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STUDY OF THE OIL – RESISTANCE OF NATURAL RUBBER*

การศึกษาคุณสมบัติความทนต่อน้ำมันของยางธรรมชาติ

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ABSTRACT

Studies were made of the oil-resistant properties of natural rubber (NR). The effects compounding ingredients on the oil-resistance of NR were determined. The results showed that compounding by changing crosslink type, crosslink density, accelerators or additions of fillers could modify oil-resistant properties of NR but the effect was small compared with the effect of chemical structure of rubbers. The improvement of oil-resistance of NR was attempted through the method of blending with NBR or ENR-50. Blending of NR with NBR or ENR-50 could lower its swelling in oils and fuels to the extent that depends on NBR or ENR content. However, it was not sufficient to modify the oil-resistance of NR to acceptable levels by blending with NBR or ENR. NR may only be used in small quantity 10-30% in order to modify prices of oil-resistant NBR or ENR.

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บทคัดย่อ

การศึกษาคุณสมบัติด้านความทนต่อน้ำมันของยางธรรมชาติ โดยการเปลี่ยนแปลงชนิดและปริมาณของสารผสมต่าง ๆ ในยางพบว่า การเปลี่ยนแปลงชนิดของสารเชื่อมโยงโมเลกุลของยาง การเพิ่มปริมาณการเชื่อมโยงโมเลกุลยาง ชนิดสารช่วยเร่งการเกิดปฏิกิริยา หรือการเพิ่มของสารเสริม สามารถเพิ่มคุณสมบัติความทนต่อน้ำมันของยางธรรมชาติได้ในระดับหนึ่ง แต่เมื่อเทียบกับอิทธิพลจากโครงสร้างทางเคมีของตัวยางเองต่อการทนต่อน้ำมัน ก็ถือได้ว่ายังอยู่ในระดับต่ำ เมื่อปรับปรุงคุณสมบัติความทนต่อน้ำมันของยางธรรมชาติ โดยการผสมยางเข้ากับยางที่ทนน้ำมัน ได้แก่ ยางไนไตรล์ (NBR) และยางธรรมชาติอิพอกซิไดซ์ (ENR) พบว่า ยางธรรมชาติจะสามารถทนต่อน้ำมันได้มากน้อยเพียงใดนั้นขึ้นอยู่กับปริมาณยางทนน้ำมันที่ผสมอยู่ การผสมยางทนน้ำมันเข้ากับยางธรรมชาติเพื่อให้ได้ยางธรรมชาติที่มีคุณสมบัติทนต่อน้ำมันในระดับที่สามารถนำไปใช้งานได้เหมือนยางทนน้ำมันนั้นไม่สามารถกระทำได้ แต่สามารถนำยางธรรมชาติมาผสมกับยางทนน้ำมันในอัตรา 10–30% โดยน้ำหนัก เพื่อลดต้นทุนการผลิตยางทนน้ำมันซึ่งมีราคาแพงได้

INTRODUCTION

Rubbers are usually selected for oil-resistance applications on the basis of their properties before and after aging in test fluids under conditions that are related to service environment and the cost and ease of processing of their compounds.[1] All of the oil-resistance rubbers are special rubbers such as nitrile rubber(NBR), chloroprene rubber(CR), polysulphide rubber(TR) and so on. There are no obvious general trends toward the use of other single rubber (i.e. general purpose rubber) in recent or predicted usage. This is because of the wide variety of properties required in industrial applications,[2] the large number of specifications for each types of industries, and the versatility of special rubbers. The successful development and use of oil-resistant synthetic rubbers has inevitably led to a slackening of interest in oil-resisting natural rubber. However, since Thailand is a natural rubber-producing country and a large volume of oil-resistant synthetic rubber has to be imported every year and is relatively expensive. This gives some importance to the problem of compounding natural rubber so as to confer the best resistance to the swelling action of fuels and petroleum hydrocarbons.

MATERIALS AND METHODS

Materials:

Natural rubber(NR), nitrile rubber(NBR) and epoxidised natural rubber(ENR) were used for this study. The characteristics of these rubbers were summarized in Table 1. All the ingredients used in the rubber formulations were commercial grade and were used without purification. The peroxide used was dicumyl peroxide(Di-Cup) which was vacuum dried at room temperature for at least 24h before being used. Test liquids used for swelling action of rubber vulcanisates were commercial grade except standard reference liquids and oils. The characteristics of these standard liquids were shown in Table 2.

Mixing procedure:

A laboratory two-roll mill (Nishimura Model NS-76) with roll size 76 × 190 mm (dia. × length) was operated at 20.3 and 18.3 rpm of the front and bade rolls for mixing the rubber compounds. The basic formulation shown in Table 3 was employed to determine the effect of compounding ingredients on oil-resistant properties of NR vulcanisates. Comparison of the oil-resistant properties of rubber vulcanisates was determined using formula in Table 4. This formulation also used to determine oil-resistant properties of NR/ENR blends by changing NR/ENR blends ratios. Formulations in Table 5 was employed to improve oil-resisting NR vulcanisates by blending with NBR. The rubber was introduced to a roll and form band on front roll and masticated for 3 min. All the ingredients were added. The time of mixing was varied so that mixes were obtained, usually within 15 min, then mixes were sheeted with a 2.0 mm gap.

Vulcanisation procedure:

Vulcanisation of the rubber compounds were carried out on a laboratory hot press (Toyoseiki A-251400363) by using stainless steel mould having the dimension of 170 × 170 × 2 mm. Vulcanisation was effected at 150 ± 1°C under the applied pressure of 10-12 MN/m^2, employing the optimum cure time determined by using Wallace Curometer marked VI. The samples obtained were kept for the minimum of 16h before their properties were measured.

Testing:

Swelling properties determined by using the ISO 1817 procedure. Two volume change specimens of each elastomer were exposed in a test tube to each of the liquid. Exposure for 7 days at room temperature and elevated temperature(100°C) were determined to be sufficient for most elastomer to equilibrium swell. Tensile properties were determined using the ISO 37 and ISO 48. An Instron Tester (Model 1026) with crosshead speed of 400 mm/min and Zwick D-7900 Hardness Tester equipped with Shore A scale were used. Phase separation in rubber blends were characterised by a differential scanning colorimetry (DSC). The DSC used was the DuPont Thermal Analyser model 990 with heating rate 10°C/min, sensitivity setting of 0.1 over the temperature range −100°C to 60°C.

RESULTS AND DISCUSSION

Effect of compounding on the oil-resistance properties of NR vulcanisates

Effect of crosslink type:

The crosslink densities of the rubber vulcanisates were adjusted to the same level and the crosslink types were varied by adjusting sulphur to accelerator ratios. Three different crosslink types were studied corresponding to characteristic crosslink type of conventional vulcanisation(CV), efficient vulcanisation(EV) and semi-efficient vulcanisation (semi-EV). It will be observed from Talbe 6 that changing the crosslink types from S_1, S_2, to S_x had only marginal effect on the swelling of NR vulcanisates at room temperature. However, the data for swelling test at high temperature (100°C) showed that NR vulcanised by EV system had slightly superior swelling resistance than the samples vulcanised by CV or semi-EV system. Carbon-carbon crosslinks existed in peroxidecured NR vulcanisates resulted in the smallest swellings in all liquids than did sulphur-sulphur crosslinks both at normal and high temperatures. The explanation is based on the strengths of the crosslinks shown in Table 7. The bond energies decrease in the order of C-C, -S-, $-S_2-$ and $-S_x-$.

Effect of crosslink density:

Moduli of rubber vulcanisates were measured at small strain to give crosslink density by the relation

crosslink density (ν) = $E/3 \times R \times T$
where E = Young's modulus
R = Gas constant = $8.314\ J\ K^{-1}\ mol^{-1}$
T = Absolute temperature

The crosslink density was varied by changing the quantity of sulphur used to effect the crosslinking from 1.0-5.0 phr. The relationship between sulphur content and crosslink density is shown in Figure 1. Results of the crosslink density on oil-resisting of NR vulcanisates will be seen from Figure 2 that for all types of oils and liquids studies, increasing the crosslink density caused the volume swell to decrease as was expected. In practice, the sulphur used is more likely to be 1.0-3.0 phr. At this sulphur level, the swellings of NR vulcanisates in oils were too large for the application as oil-resistant materials.

Effect of types of accelerator:

It will be seen from Table 8 that difference accelerators gave rubber vulcanisates exhibited different percent volume change in a given liquids. The improvement that was obtained by changing the accelerator type, however, was not sufficiently great as to be useful as the mean to improve the oil-resistance of NR. The differences between the largest and the smallest swelling as a result of varying accelerator types were 74% for liquid A, 126% for liquid B, 3% for brake fluid, 48% for engine oil and 38% for gear oil. The results obtained might be explained, to the certain extent, by the differences in crosslink density exhibited by the rubber vulcanisates that were vulcanised by using different accelerators.

Effect of type and amount of fillers:

For both carbon black and silica, it will be observed from Table 9 and Figure 3 that their inclusion to NR vulcanisates caused reduction in the percent volume swell in oils, the extent of reduction being dependent upon the amount of fillers. Increasing the quantity of carbon black or silica caused the volume swell of rubber vulcanisates in liquid A and liquid B to be reduced by 10-20% for 10 phr of fillers to 40-50% for 50 phr of fillers. The effect on fuel oil, gear oil and brake fluid being much less. The effect due to carbon black might be explained on the basis of increasing crosslinking between the rubber and the carbon black particles, which thus causing reduced volume swell of the vulcanisates. On the other hand, the decreases in volume swell of NR vulcanisates in the presence of silica was to be due to the polar nature of silica which repelled the non polar oils.

Effect of antioxidant:

A brief study was made in order to see whether antioxidant (Wingstay-L) will have any influence on the swelling properties of NR vulcanisates in oils. The results shown in Figure 4 revealed that NR vulcanisates might benefit from the inclusion of antioxidant into their recipe since the rubber samples were comparatively much less swollen. The decrease in percent volume swell in engine oil at 100°C was about 100% when 1 phr of Wingstay-L was included. The decrease, however, levelled off at around 100-120% volume swell even though larger quantity of antioxidant was added. It appeared, therefore, that only 1-2 phr of antioxidant will be required to protect NR vulcanisate against swelling in engine oil at high temperature.

Comparison the oil-resistance of rubber vulcanisates

Comparison between swelling properties of NR and NBR (or ENR) shown in Table 10 revealed that oil-resistant properties of NR vulcanisates are much poorer than NBR (or ENR) vulcanisates. The volume swelling of NR vulcanisates range from 55-70% in engine oil, 36-80% in gear oil and 120-370% in liquid A and liquid B whereas NBR and ENR vulcanisates showed nearly equivalent resistance properties both in oils and liquids. In brake fluid, swelling resistance properties of NR vulcanisates exhibited better swelling resistance than NBR and ENR. This could be understood in terms of solubility parameter (χ) of the rubbers and brake fluid (ethylene glycol). The difference in solubility parameter between NR ($\chi = 16.49\text{-}16.62 \times 10^{-3} J^{1/2}/m^{3/2}$) and ethylene glycol ($\chi = 29.9 \times 10^{-3} J^{1/2}/m^{3/2}$) is greater than that between ENR or NBR ($\chi = 21.28\text{-}21.36 \times 10^{-3} J^{1/2}/m^{3/2}$) and the glycol, therefore, the swelling of NR vulcanisates were less.

The improvement of oil-resistance NR vulcanisates

Oil-resistance of filled NR/NBR blends:

The general trend that oil-resistance of the blends increased with increasing NBR content are shown in Table 11. It is of particular interest to look at the volume swell of blends in the highly swelling ISO oil no. 3. It will be observed that NBR vulcanisates showed 4% volume swell and the only NR/NBR blend which possessed comparable level of swelling was 20/80 NR/NBR blend. All the remaining blend showed volume swelling of greater than 20%. At elevated temperature of 110°C, 20/80 NR/NBR blend swelled to almost 40% by volume, thus became less useful for oil-resistance applications. Physical properties of filled NR/NBR blends were also measured and results are presented in Table 12. It will be observed that blends of NR/NBR were poorer in properties to the individual rubber from which they were prepared. They exhibited lower moduli and tensile strength. Since NR and NBR cured at different rate, it was likely that the poor properties of blends resulted from incomplete curing of any of the two rubber components or poor distribution of fillers in NR and NBR phases. The lower tensile strength of the blends might also originated from poor adhesion between the widely-different polarity NR and NBR phases.

Oil-resistance of NR/ENR blends:

The percent volume swelling of NR/ENR blends in various oils and liquids are shown in Table 13. The swelling behaviour of NR/ENR blends were somewhat similar to those of NR/NBR blends, in that the oil-resistant components, viz NBR and ENR, had to be present in much greater quantity than NR. Tensile properties of NR/ENR were measured and the results are given in Table 14. It will be seen that whereas ENR and NR showed the same level of strength, moduli and elongation at break, their blends were much inferior in these properties. The relatively poor properties of the blends were thought to arise from the difference in cure rate of NR (45 min) and ENR (25 min). It was quite possible that NR phase in the blends was undercured, resulting, therefore, in overall low strength and moduli. The poor tensile strength of NR/ENR blends might also arise from poor adhesion between NR and ENR phases.

Compatibility in rubber blends:

DSC thermogram of rubber blends of NR and oil-resistance rubbers are shown in Figures 5 and 6. Two distinct of glass transition (T_g) that of NR (−66°C) and NBR (−24°C) or ENR (−18°C) were observed, indicating that NR and NBR (or ENR) are immisible and form two separate phases. Incompatibility between the two rubbers is a disadvantage and make poor oil-resistance properties, including physical properties of blend. Further study is required in order to improve the compatibility of rubber blends using a compatibilising agent.

CONCLUSION

The experimental results indicated that chemical structure of rubber was the determining factor for oil-resistance properties. Thus, NBR and ENR are oil-resistant but NR was not. Blending of NR with oil-resistant rubbers were not sufficient to modify the oil-resistance of NR to acceptable levels. Phase separation in rubber blends caused poor oil-resistance and poor physical properties of the blends.

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Table 1. Rubber properties

Rubber	Properties	Suppliers
NR	No.2 smoked sheet rubber, density 0.923, plasticity number (P_0) = 54.0	Commercial
NBR	39% acrylonitrile content, density 1.0, mooney viscosity ML 4′ (@) 100°C = 50-63	Goodyear
ENR-50	50% epoxidation, MW = 5×10^6 P_0 = 45.0	Rubber Research Institute of Malaysia (RRIM)

Table 2. ISO reference oils and liquids

ISO reference oils	no. 1	no. 3
Aniline point, °C	124.0 ± 1.0	70.0 ± 1.0
Kinematic viscosity ($mm^2/S(cst)$)	18.7 - 21.0	31.0 - 34.1
Flash point min, °C	243	163
ISO reference liquids liquid A - isooctane liquid B - isooctane (70 volume %) + toluene (30 volume %)		

Table 3. Basic formula of rubber compound

NR	100.00	phr
ZnO	6.00	,,
Stearic acid	0.50	,,
Accelerator (MBT)	varied	,,
S	varied	,,
Cure temperature	150 ± 1°C	

Table 4. Formulations for rubber vulcanisates

Material	Formulation		
	1	2	3
NR	100.0	—	—
NBR(N300)	—	100.0	—
ENR-50	—	—	100.0
Filler(N220)	30.0	30.0	30.0
Napthenic oil	5.0	5.0	5.0
ZnO	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0
Flectol H	2.0	2.0	2.0
S	0.30	0.30	0.30
MBS	2.4	2.4	2.4
TMTD	1.6	1.6	1.6
Santogard PVI	—	—	0.15
Anhydrous Na_2CO_3	—	—	0.30
Cure time (min)	45	50	25

Table 5. Formulation for the study of oil-resistance of filled NR/NBR blends

Material	Formulation							
	1	2	3	4	5	6	7	8
NR	0.0	20.0	30.0	40.0	60.0	70.0	80.0	100.0
NBR(N300)	100.0	80.0	70.0	60.0	40.0	30.0	20.0	0.0
ZnO	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
CBS	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
S	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
C-black(N330)	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0
Wingstay-L	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Napthenic oil	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Cure time (°C)	45	45	50	45	50	50	50	45

Table 6. Volume swell of each system of NR vulcanisates in various liquids

System	Crosslink Density (1×10^{-4} mole/cm^3)	% Volume change (7 days, room temp.)					% Volume change (7 days, 100°C)				
		Liquid A	Liquid B	Engine oil	Gear oil	Brake fluid	Liquid A	Liquid B	Engine oil	Gear oil	Brake fluid
CV	1.809	232	371	79	52	2.1	a	a	237	209	13
Semi-EV	1.791	243	388	79	60	2.2	a	a	228	290	11
EV	1.866	243	390	80	61	3.1	757	b	213	200	9
Peroxide Cured NR	1.857	200	298	75	52	0	475	587	154	147	7

a = Samples disintegrated after 4 days

b = Samples disintegrated after 6 days

Table 7. Bond energy of different crosslink type

Type of linkage in rubber network	Bond energies (kJ/mol)
$-C-S_x-C(X>2)$	< 268
$-C-S_2-C-$	268
$-C-S-C-$	285
$-C-C-$	352

Table 8. Volume swell of NR vulcanisates different in types of accelerator

Types of accelerator	Crosslink density (1×10^{-4}mole/cm^3)	% Volume change (7 days, room temp.)				
		Liquid A	Liquid B	Brake fluid	Gear oil	Engine oil
Thiazole:						
MBTS	1.013	270	434	5	130	96
MBT	1.348	277	451	3	85	60
Guanidine:						
DPG	1.409	273	451	5	133	98
Sulphenamide:						
CBS	1.705	203	329	2	105	70
Thiuram:						
TMTM	2.067	207	325	4	102	76

Table 9. Volume swell of filled NR vulcanisates in various liquid

Filler(phr)	% Volume swell (7 days, room temp.)					% Reduction in volume swell			
	Liquid A	Liquid B	Engine oil	Gear oil	Brake fluid	Liquid A	Liquid B	Engine oil	Gear oil
C-black (N330):									
0	232	371	79	53	2.1	0	0	0	0
10	186	302	77	53	2.1	20	19	3	0
20	167	263	73	53	3.1	28	29	8	0
30	141	227	68	46	3.1	39	39	14	13
40	129	209	61	41	3.7	44	44	23	23
50	119	190	57	38	3.5	48	49	28	29
Silica:									
0	232	371	79	53	2.1	0	0	0	0
10	215	353	79	53	2.7	7	5	0	0
20	181	302	69	53	3.6	22	18	13	0
30	171	271	68	51	3.8	26	27	14	4
40	139	239	60	47	5.3	40	36	24	11
50	132	214	46	36	6.2	43	42	42	32

Table 10. Comparison between the oil-resistant properties of NR, NBR and ENR vulcanisates in various liquids

Types of Liquid	% Volume change (7 days, room temp.)		
	NR	NBR	ENR
Liquid A/liquid B	120 - 370	4 - 45	5 - 45
Gear oil	36 - 80	1 - 4	−3 - 4
Engine oil	55 - 70	0 - 3	−3 - 0
Brake fluid	2 - 6	18 - 20	11 - 12

Table 11. Volume swell of filled NR/NBR vulcanisates in various liquids

NR : NBR	% Volume swell (7 days, room temp.)							(7 days, 100°C)	
	Liquid A	Liquid B	Engine oil	Gear oil	Brake fluid	ISO oil		ISO oil	
						no.1	no.3	no.1	no.3
0 : 100	2	80	1	0	14	1	4	−5	15
20 : 80	11	42	−2	−3	14	−3	8	−1	37
30 : 70	14	52	2	0	9	−2	17	6	56
40 : 60	31	18	6	2	5	2	28	17	84
60 : 40	61	108	17	10	−2	6	64	58	173
70 : 30	62	109	21	11	−3	7	66	61	204
80 : 20	82	133	28	16	−3	10	90	84	292
100 : 0	121	188	48	34	2	24	119	144	340

Table 12. Physical properties of filled NR/NBR vulcanisates

NR : NBR	Tensile strength (MPa)	Modulus (MPa)		Elongation at break, %
		100%	300%	
0 : 100	12.92 ± 0.83	3.74 ± 0.15	16.27 ± 0.09	312 ± 28
20 : 80	3.70 ± 0.44	1.67 ± 0.11	—	200 ± 40
30 : 70	7.28 ± 0.22	2.00 ± 0.06	6.69 ± 0.09	308 ± 10
40 : 60	7.17 ± 0.54	1.71 ± 0.09	5.58 ± 0.14	359 ± 26
60 : 40	6.46 ± 0.56	1.19 ± 0.04	4.34 ± 0.13	403 ± 32
70 : 30	6.06 ± 0.59	1.50 ± 0.06	5.43 ± 0.14	304 ± 19
80 : 20	6.90 ± 0.49	1.35 ± 0.03	5.18 ± 0.05	336 ± 20
100 : 0	27.78 ± 0.82	3.24 ± 0.22	14.15 ± 0.25	477 ± 15

Table 13. **Percent volume swell of NR/ENR-50 blends in various liquids**

NR : NBR	% Volume swell (7 days, room temp.)							(7 days, 100°C)	
	Liquid A	Liquid B	Engine oil	Gear oil	Brake fluid	ISO oil		ISO oil	
						no.1	no.3	no.1	no.3
0 : 100	5	43	−3	−5	11	−3	0.7	−38	39
20 : 80	28	87	1	0.3	11	0.4	8.0	5	72
30 : 70	39	103	2	0.8	10	0.5	14.0	11	93
40 : 60	51	113	11	7.0	8	7	36.0	24	108
60 : 40	80	155	38	7.0	16	17	80.0	48	149
70 : 30	95	164	47	7.0	24	19	96.0	56	162
80 : 20	115	191	55	5.0	33	24	114.0	75	200
100 : 0	151	227	61	−0.4	41	31	147.0	89	250

Table 14. **Physical properties of NR/ENR-50 vulcanisates**

NR : ENR	Tensile strength (MPa)	Modulus (MPa)		Elongation at break, %
		100%	300%	
0 : 100	22.80 ± 0.42	2.26 ± 0.03	9.53 ± 0.37	535 ± 22
20 : 80	6.75 ± 0.24	0.42 ± 0.03	3.05 ± 0.12	457 ± 39
30 : 70	6.89 ± 0.24	0.60 ± 0.04	2.86 ± 0.05	482 ± 35
40 : 60	7.95 ± 0.26	0.89 ± 0.04	3.42 ± 0.05	490 ± 22
60 : 40	8.09 ± 0.28	0.70 ± 0.06	3.01 ± 0.03	517 ± 16
70 : 30	8.17 ± 0.34	0.74 ± 0.02	3.20 ± 0.05	495 ± 12
80 : 20	7.44 ± 0.26	0.63 ± 0.00	3.04 ± 0.10	475 ± 11
100 : 0	23.91 ± 0.83	2.04 ± 0.21	8.22 ± 0.76	540 ± 39

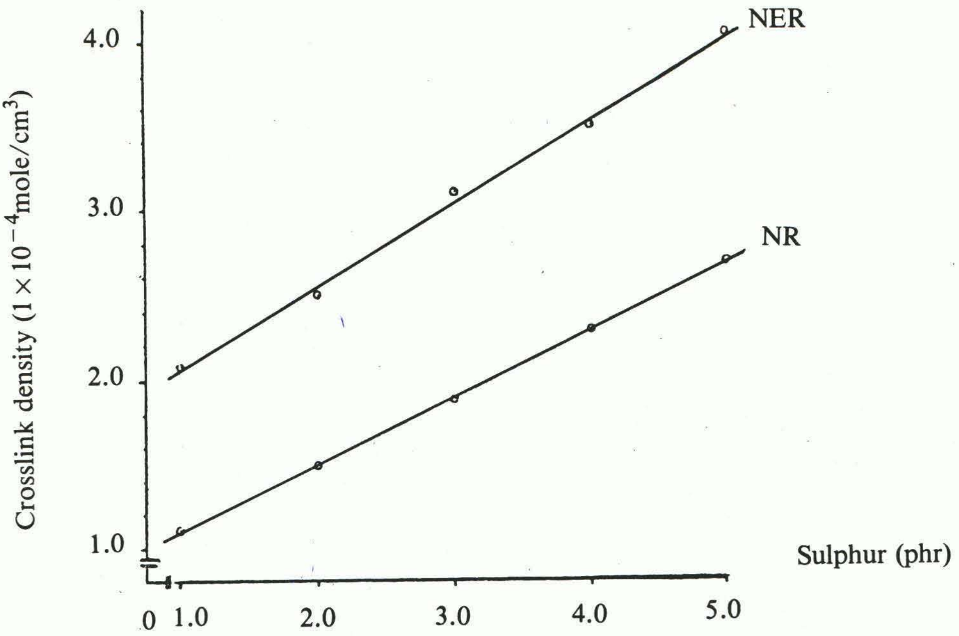

Fig.1 **The relation between crosslink density and sulphur content**

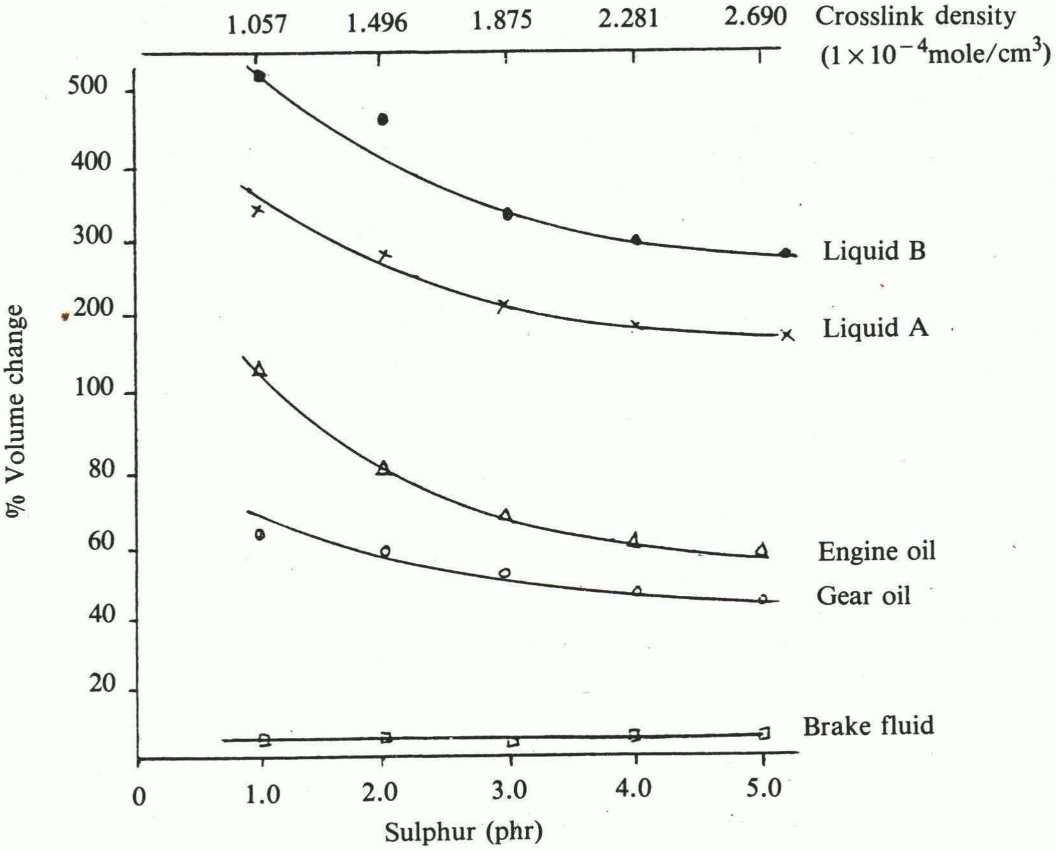

Fig. 2 **Effect of crosslink density on the volume swell of NR vulcanisates in various liquids**

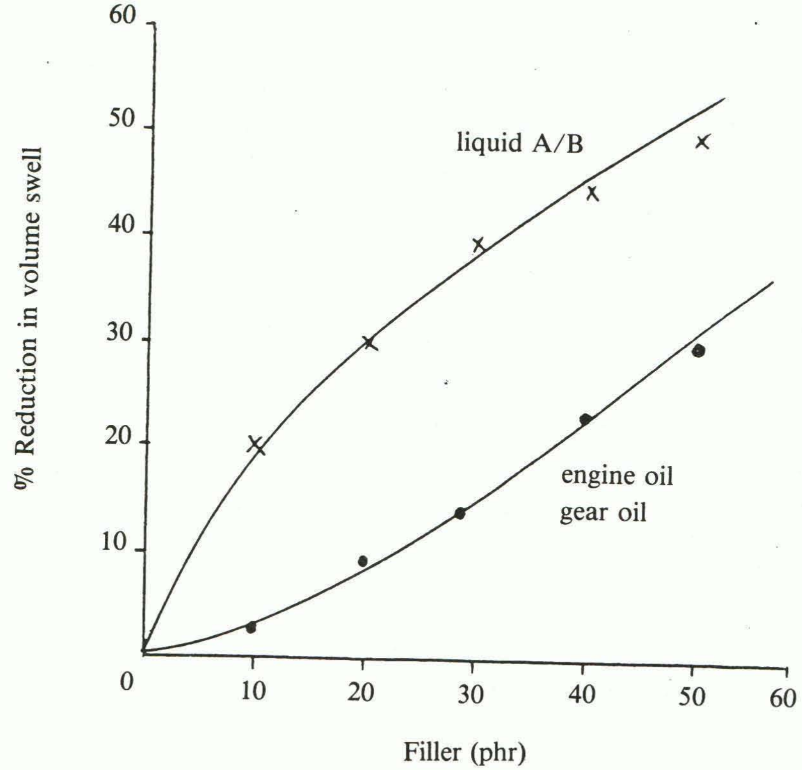

Fig. 3 Reduction in volume swell of filled NR vulcanisates in oils and liquids

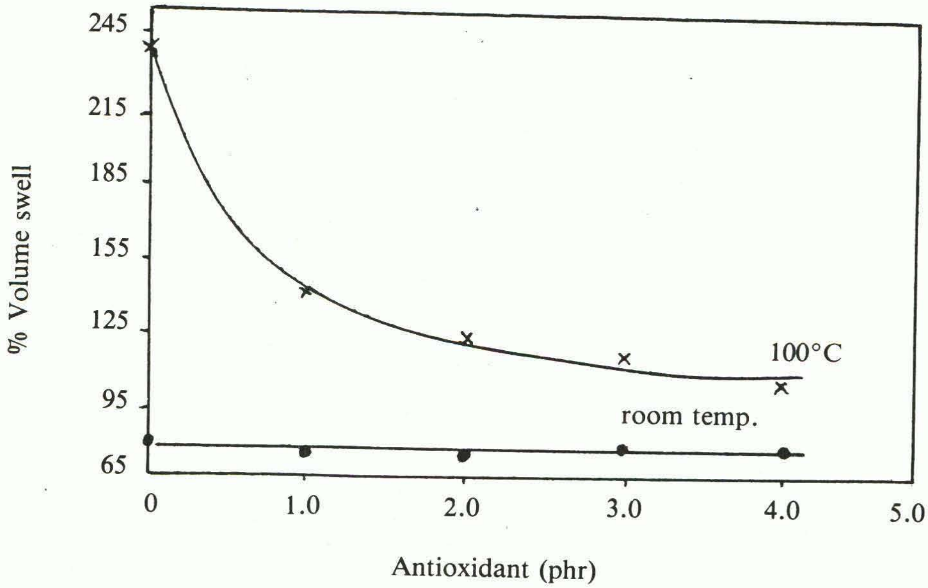

Fig. 4 Effect of antioxidant on volume swell of NR vulcanisates in engine oil at room temperature and elevated temperature

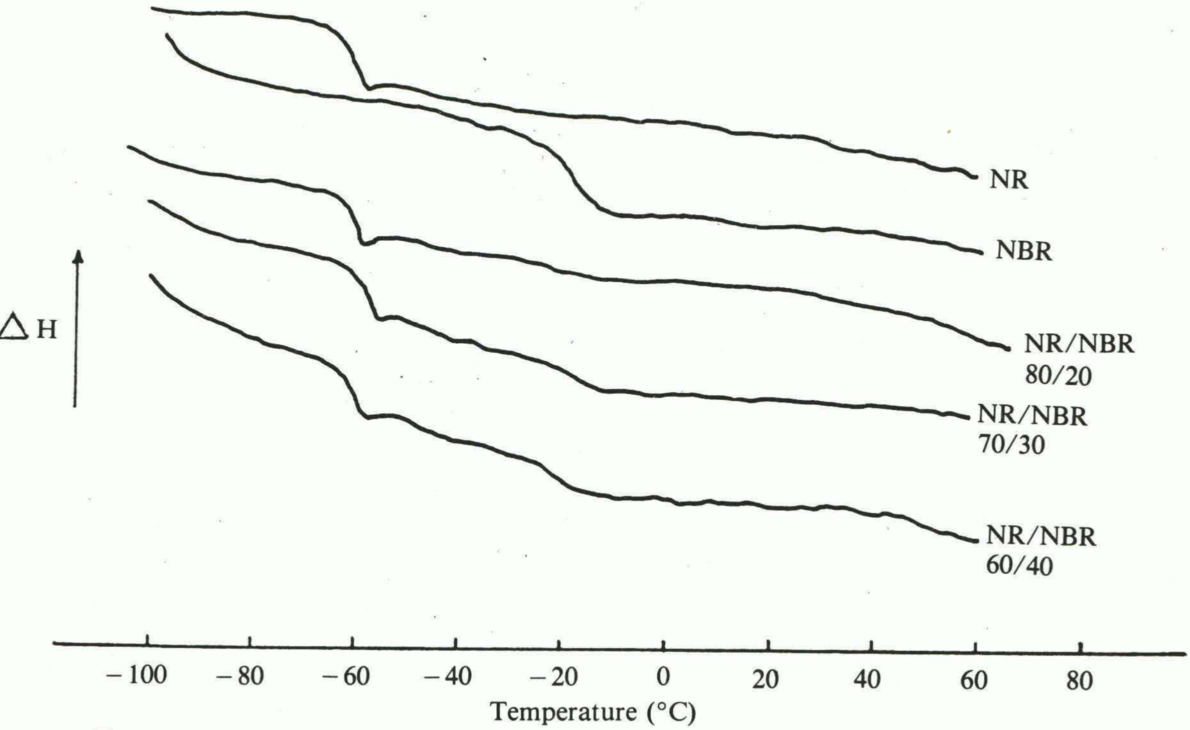

Fig. 5 DSC thermogram of NR/NBR blends

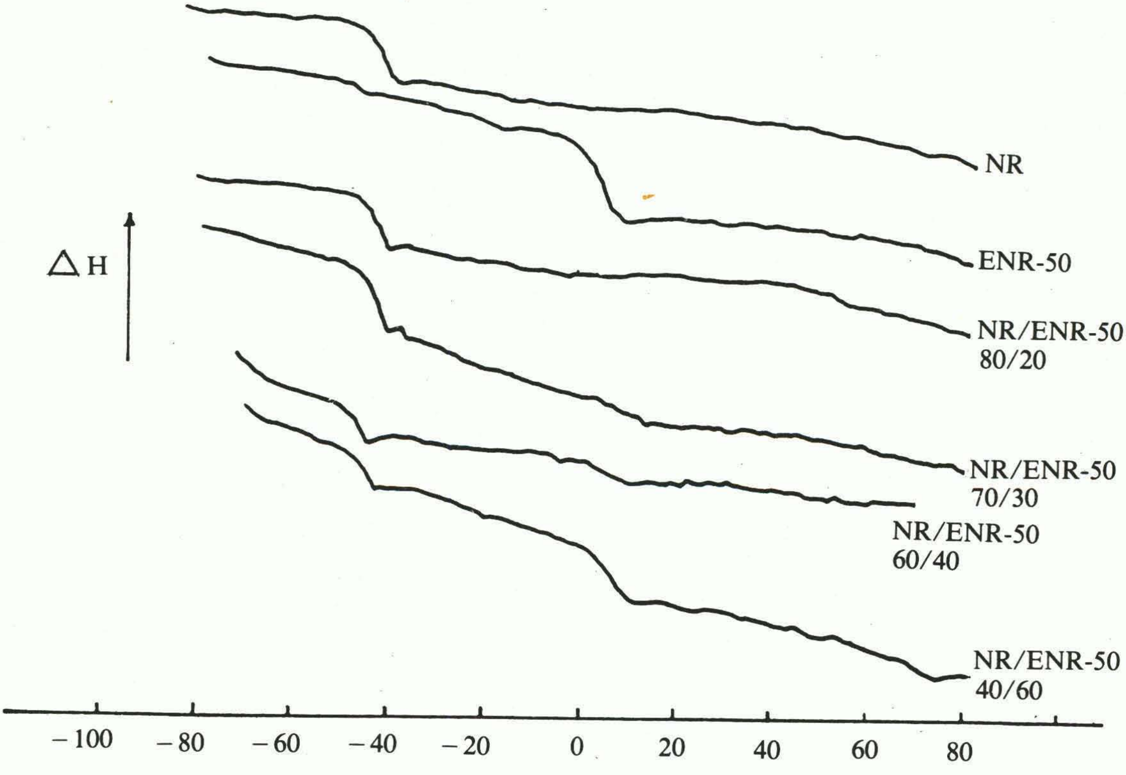

Fig. 6 DSC thermogram of NR/ENR blends