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Amidinothiourea as a secondary accelerator in a binary system for the sulphur vulcanization of natural rubber

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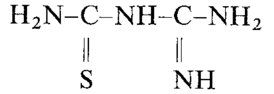
A study of a binary accelerator system using amidinothiourea as a secondary accelerator with mercaptobenzothiazyl disulfide (MBTS), in sulphur vulcanization of natural rubber has been undertaken. This system was found to boost MBTS accelerator activity considerably. From the results, a nucleophilic reaction mechanism was established for this system. Different compositions of the amidinothiourea were tried in different mixes using standard recipes, and reference mixes were also vulcanized. Different cure characteristics of the mixes and important physical properties of the vulcanizates were evaluated. Optimum concentrations of amidinothiourea required were derived and the experimental mixes were found to have better cure characteristics, including an advantageous reduction in the optimum cure time. Many of the physical properties of the vulcanizates studied were also found to be better compared to those of the reference mixes. Evaluation of these properties both before and after ageing showed good retention of these properties as well. An attempt was also made to correlate the variation in physical properties to chemical crosslink formation in the various vulcanizates.

1. Introduction

The use of mixed accelerator systems in rubber vulcanization has received considerable attention, since such systems often show synergism and are very efficient under suitable conditions. Better physical and chemical properties are exhibited by the vulcanizates obtained using mixed accelerator systems [1–4]. Thiourea and its derivatives have been proved to have advantageous properties in this context, especially in the vulcanization of natural rubber latex and neoprene rubber [5–8]. A perusal of the literature indicates that a number of thiourea (TU) derivatives have been tried as accelerators in rubber vulcanization. Many of them, namely ethylene thiourea, *N,N′*-dimethyl thiourea, diphenyl thiourea, sym di-*o*-tolyl thiourea etc., are known, though the most important one is ethylene thiourea. Philpot [5] suggested a nucleophilic reaction mechanism in the thiourea–tetramethylthiuram disulfide (TMTD) binary system of natural rubber latex vulcanization, even though no conclusive evidence was shown. He found that sulphur containing nucleophiles, such as thiourea, enabled accelerators like TMTD to operate at sufficiently lower temperatures. He suggested an ionic mechanism where the S–S bond in TMTD was cleaved by the nucleophile produced from thiourea. Kuriakose and coworkers [9, 10] investigated this further, and found that the higher the nucleophilic character of the thiourea derivative, the higher the rate of vulcanization in the systems under review. They extended the study to different dithiobiuret derivatives of thiourea, ranging in their nucleophilic reactivity. Also different polymers, their blends and lattices were vulcanized using these systems, and they [9–11] were able to give conclusive proof to the suggestions made by Philpot. The cure characteristics of the mixes, physical properties of the vulcanizates and the formation of chemical crosslinks in these systems were also investigated. In many of these properties the systems under review were shown to be better than the control mixes. The optimum concentration of the accelerator requirement was also derived. They extended the study to sulfenamide type accelerators also, and proved the existence of a similar nucleophilic reaction mechanism in such systems.

On the basis of these facts and findings one was encouraged to initiate a study on the accelerator activity of an amidinothiourea derivative. This secondary accelerator was used along with MBTS, aiming at nucleophilic reaction in such a system also. Control mixes were prepared using TU, TMTD and diphenyl guanidine (DPG) along with MBTS. The choice of an amidinothiourea derivative of the general formula given in Equation 1 as a secondary accelerator was made, assuming that it would show greater nucleophilic reactivity than simple thiourea, and that its guanidine-like structure would be advantageous in this respect.



$$H_2N{-}\underset{\displaystyle S}{\underset{\|}{C}}{-}NH{-}\underset{\displaystyle NH}{\underset{\|}{C}}{-}NH_2 \qquad (1)$$

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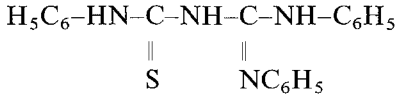
In the present study, 1-phenyl-3-(*N*,*N*'-diphenylamidino)thiourea (ATU), Equation 2, was used, synthesized according to [12].



$$H_5C_6\text{-HN-}\underset{\underset{S}{\|}}{C}\text{-NH-}\underset{\underset{NC_6H_5}{\|}}{C}\text{-NH-}C_6H_5 \qquad (2)$$

This compound was used along with MBTS in standard formulations in the sulphur vulcanization of natural rubber. It may be noted that in this structure, Equation 2, the guanidinyl group will facilitate the polarization of the C=S bond. The fact that Equation 2 can condense with aryl isothiocyanates in the absence of alkali, unlike thiourea, shows its greater nucleophilicity [13]. These, as well as steric considerations, may play a positive role in the use of ATU as a secondary accelerator.

The cure characteristics obtained in the different systems studied clearly indicate a nucleophilic reaction mechanism initiated by the amidinothiourea. In the evaluation of physical properties of the vulcanizates also, some of these mixes were shown to be better; while others gave comparable values with the control mixes. After-ageing properties of many of these vulcanizates were also found to be superior. The total crosslink formation in these different systems was investigated in order to correlate the variation in physical properties obtained. Also derived is the optimum dosage of ATU required to achieve satisfactory physical properties of the vulcanizates and optimum cure characteristics of the mixes.

2. Experimental procedure

Natural rubber: ISNR-5 of Mooney viscosity (ML 1 + 4, 100 °C) equal to 85 was used. The rubber additives, namely zinc oxide, stearic acid, MBTS, TMTD, DPG, thiourea and sulphur, used were all of rubber grade. Amidinothiourea, Equation 2, was synthesized by reaction of phenyl isothiocyanate (0.01 mol) and *N*,*N*'-diphenyl guanidine (0.01 mol) in benzene (50 ml) by refluxing for 2 h, as reported by [12]. The reaction mixture was concentrated and then petroleum ether was added until the solution turned turbid. The ATU which separated after keeping the solution for about 12 h was filtered out and recrystallized from 1:1 mixture of acetone and ethanol (melting point, m.p. = 163 °C). Chemical reagents used for the synthesis of amidinothiourea were of analar grade.

Formulations of the different mixes are shown in Table I. Eight different mixes were prepared, out of which three contained varying concentrations of ATU. Mixes A_1, A_2 and A_3 contained ATU ranging from 0.5 to 1.5 phr with 1 phr (parts per hundred of rubber) of MBTS. Mix B_5 contained only ATU as accelerator. This mix cured so slowly that it did not proceed further. Mix B_1 contained only MBTS as accelerator. Mixes B_2–B_4 contained 1 phr each of TMTD, DPG and TU, with 1 phr of MBTS. The mixes were prepared on a laboratory size two-roll mixing mill (15.3 × 30.5 cm) as per ASTM designation D3182–89.

The optimum cure time of the mixes (time to reach 90% of the maximum torque) was determined on a Goettfert elastograph, model 67.85, at 150 °C. The compounds were then vulcanized upto the optimum cure time in an electrically heated laboratory type hydraulic press at 150 °C at a pressure of 120 kg cm^{-2}. The cure characteristics of these formulations were evaluated from the cure curves (Figs 1 and 2) and the values are given in Table II. Induction time is the time required for one unit (1.0 dN m) to rise above the minimum torque (i.e. about 5% vulcanization). Elastographic scorch time is the time required for two units to rise above the minimum torque (about 10% vulcanization). The cure-rate index is reported as $100/(t_{90} - t_{10})$, where t_{90} and t_{10} are the times corresponding to the optimum cure and elastograph scorch, respectively. The tensile properties of the vulcanizates

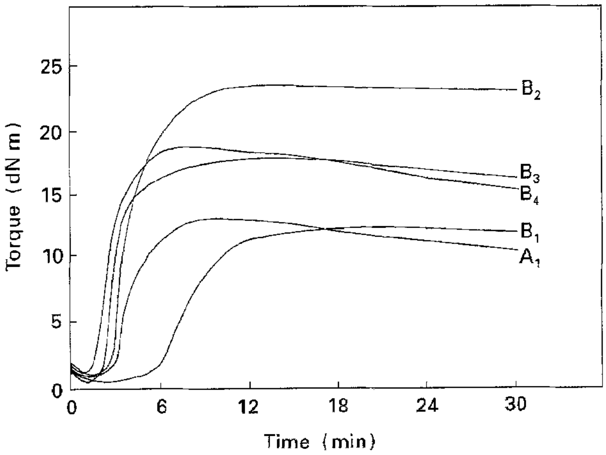


Figure 1 Cure curves of mixes A_1, B_1, B_2, B_3 and B_4.

TABLE I Formulation of the mixes (parts per hundred of rubber)

Ingredients	A_1	A_2	A_3	B_1	B_2	B_3	B_4	B_5
Natural rubber	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Zinc oxide	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
MBTS	1.0	1.0	1.0	2.0	1.0	1.0	1.0	–
TMTD	–	–	–	–	1.0	–	–	–
DPG	–	–	–	–	–	1.0	–	–
Thiourea	–	–	–	–	–	–	1.0	–
ATU	0.5	1.0	1.5	–	–	–	–	2.0
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

were determined on a Zwick universal testing machine, model 1445, using a crosshead speed of 500 mm min^{-1} as per ASTM D412–87 (method A). Dumbbell specimens for the test were punched out of the moulded sheets along the mill grain direction. Heat ageing resistance of the vulcanizates was studied as per ASTM D865–88 at 70 °C for 48 h. Angular test specimens were used to measure the tear resistance on a Zwick universal testing machine according to ASTM D624–86. Compression set, hardness and heat build-up were tested as per ASTM D395–89 (method B), D2240–86 and D623–88 (method A), respectively. Rebound resilience was measured using a Dunlop tripsometer (BS 903, Part A8) and abrasion resistance was measured using DIN abrader (DIN 53516). The data obtained are reported in Tables III and IV.

The chemical crosslink density of the vulcanizates was evaluated as follows. Samples of approximately 1 cm diameter and 0.2 cm thickness and 0.2 g weight were punched out from the central portion of the vulcanizate and allowed to swell in toluene for 24 h. The swollen samples were taken out and weighed. The solvent was removed in vacuum and the samples weighed again. The volume fraction of rubber, V_r, in the swollen network was then calculated by the method reported by [14, 15] from the following equation

$$V_r = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_o\rho_s^{-1}} \qquad (3)$$

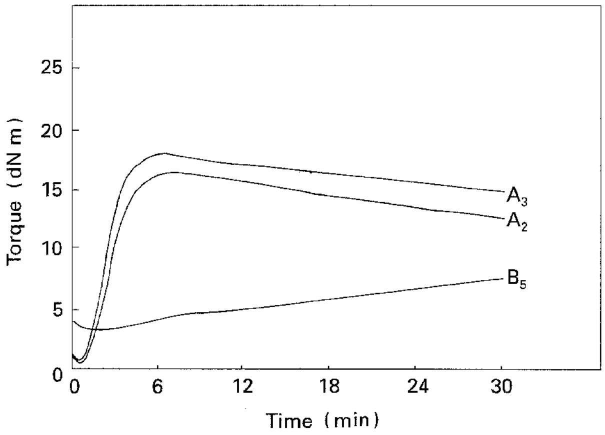


Figure 2 Cure curves of mixes A_2, A_3 and B_5.

TABLE II Cure characteristics of the mixes (cured at 150 °C)

	Mix No.						
	A_1	A_2	A_3	B_1	B_2	B_3	B_4
Minimum torque, dN m	0.7	0.5	0.5	0.5	0.6	0.4	1.0
Maximum torque, dN m	13.2	16.4	17.7	12.9	24.0	17.1	18.9
Optimum cure time, t_{90}, min	6.0	4.0	3.6	11.4	7.4	4.6	5.0
Elastograph scorch time, t_{10}, min	2.6	1.4	1.2	6.0	3.0	2.2	1.6
Induction time, t_5, min	2.1	1.0	0.9	5.7	2.1	1.8	0.6
Cure-rate index	29.41	38.46	41.67	18.52	22.73	41.67	29.41

TABLE III Tensile properties of the various vulcanizates

Mix No.	Tensile strength (MPa)			100% modulus (MPa)			Elongation at break (%)		
	Before ageing	After ageing	Retention (%)	Before ageing	After ageing	Retention (%)	Before ageing	After ageing	Retention (%)
A_1	17.78	22.68	127.6	0.66	1.10	166.7	838.27	818.16	97.6
A_2	20.90	21.07	100.8	1.29	1.75	135.7	790.76	724.82	91.7
A_3	24.05	17.84	74.2	1.48	1.79	120.9	793.45	689.28	86.9
B_1	20.96	20.82	99.3	0.74	0.81	109.5	886.95	837.33	94.4
B_2	2.39	1.88	78.7	1.32	1.38	104.5	192.36	143.05	74.4
B_3	24.78	28.53	115.1	0.95	1.17	123.2	775.85	763.03	98.3
B_4	15.95	20.48	128.4	0.66	0.93	140.9	834.00	799.06	95.8

TABLE IV Other physical properties evaluated

Mix No.	Hardness (Shore A)	Compression set (%)	Heat build-up (ΔT °C)	Resilience (%)	Abrasion loss (cm^3 h^{-1})	Tear strength (N mm^{-1})	Total crosslink density, × 10^5 (gm mol cm^{-3})
A_1	20	26.85	13.3	70.94	9.33	23.24	4.16
A_2	17	27.54	13.7	76.85	6.25	24.04	4.23
A_3	23	29.43	11.2	78.76	4.82	26.88	4.63
B_1	27	18.88	12.7	72.38	9.88	25.47	4.03
B_2	36	13.55	5.0	85.32	15.20	31.66	6.87
B_3	29	38.46	9.4	78.73	6.20	37.29	5.70
B_4	30	57.93	20.0	72.37	14.17	23.21	4.53

where T is the weight of the test specimen, D the weight of the unswollen test specimen, F the weight fraction of insoluble components, A_o the weight of the absorbed solvent corrected for the swelling increment, ρ_r the density of the test specimen, and ρ_s the density of the solvent.

The values of ρ_r and ρ_s taken are

$$\rho_r = 0.921\ \mathrm{g\,cm^{-3}}$$

$$\rho_s = 0.886\ \mathrm{g\,cm^{-3}}$$

Knowing the value of V_r, the total chemical crosslink density $1/2M_c$ was calculated using the Flory–Rehner equation [16]

$$-[\ln(1 - V_r) + V_r + \chi V_r^2] = \frac{\rho_r V_s (V_r)^{1/3}}{M_c} \quad (4)$$

where V_s is the molar volume of the solvent [V_s(toluene) = 106.2 $\mathrm{cm^3\,mol^{-1}}$]; χ the parameter characteristics of interaction between natural rubber, NR, and solvent [17] [χ(NR-toluene) = 0.42]; and M_c the number average molecular weight of the rubber chains between crosslinks.

3. Results and discussion

The acceleration effect of the amidinothiourea in the vulcanization of natural rubber is very evident from the results obtained. The vulcanization systems containing MBTS and ATU are found to be better than the reference systems as far as the cure characteristics are concerned (Table II and Figs 1 and 2). In comparison to mix B_1, which contains MBTS alone as accelerator, the addition of 1.5 phr of ATU (mix A_3) reduces the optimum cure time to almost one-third (11.4–3.6 min). This points to a very effective accelerator activity of the amidinothiourea derivative. However, the very low scorch time of this mix is likely to cause processing problems. On the other hand, the mix containing 0.5 phr ATU (mix A_1) gives a practical system with reasonable optimum cure time and sufficient scorch safety. This can be taken to be the optimum dosage of the amidinothiourea required.

ATU is found to improve many of the tensile properties of the vulcanizates in the systems under review. The effect of amidinothiourea concentration on tensile properties is shown graphically in Figs 3–5. A steady increase in the values of tensile strength and 100% modulus is seen with increasing concentration of ATU from 0.5 to 1.5 phr. The percentage retention of these properties is seen to be maximum for mix A_1, which has optimum cure characteristics also. A bar graphical comparison of the tensile properties of the reference mixes with those of MBTS–ATU systems of equivalent concentration (1 : 1) both before and after ageing is also given (Figs 6–8).

Other physical properties studied are hardness (Shore A), compression set, heat build-up, resilience, abrasion loss and tear strength. The values of tear strength, compression set and resilience of the vulcanizates are seen to increase with increasing concentration of ATU (Table IV), whereas abrasion loss shows a decrease. Heat build-up and hardness do not show

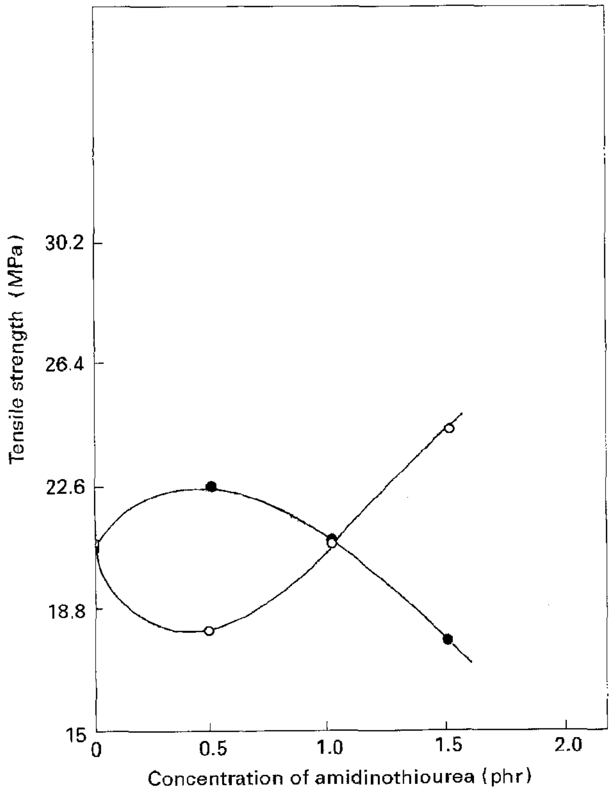


Figure 3 Effect of concentration of amidinothiourea on tensile strength of vulcanizates: MBTS–ATU (○) before ageing, (●) after ageing.

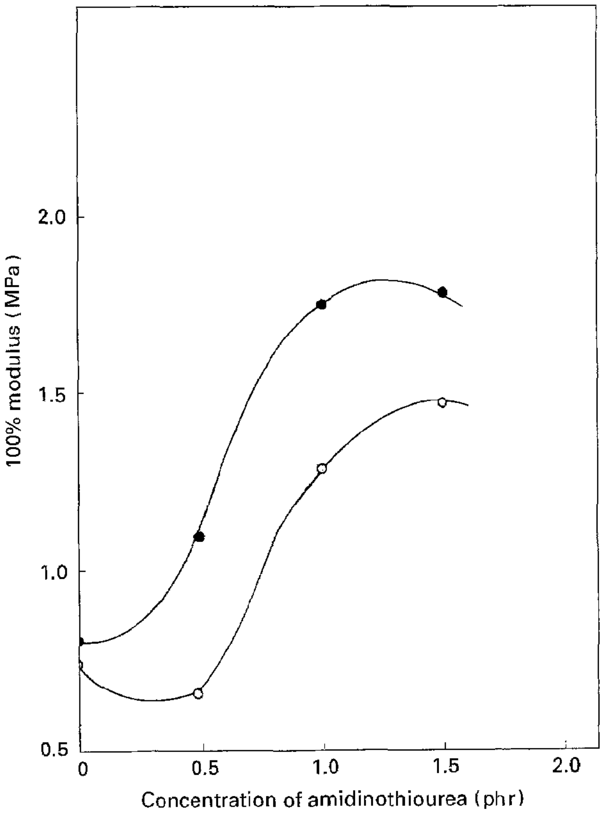


Figure 4 Effect of concentration of amidinothiourea on 100% modulus of vulcanizates: MBTS–ATU (○) before ageing, (●) after ageing.

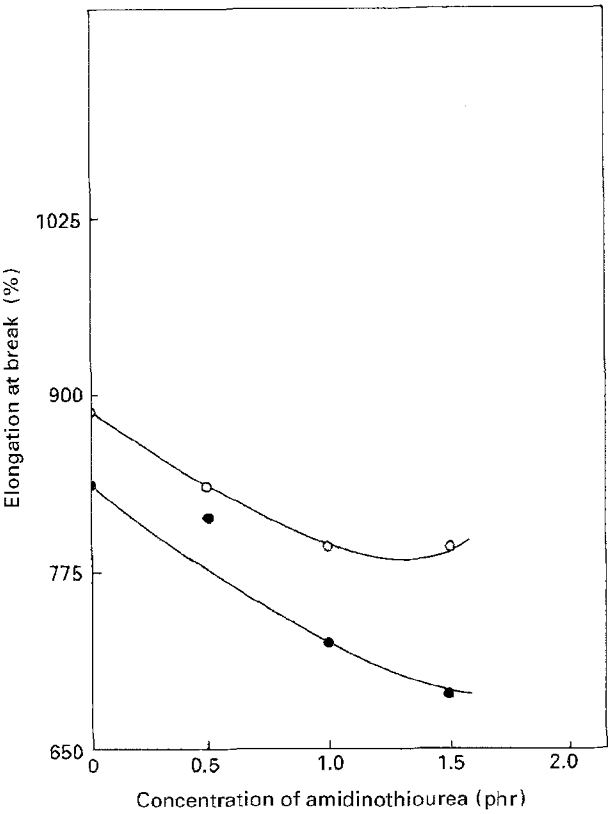


Figure 5 Effect of concentration of amidinothiourea on elongation at break of vulcanizates: MBTS–ATU (○) before ageing, (●) after ageing.

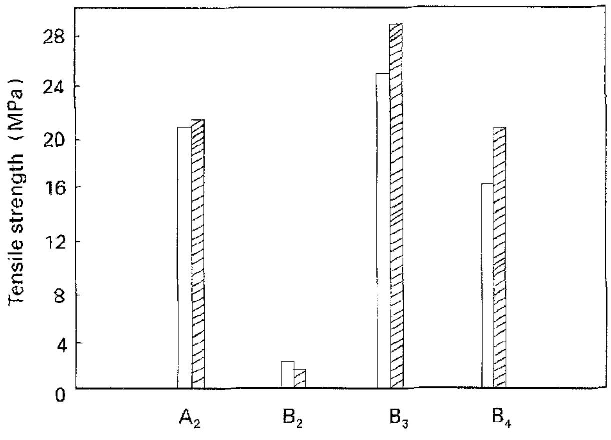


Figure 6 Tensile strength of vulcanizates containing equivalent concentrations of MBTS with ATU, TMTD, DPG and thiourea before (□) and after (▨) ageing.

appreciable changes with change in the concentration of ATU. Some of these values are comparable to those of reference mixes. Variations observed in crosslink density are more or less consistent with the variation in the physical properties of the different vulcanizates.

4. Conclusions

1-phenyl-3-(*N*,*N*′-diphenylamidino)thiourea can be very effectively used as a secondary accelerator in the sulphur vulcanization of natural rubber along with MBTS. The results of the study indicate a nucleophilic reaction mechanism in the systems under review. Amidinothiourea reduces the optimum cure time of the mixes considerably, and practical cure systems with optimum concentrations of amidinothiourea have been developed. This will be of definite advantage to the rubber product manufacturing industry. In many of the tensile properties studied, mixes containing amidinothiourea showed better performance. In the other physical properties, values comparable to those of the reference mixes were obtained. In the study of after-ageing properties also, mixes containing ATU showed favourable trends.

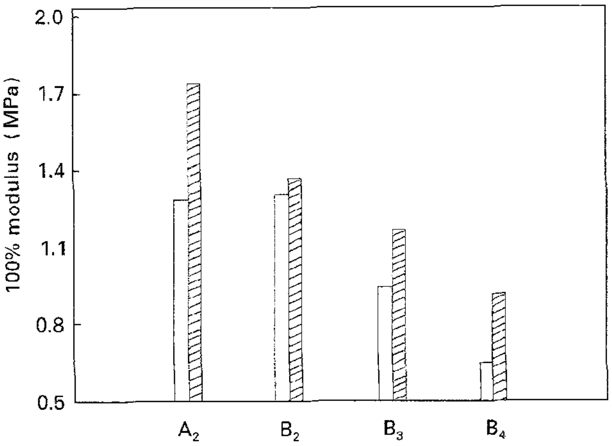


Figure 7 100% modulus of the vulcanizates containing equivalent concentrations of MBTS with ATU, TMTD, DPG and thiourea before (□) and after (▨) ageing.

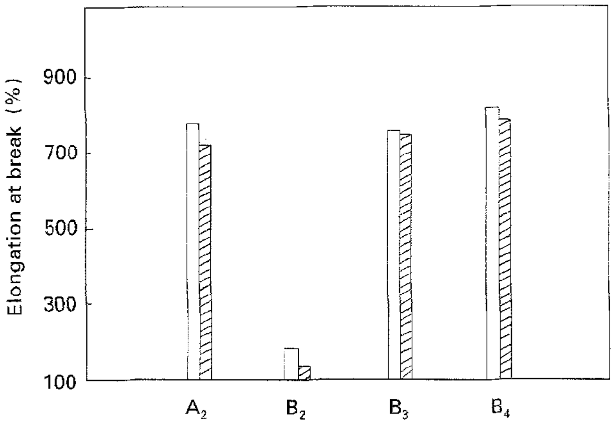


Figure 8 Elongation at break of vulcanizates containing equivalent concentrations of MBTS with ATU, TMTD, DPG and thiourea before (□) and after (▨) ageing.

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References

1. M. M. DAS, D. K. BASU and A. K. CHAUDHARI, *Kautsch Gummi Kunstst.* **36** (1983) 569.
2. S. KUCHARIK, *Sb. Vys. Sk. Chem. Technol. Praze* (*Oddil*) **58** (1982) 203.
3. B. A. DOGADKIN and V. A. SHERSHNEV, *Rubber Chem. Technol.* **35** (1962) 1.

4. T. D. SKINNER and A. A. WATSON, *Rubber Chem. Technol.* **42** (1969) 404.
5. M. W. PHILPOT, Paper presented at the Institution of Rubber Industry IVth Rubber Technology Conference, London 39th article.
6. L. A. BROOKS and J. C. BACON, US Patent No. 29, 111 394.
7. T. R. DAWSON, *J. Res. Assoc. Brit. Rubber Manufact.* **9** (1940) 11.
8. A. PERMINOV, *Kauch Rezina* **10** (1938) 85.
9. A. P. KURIAKOSE and G. MATHEW, *Indian J. Technol.* **26** (1988) 344.
10. G. MATHEW, P. V. PILLAI and A. P. KURIAKOSE, *Rubber Chem. Technol.* **65** (1992) 277.
11. G. MATHEW, B. KURIAKOSE and A. P. KURIAKOSE, *Kautsch Gummi Kunstst.* **45** (1992) 490.
12. F. KURZER and P. M. SANDERSON, *J. Chem. Soc.* (1960) 3240.
13. V. T. E. MINI, PhD Thesis, University of Kerala (1990).
14. B. ELLIS and G. W. WELDING, "Techniques of Polymer Science", (Society of Chemical Industries, London, 1964) p. 46.
15. *Idem, Rubber Chem. Technol.* **37** (1969) 571.
16. P. J. FLORY and J. REHNER, *J. Chem. Phys.* **11** (1943) 512.
17. C. J. SHEELAN and A. L. BASIO, *Rubber Chem. Technol.* **39** (1966) 144.

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