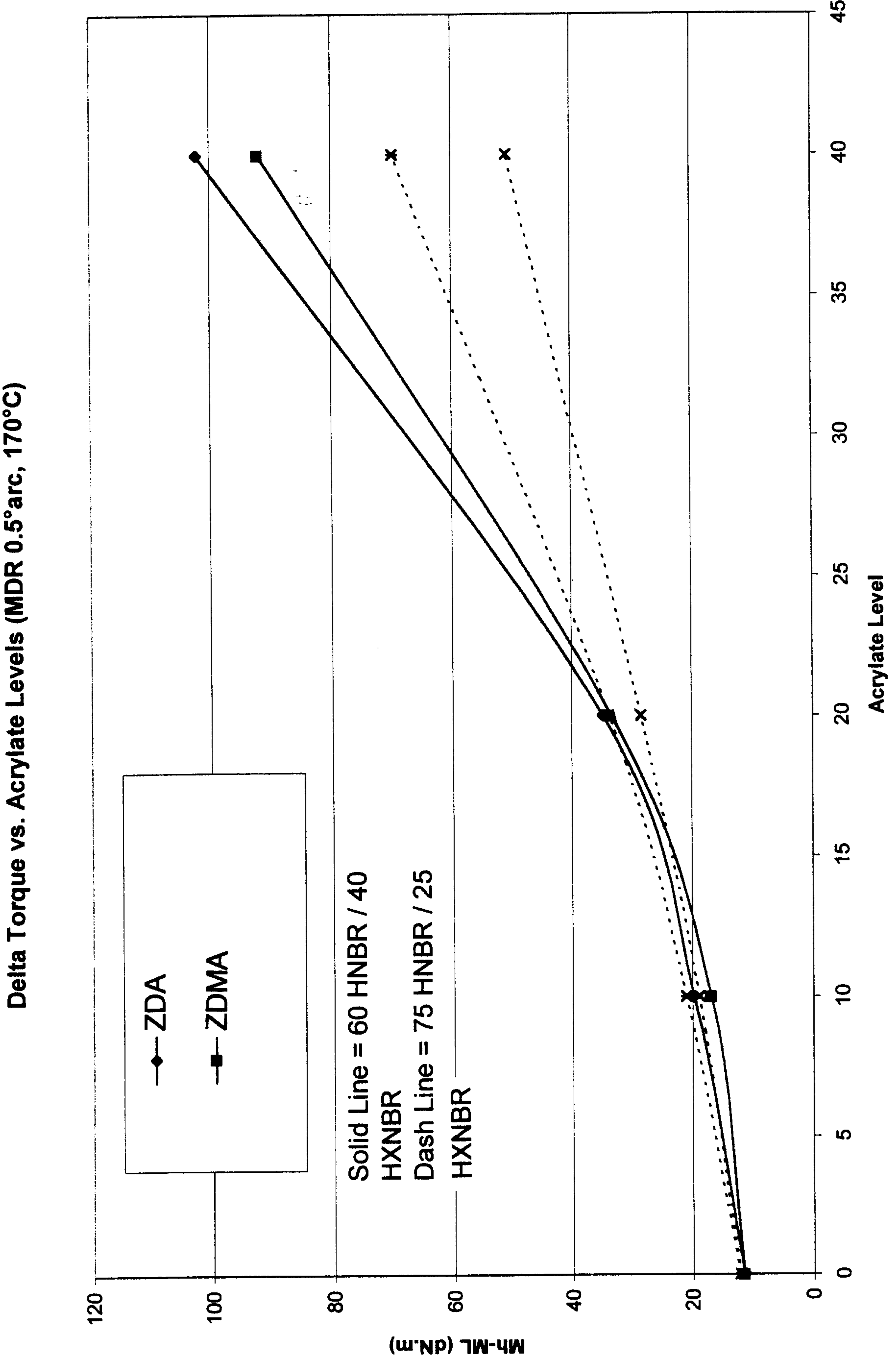

Delta Torque vs. Acrylate Levels (MDR 0.5°arc, 170°C)
ZDA
ZDMA
Solid Line = 60 HNBR / 40 HXNBR
Dash Line = 75 HNBR / 25 HXNBR
Mh-ML (dN.m)
0
20
40
60
80
100
120
Acrylate Level
0
5
10
15
20
25
30
35
40
45

FIG. 5

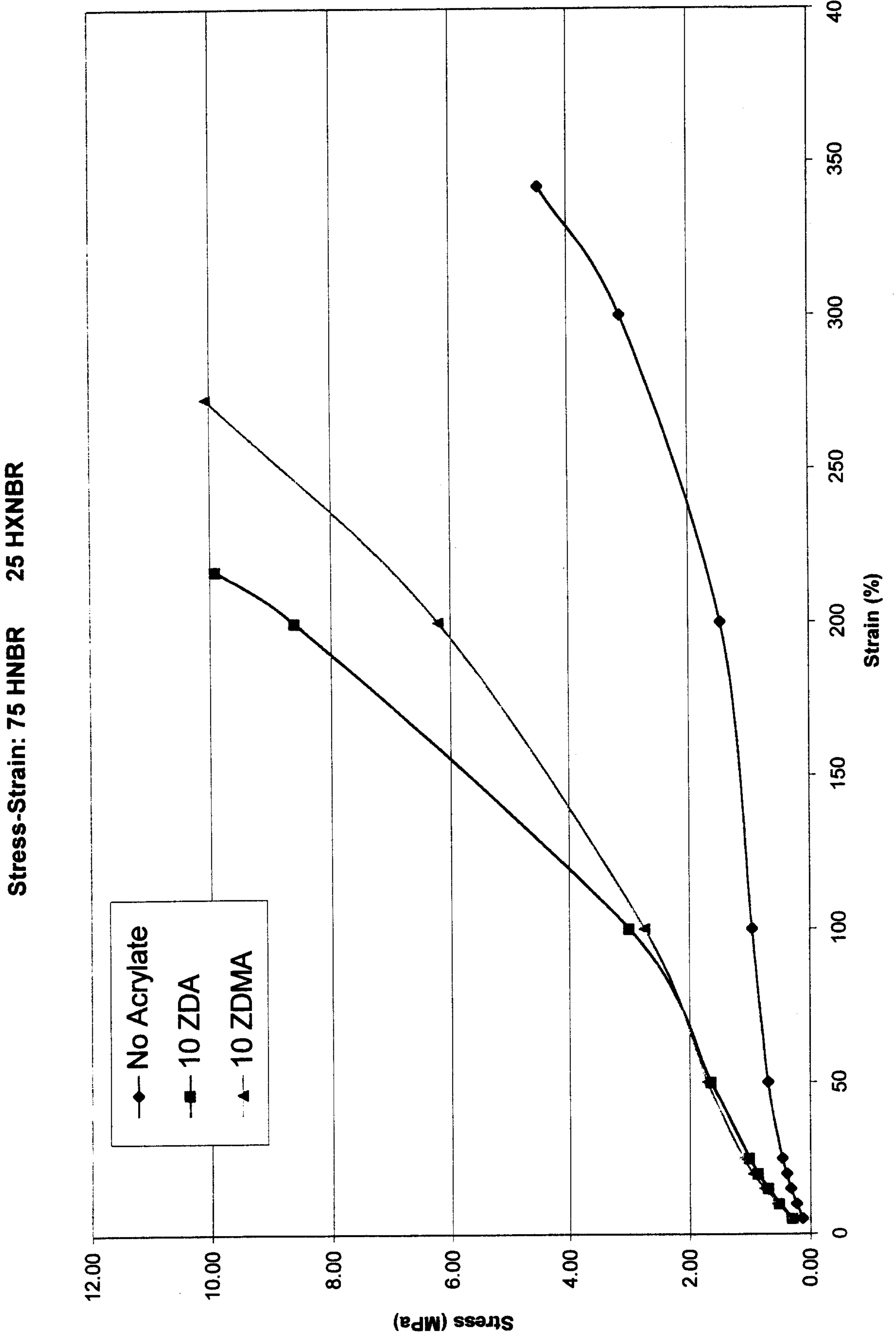

Stress-Strain: 75 HNBR 25 HXNBR
No Acrylate
10 ZDA
10 ZDMA
Stress (MPa)
0.00
2.00
4.00
6.00
8.00
10.00
12.00
Strain (%)
0
50
100
150
200
250
300
350
400

FIG. 6

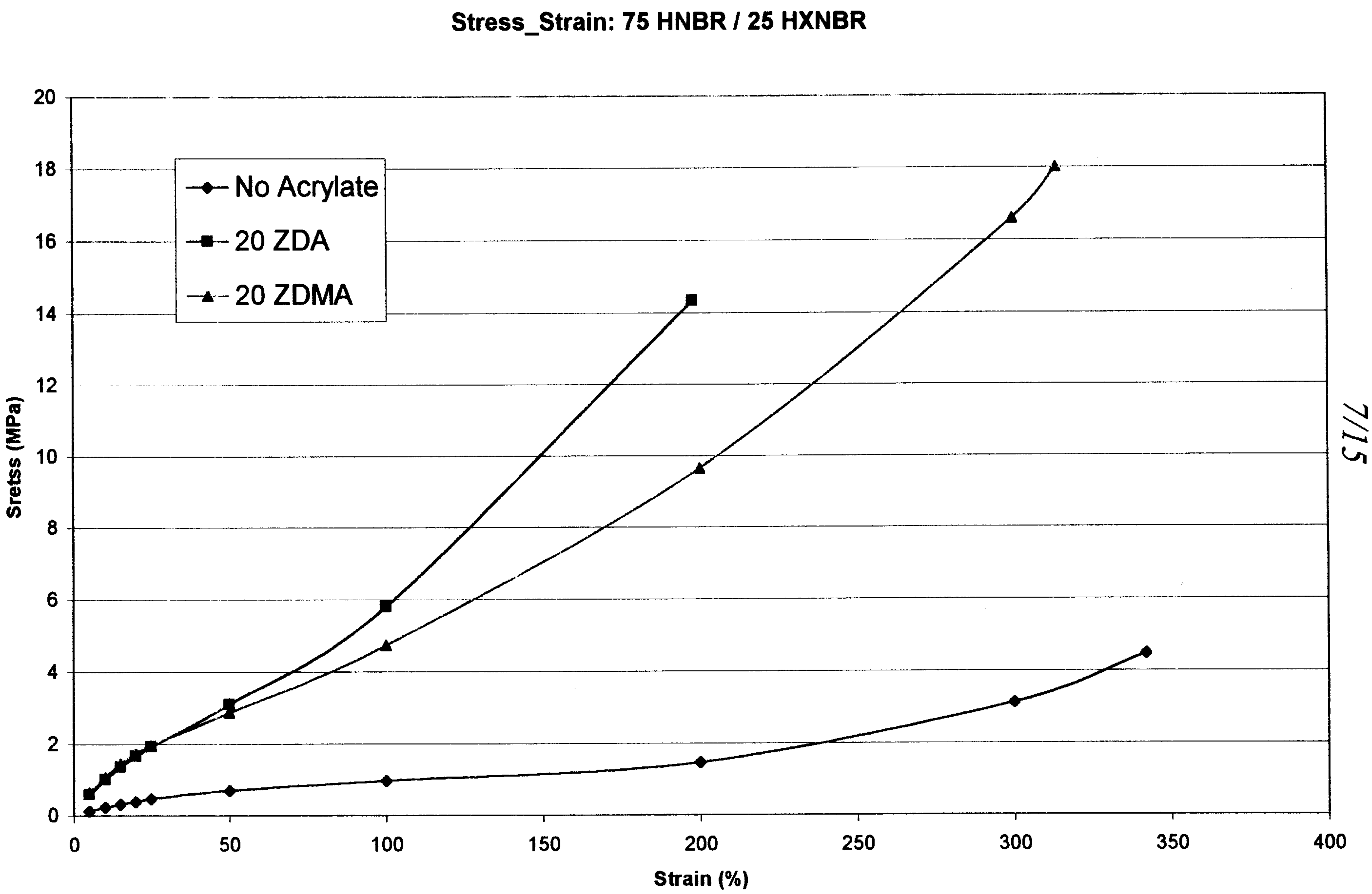

Stress_Strain: 75 HNBR / 25 HXNBR
No Acrylate
20 ZDA
20 ZDMA
Sretss (MPa)
0
2
4
6
8
10
12
14
16
18
20
Strain (%)
0
50
100
150
200
250
300
350
400

FIG. 7

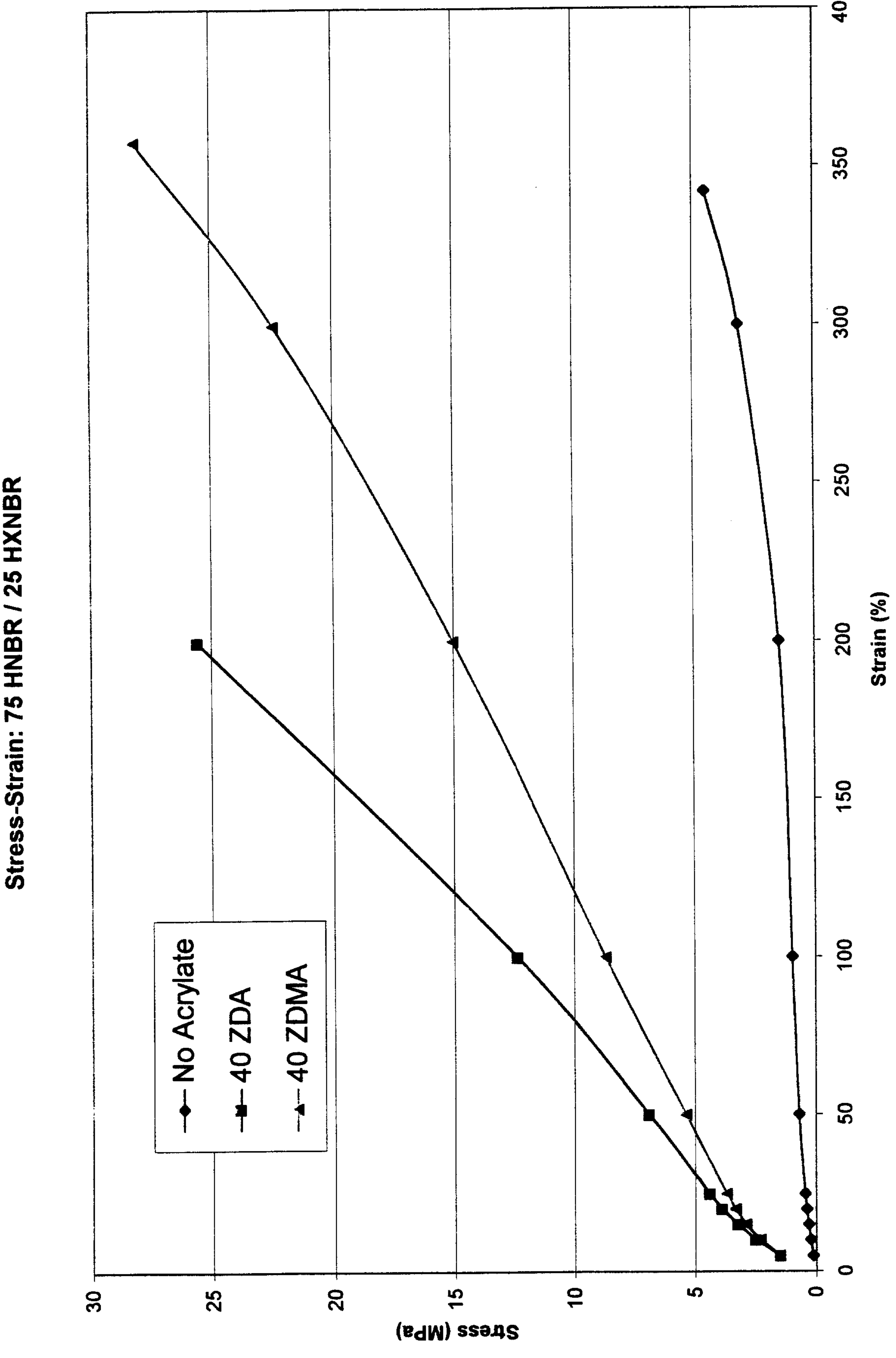

Stress-Strain: 75 HNBR / 25 HXNBR
No Acrylate
40 ZDA
40 ZDMA
Stress (MPa)
0
5
10
15
20
25
30
Strain (%)
0
50
100
150
200
250
300
350
400

FIG. 8

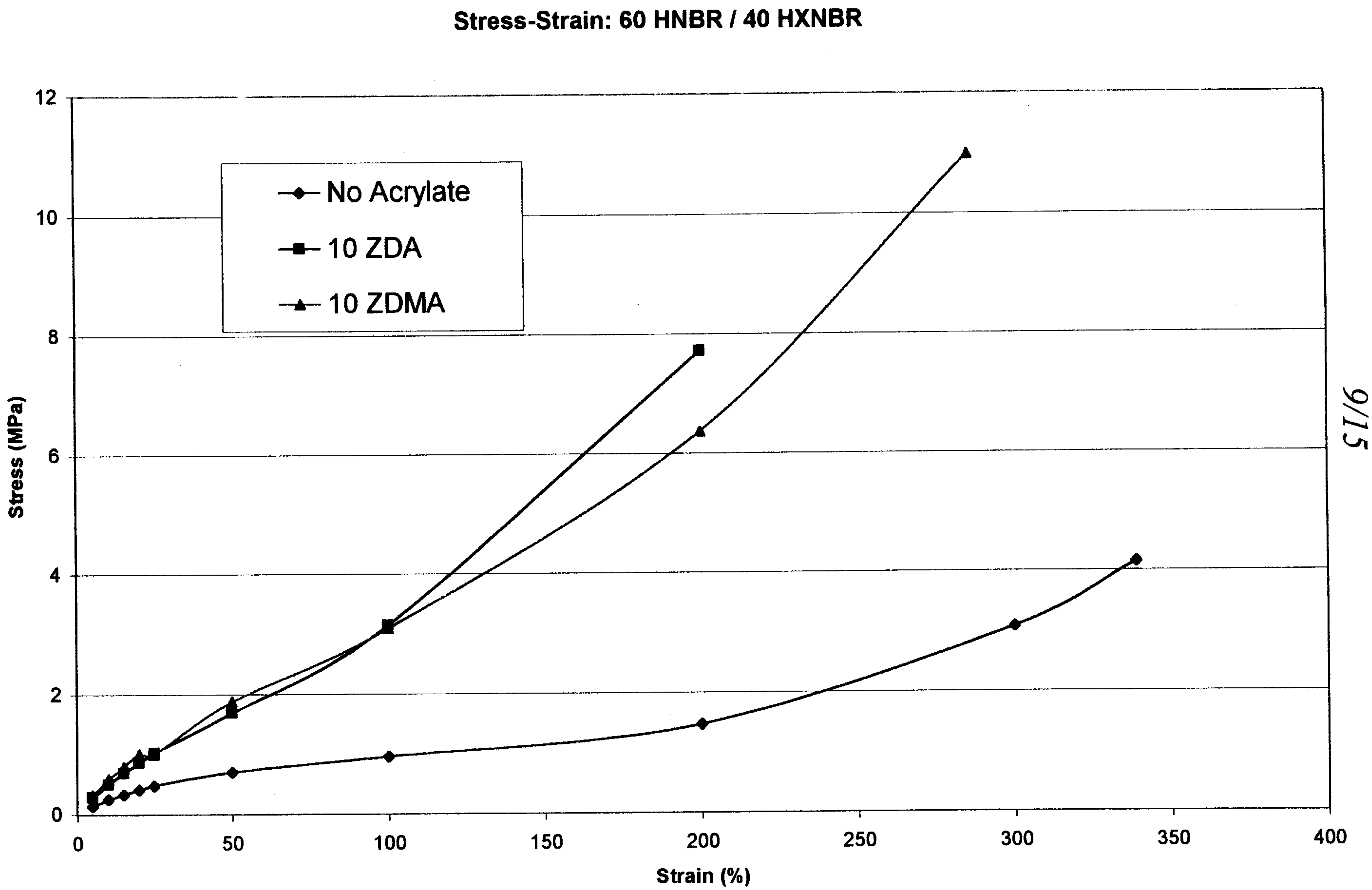

Stress-Strain: 60 HNBR / 40 HXNBR
No Acrylate
10 ZDA
10 ZDMA
Stress (MPa)
0
2
4
6
8
10
12
Strain (%)
0
50
100
150
200
250
300
350
400

FIG. 9

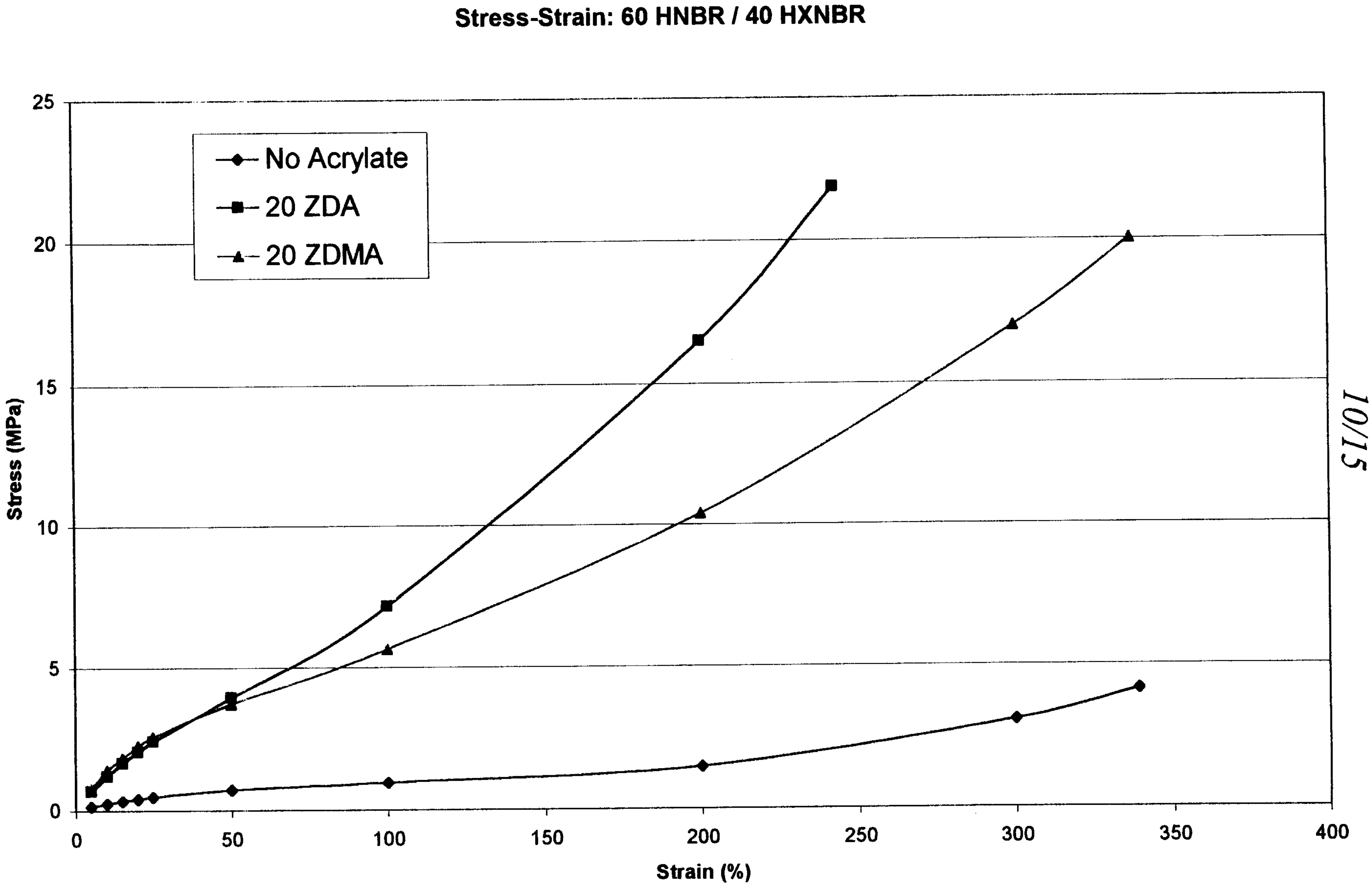

Stress-Strain: 60 HNBR / 40 HXNBR
No Acrylate
20 ZDA
20 ZDMA
Stress (MPa)
25
20
15
10
5
0
0
50
100
150
200
250
300
350
400
Strain (%)

FIG. 10

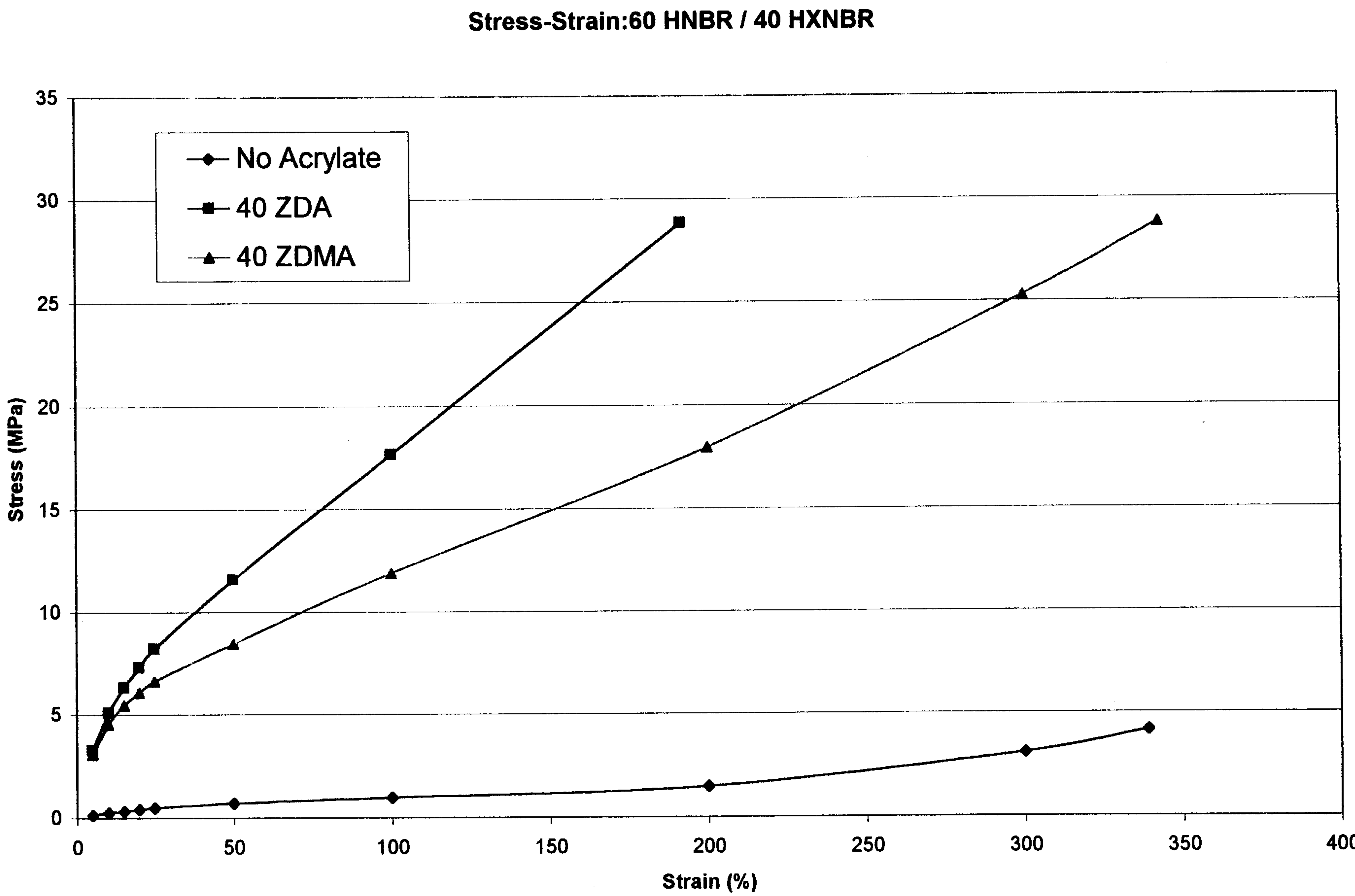

Stress-Strain:60 HNBR / 40 HXNBR
No Acrylate
40 ZDA
40 ZDMA
Stress (MPa)
35
30
25
20
15
10
5
0
Strain (%)
0
50
100
150
200
250
300
350
400

FIG. 11

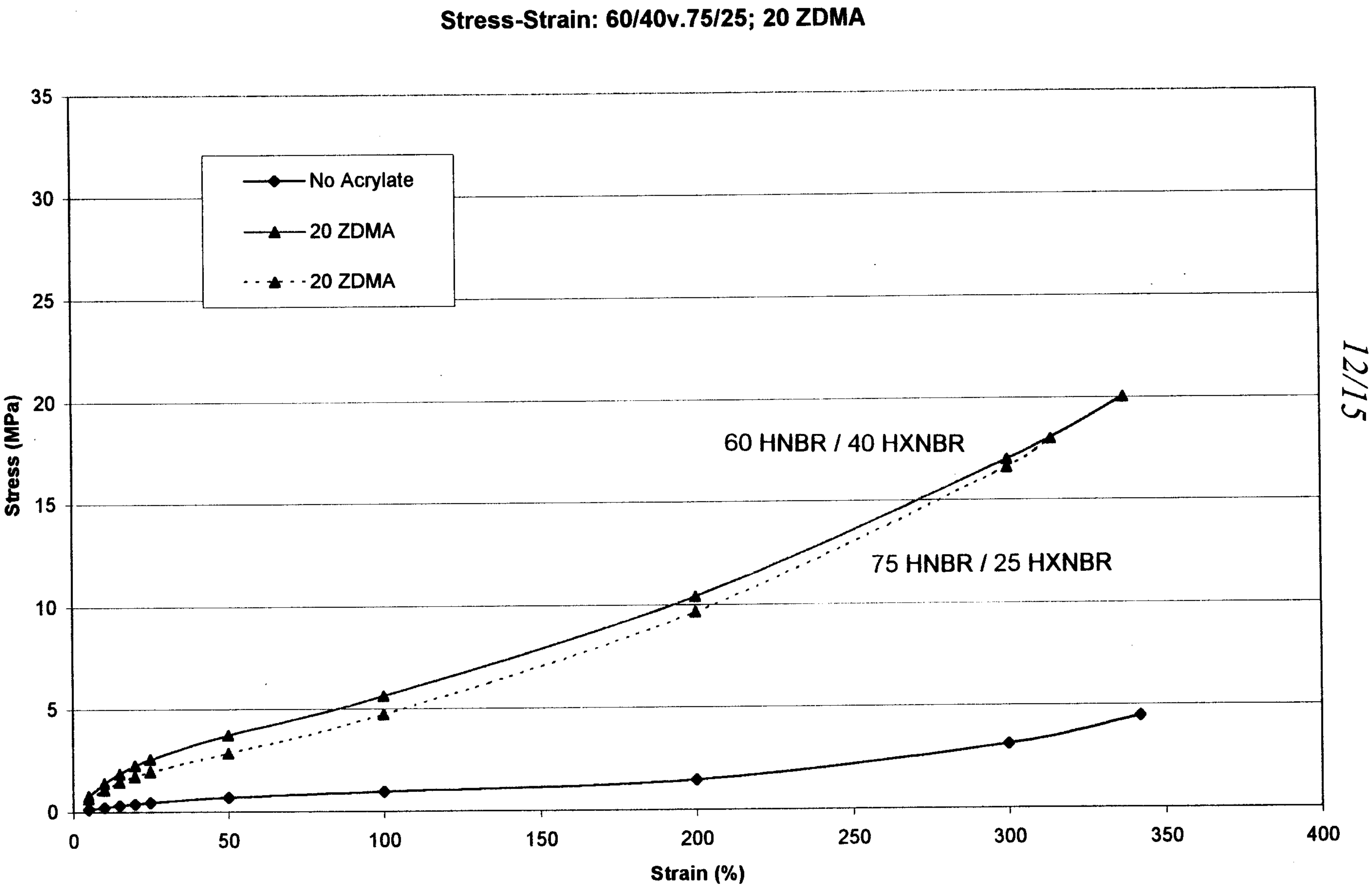

Stress-Strain: 60/40v.75/25; 20 ZDMA
No Acrylate
20 ZDMA
20 ZDMA
60 HNBR / 40 HXNBR
75 HNBR / 25 HXNBR
Stress (MPa)
35
30
25
20
15
10
5
0
Strain (%)
0
50
100
150
200
250
300
350
400

FIG. 12

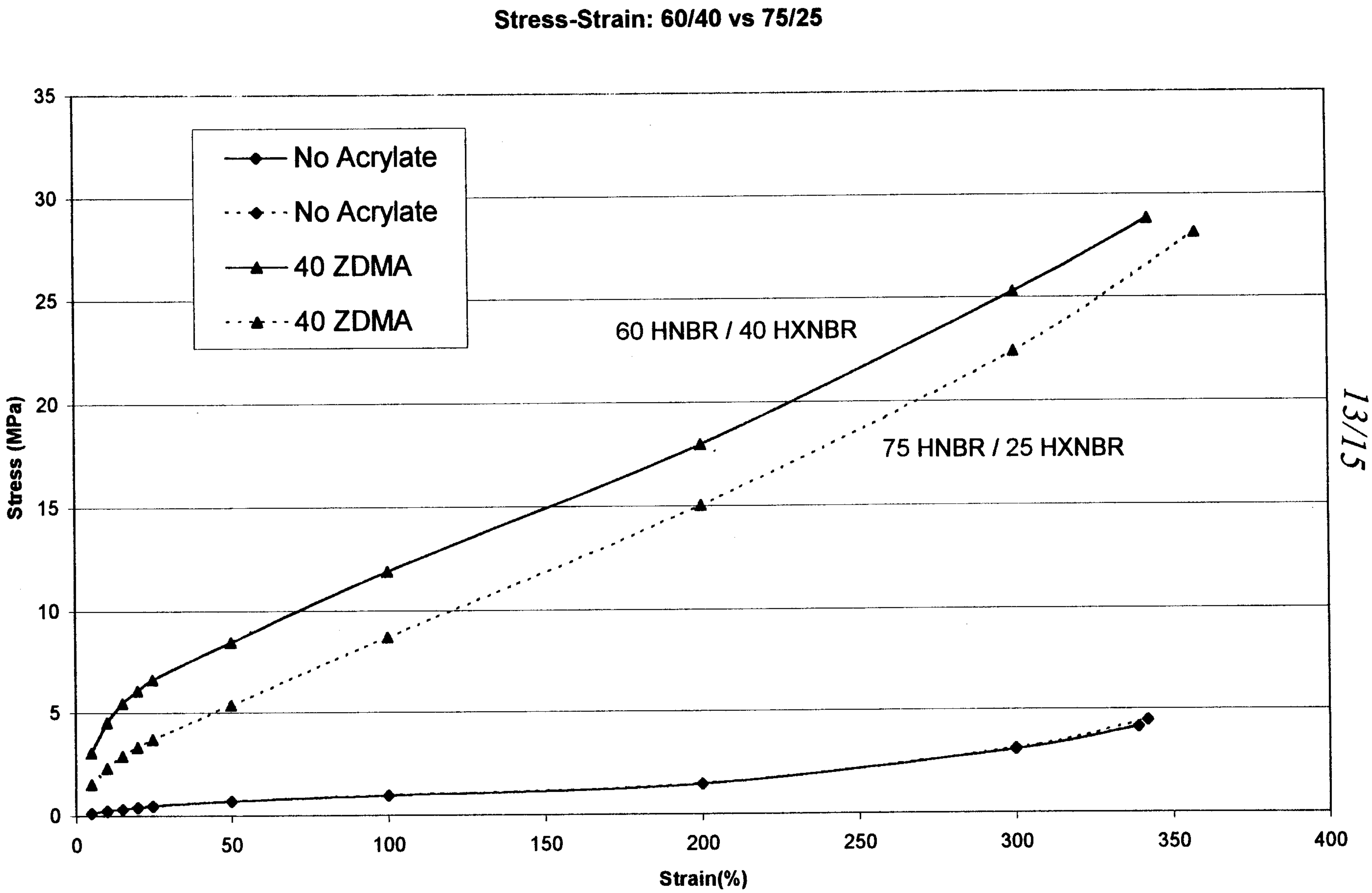

Stress-Strain: 60/40 vs 75/25
Stress (MPa)
35
30
25
20
15
10
5
0
Strain(%)
0
50
100
150
200
250
300
350
400
—◆— No Acrylate
··◆·· No Acrylate
—▲— 40 ZDMA
··▲·· 40 ZDMA
60 HNBR / 40 HXNBR
75 HNBR / 25 HXNBR

FIG. 13

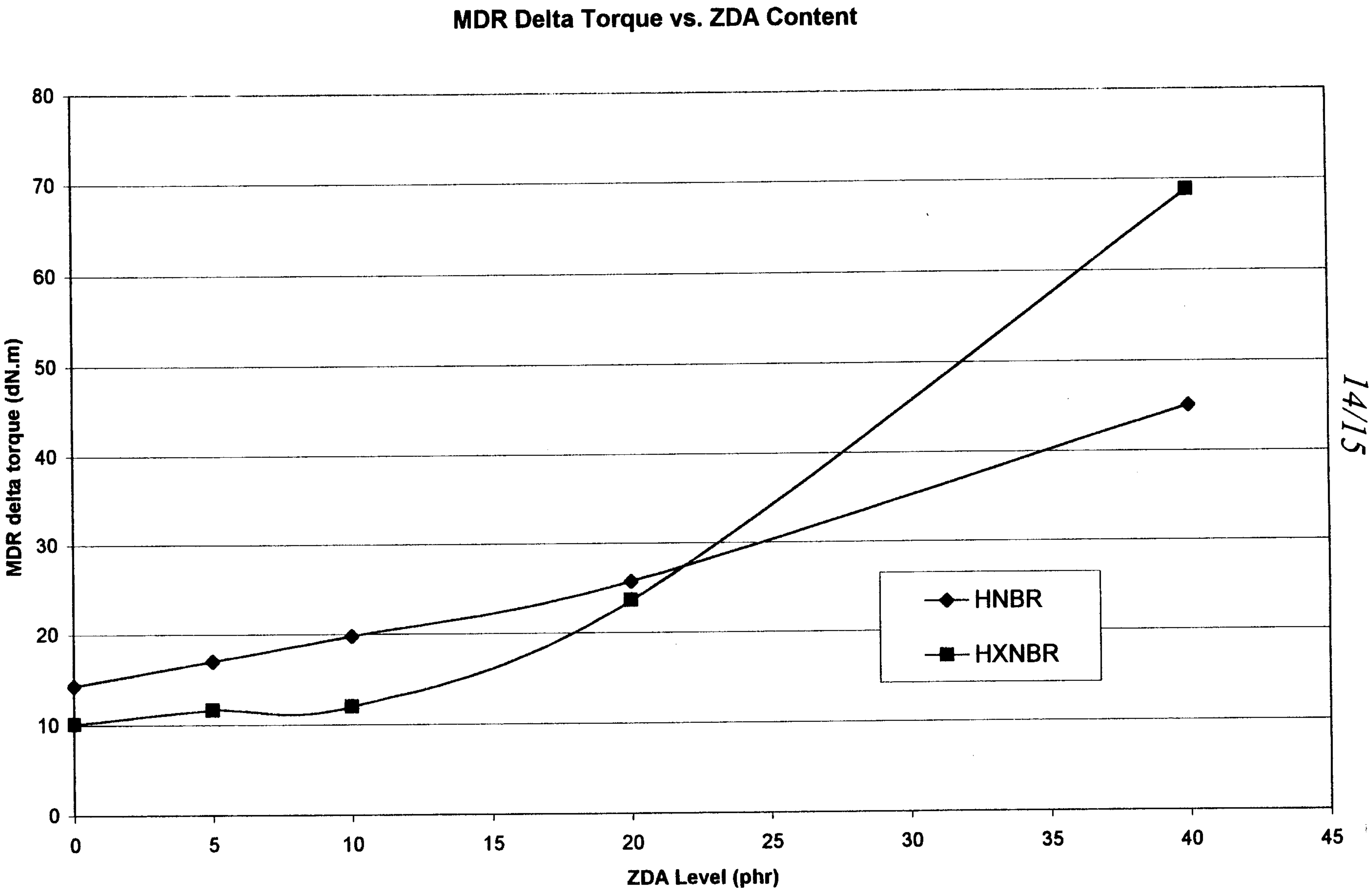
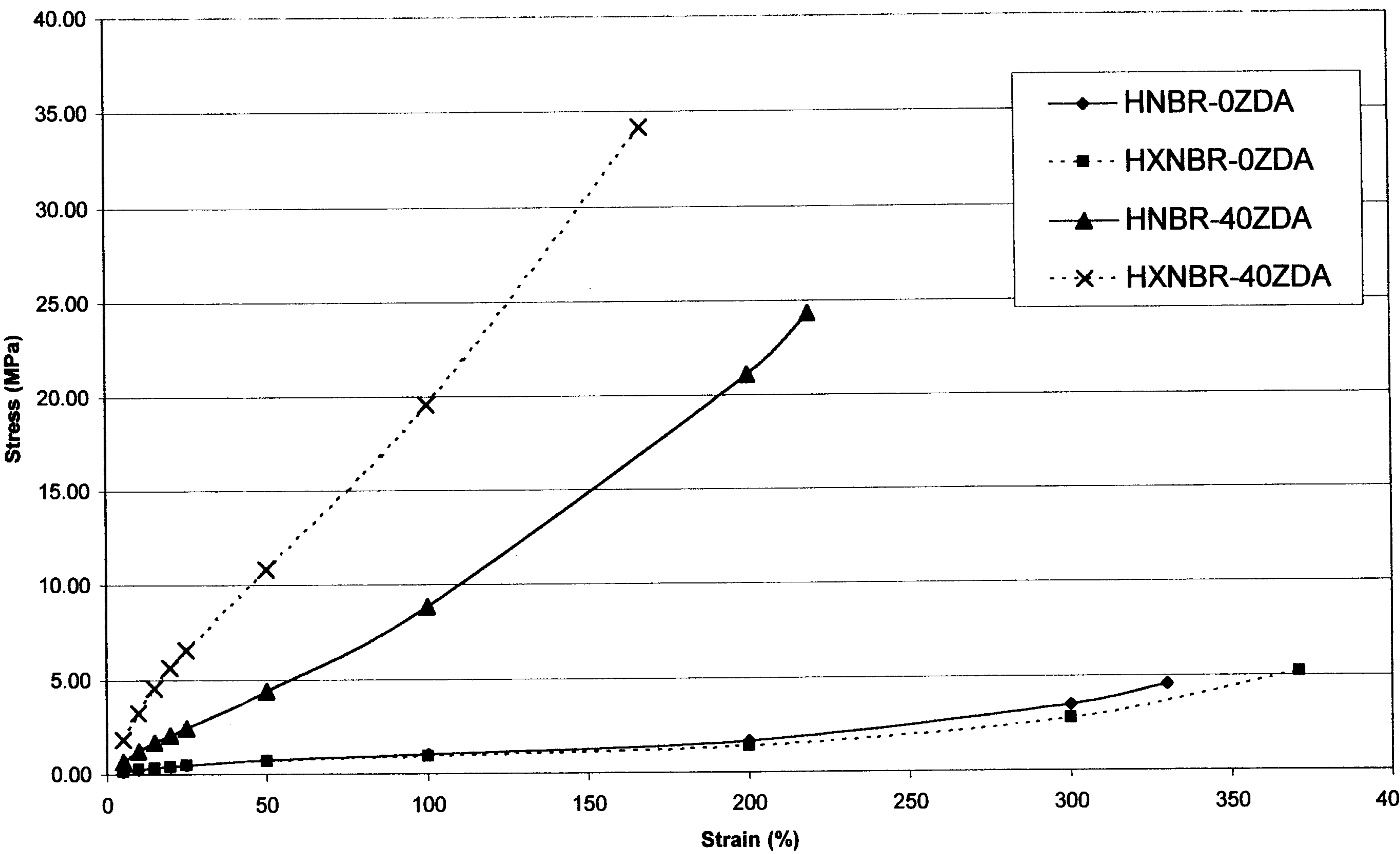
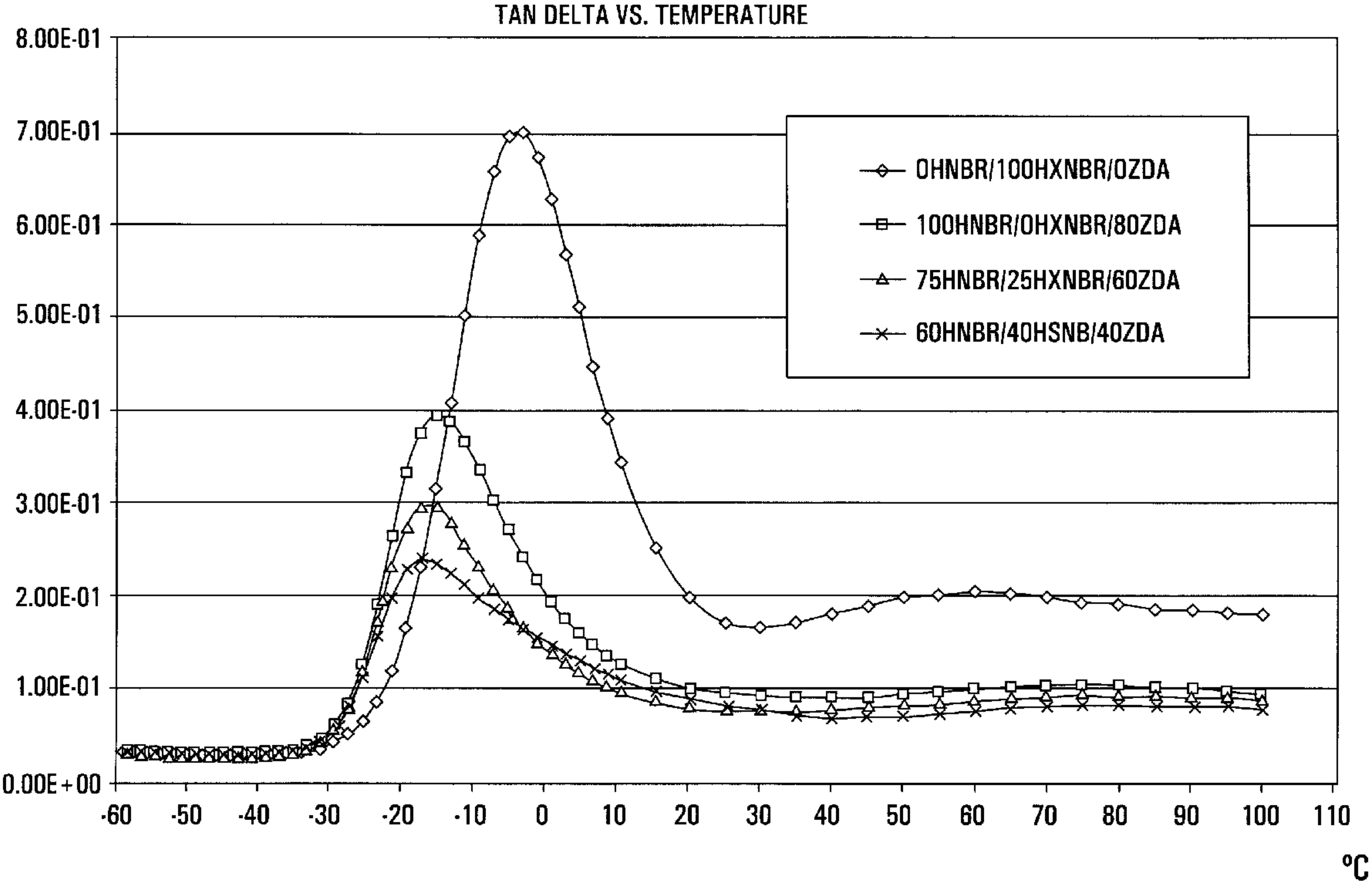

MDR Delta Torque vs. ZDA Content
MDR delta torque (dN.m)
80
70
60
50
40
30
20
10
0
0
5
10
15
20
25
30
35
40
45
ZDA Level (phr)
HNBR
HXNBR

FIG. 14



Stress-Strain: Comparison of 100 HNBR or HXNBR @ 0 and 40 ZDA

FIG. 15


TAN DELTA VS. TEMPERATURE
8.00E-01
7.00E-01
6.00E-01
5.00E-01
4.00E-01
3.00E-01
2.00E-01
1.00E-01
0.00E+00
-60
-50
-40
-30
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
°C
0HNBR/100HXNBR/0ZDA
100HNBR/0HXNBR/80ZDA
75HNBR/25HXNBR/60ZDA
60HNBR/40HSNB/40ZDA