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Amidino Phenyl Thiourea as a Secondary Accelerator for the Vulcanisation of Natural Rubber - Polychloroprene Blends

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All rubbers have shortcomings in one or more properties. There are therefore technical reasons for blending different elastomers as it makes it possible to obtain the desired compromise in properties. Natural rubber (NR) is a versatile raw material on account of its unique chemical and physical properties. Polychloroprene rubber (CR) is known for its good flame resistance, resistance to oil and ozone but is more costly. A blend of NR and CR will make a desirable compromise in the individual properties. Thiourea (TU) and its derivatives are widely used in CR and NR latex vulcanisation. Ethylene thiourea (NA22), the conventional accelerator used in CR vulcanisation is reported to be toxic in nature.

We synthesised a thiourea derivative viz. *N-amidino-N'-phenyl thiourea (APT) which is a non-toxic chemical and attempted the use of APT, as a secondary accelerator for the vulcanisation of NR-CR blends. Systems with varying concentrations of APT along with tetramethyl thiuram disulphide (TMTD) and other compounding ingredients were prepared in unfilled and filled systems. TMTD-TU and TMTD-NA22 binary combinations were taken as controls. Different cure characteristics and various physical properties of the experimental and control systems were investigated.*

Studies showed that APT could be advantageously used as a secondary accelerator along with TMTD. The different vulcanisates prepared with this non-toxic accelerator showed better/ comparable tensile and other physical properties compared with the reference formulations.

Key words: Amidino Phenyl Thiourea; secondary accelerator; natural rubber; polychloroprene rubber; blend vulcanisation; unfilled and filled systems

It is recognized that a single elastomer cannot necessarily meet all the requirements of a rubber product like oil and chemical resistance, dynamic properties, weathering resistance *etc*. There are therefore technical reasons for blending, as it makes possible the right compromise in properties by blending different elastomers. The difficulties encountered in the processing and vulcanisation of some rubbers also emphasise the need for blending.

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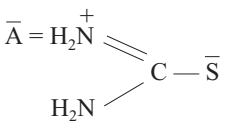
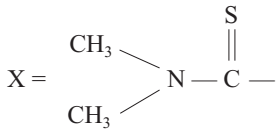
Economic reasons can also be given for blending since appreciable price differences exist between different rubbers. For example the resistance of polychloroprene to ozone is outstandingly good but its price is high and accordingly blending of CR with cheaper rubbers is normally practiced for various applications[1]. Blends make up over 30% of the market of polymeric materials[2].

It is well known that the use of binary accelerator systems in rubber vulcanisation provides better acceleration and that it improves the physical and chemical properties of the vulcanisates. In spite of the widespread use of binary accelerator systems, the mechanism of the combined action of accelerators in rubber vulcanisation is not fully understood even now. It is known that the accelerators in which sulphur is combined as S-S, C-S-C, and S-N *etc*. are generally inactive at lower vulcanisation temperatures because of the high thermal stability of the sulphur bonds. Thiourea (TU) and its derivatives definitely have an edge over others, especially in the vulcanisation of natural rubber (NR) and neoprene lattices. Scientist Philpot[3] has shown that, sulphur - containing nucleophiles enable accelerators like tetramethylthiuram disulphide (TMTD) to operate even at lower vulcanisation temperatures. He suggested an ionic mechanism for vulcanisation reactions where the S-S bond in TMTD is cleaved by the nucleophile produced from thiourea as:

Where  and



Kuriakose *et al*[4–8] investigated this further and found that the higher the nucleophilicity of the thiourea derivative the greater is the rate of vulcanisation of the systems under review.

One of the aims of this study is to see whether the theory of nucleophilic reaction in such binary systems is applicable to the blend systems as well. A new method is adopted here, as monitoring a vulcanisation reaction is otherwise difficult. We have evaluated the rate of the reaction based on a nucleophilic character of the secondary accelerator used. The effect of APT as a secondary accelerator was compared with that of TU in these binary combinations of TMTD. By virtue of the presence of guanidinyl group in it, APT is more nucleophilic than TU as polarisation of the C=S bond to create a nucleophilic centre will be easily facilitated. Hence, we have compared optimum cure time obtained for APT with that for TU.

Many of the rubber compounding ingredients, especially antioxidants and accelerators, are reported to be toxic[9,10]. For example, NA22, the single popular accelerator used in CR vulcanisation is toxic and reported to be carcinogenic[11–13]. In recent times, there has been a revival of interest in studies related to safe accelerators. Amidinophenyl thiourea is reported to be non-toxic and is used in many pharmaceutical applications[14–16]. One of the aims of our study with NR-CR blend therefore is to investigate the possibility of replacing the conventionally used thiourea derivative NA22 with a non-toxic derivative of thiourea like APT.

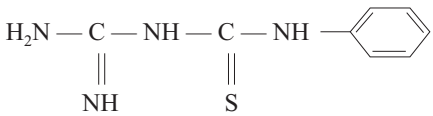
In view of the fact that APT functions effectively as a secondary accelerator in

NR and CR formulations[17,18] we thought it worthwhile to investigate the effect of this non-toxic amidino thiourea derivative in different vulcanisation systems of NR-CR blends. The variation in cure characteristics of compounds and the tensile properties of the vulcanisates brought about by APT as an accelerator in unfilled and filled NR-CR blends have also been investigated. The blends were prepared in 50:50 ratio by mass of NR and CR. Binary accelerator systems containing TMTD-TU and TMTD-NA22 were evaluated as control mixes. The cure and tensile properties of vulcanisates of the experimental mixes were compared with those of control formulations. Heat ageing characteristics and swelling studies were also carried out for various formulations of blends.

EXPERIMENTAL

Synthesis of N-Amidino-N'-phenyl thiourea (APT)

Guanidine carbonate (0.05 mol) and powdered sodium hydroxide (0.01 mol) were suspended in acetonitrile (50 mL). Phenyl isothiocyanate (0.1 mol) was added dropwise with stirring until the smell of thiocyanate vanished. The reaction mixture was then diluted with cold water and the precipitate obtained was filtered out and was recrystallised from aqueous alcohol (m.p 174ºC).



(APT)

Natural rubber conforming to Indian Standard Natural Rubber (ISNR-5) of Mooney viscosity (M L 1+4,100ºC) 85, used in the present study, was obtained from the Rubber Research Institute of India, Kottayam, Kerala. Chloroprene rubber used in this study was W type (CR B 30) with Mooney viscosity [M L (1+4), 100ºC] 47, Du Pont, USA supplied the rubber. Other compounding ingredients, *viz*. ZnO, Stearic acid, TMTD, ethylene thiourea (NA22), carbon black (HAF 330), precipitated silica, naphthenic oil and aromatic oil were all of rubber grade and MgO was calcined light magnesia. Chemical reagents, *viz*. guanidine carbonate, acetonitrile, phenylisothiocyanate and sodium hydroxide used for the synthesis and benzene used for swelling studies were of Analar grade. The procedure adopted for blending NR and CR was preblending, in which the compounding ingredients were added to the premixed NR and CR in a manner similar to the one followed in mixing a single elastomer. The formulations used for unfilled and filled mixes are given in *Table 1*.

All these mixes were prepared on a two-roll mixing mill as per *ASTM D 3182-89* at a friction ratio of 1:1.25. In the formulations used A series indicate unfilled mixes, Ac series indicate carbon-black filled mixes and As series indicate silica-filled systems. Mixes A1 to A4 are blends containing various concentrations of APT ranging from 0.25 to 1.5 molar equivalent with 1 molar equivalent TMTD. An attempt was made to find out the optimum concentration of APT required in these vulcanisation reactions. Mixes R1 and R3 contained, respectively, TMTD-TU and TMTD-NA22 in 1:1 ratio. Mix R2 contained TMTD alone (2 molar equivalents) as accelerator for unfilled systems. Mixes Ac1–Ac4 were carbon-black filled mixes containing various concentrations of APT, *viz*. 0.25, 0.5,1 and 1.5 molar levels with 1 molar equivalent TMTD and with 50 p.h.r. carbon black. Rc1, Rc2 and Rc3 were control formulations of the black-filled series. Mixes As1–As4 and Rs1,

TABLE 1. FORMULATIONS OF MIXES

Mix No	Carbon black	Aromatic oil	Silica	Naphthenic oil	DEG	TMTD	TU	NA22	APT
A1	–	–	–	–	–	1.2	–	–	0.243
A2	–	–	–	–	–	1.2	–	–	0.485
A3	–	–	–	–	–	1.2	–	–	0.970
A4	–	–	–	–	–	1.2	–	–	1.455
Ac1	50	5	–	–	–	1.2	–	–	0.243
Ac2	50	5	–	–	–	1.2	–	–	0.485
Ac3	50	5	–	–	–	1.2	–	–	0.970
Ac4	50	5	–	–	–	1.2	–	–	1.455
As1	–	–	30	5	2	1.2	–	–	0.243
As2	–	–	30	5	2	1.2	–	–	0.485
As3	–	–	30	5	2	1.2	–	–	0.970
As4	–	–	30	5	2	1.2	–	–	1.455
R1	–	–	–	–	–	1.2	0.38	–	–
R2	–	–	–	–	–	2.4	–	–	–
R3	–	–	–	–	–	1.2	–	0.51	–
Rc1	50	5	–	–	–	1.2	0.38	–	–
Rc2	50	5	–	–	–	2.4	–	–	–
Rc3	50	5	–	–	–	1.2	–	0.51	–
Rs1	–	–	30	5	2	1.2	0.38	–	–
Rs2	–	–	30	5	2	2.4	–	–	–
Rs3	–	–	30	5	2	1.2	–	0.51	–

Basic recipe: NR-50, CR-50, MgO-2, Stearic acid-2, ZnO-5, Sulphur- 1.5

Rs2 and Rs3 were corresponding filled mixes containing 30 p.h.r. precipitated silica.

The cure characteristics of the various mixes were evaluated at 150ºC using a Geottfert elastograph. Vulcanisation of the various mixes was carried out in an electrically heated hydraulic press of 18 inches × 18 inches platens maintained at 150ºC and at a pressure of 11.76 MPa. Tensile properties were determined using a Zwick Universal Testing machine at a pulling rate of 500 mm/min.at 27°C. Tear strength, hardness, compression set and abrasion loss of gum and filled vulcanisates were determined as per *ASTM* standards. Ageing studies on the vulcanisates were carried out at 100ºC for 24 hours in an air oven (*ASTM D 573-88*). Rebound resilience was measured using a vertical rebound resilience tester as per *ASTM D2632-88*. The swelling index, an indirect way of measuring total crosslink density, was determined by immersing 0.2 g of the sample in benzene for 24 hrs at room temperature. The swollen samples were weighed, solvent removed in vacuum and weighed again. Swelling index was calculated using the equation given below:

$$\text{Swelling index} = \frac{\text{Swollen weight} - \text{deswollen weight}}{\text{Original weight of sample}}$$

RESULTS AND DISCUSSION

Figures 1 and *2* show the cure curves and *Tables 2* and *3* give the different cure characteristics of NR-CR unfilled and filled mixes containing TMTD-APT and the control systems. In the case of the unfilled formulations of NR-CR blends, corresponding to the decrease in optimum cure time, scorch time is also found to decrease with the addition of APT. Based on the cure characteristics such as cure rate index, optimum cure time, scorch time and maximum torque developed, a 1: 1 molar combination of TMTD and APT can be considered to be the optimum level of accelerator combination but the scorch time is low. Comparing this mix with the control formulations, the t_{90} value of the experimental mix containing APT is below that of the TMTD-TU and TMTD-NA22 systems of similar concentration of accelerator (*Table 2*). Taking the black-filled formulations the reduction in cure time with increase in concentration of APT is not so pronounced as in unfilled systems. Considering the cure characteristics such as t_{90}, t_5 values, cure rate index and maximum torque developed, mix Ac2 containing 0.5 molar equivalent APT with 1 molar TMTD can be considered as the optimum cure system and the scorch time is found to be lower. Comparing mixes with equivalent concentration of accelerators, the experimental mix containing APT shows a lesser t_{90} value compared to the TMTD-TU and TMTD-NA22 control mixes in filled formulations (*Table 3*). APT being more nucleophilic than TU, the proposed nucleophilic reaction mechanism for sulphur vulcanisation applied to single elastomer systems of NR is seen to be applicable to these NR-CR blends. This is true for both filled and unfilled formulations.

Table 4 shows a comparative evaluation of the cure characteristics of NR, CR and NR-CR blends containing TMTD and APT in 1:1 ratio. Some of the favourable cure properties of these blends in comparison to the individual polymers may also be stated here. Considering the unfilled formulations of NR, CR and blend, the optimum cure time is much less for the blend system than that of CR. The scorch time value of the NR mix is 0.5 min. where as that of the corresponding blend is 1.12 min. Thus scorch safety of NR-APT system is found to have improved in the blend formulation. Taking the case of filled systems, the optimum cure time of CR mix containing this amidinothiourea derivative is much higher than that of the blend formulation. However the black filled APT mixes are little scorchier in the blend compared to the individual elastomer systems. One of the other advantages of the blend systems to be noted is the fact that while all the systems based on CR show marching cure[18], the blend systems show plateau cure.

The tensile properties such as tensile strength, elongation at break and 100% modulus of unfilled and filled systems are shown in *Table 5*. As the concentration of APT increases, the tensile strength of unfilled vulcanisates are found to increase up to an optimum level. Mix A3 containing optimum concentration of APT shows tensile strength of 27.6 MPa, which is much higher than those of control mixes containing equivalent amounts of TU and NA22. 100% Modulus and elongation at break values are comparable with those of the control formulations.

The retention of the tensile properties after heat ageing is also better / comparable to that of the control systems (*Figures 4–6*). Considering the tensile properties of carbon filled vulcanisates, it is to be noted that there is not much improvement in tensile strength values compared to those of the unfilled formulations. The case of unfilled and carbon filled vulcanisates of individual elastomers *viz*. NR and CR is similar. This may be attributed to the high stress-crystallising nature of NR

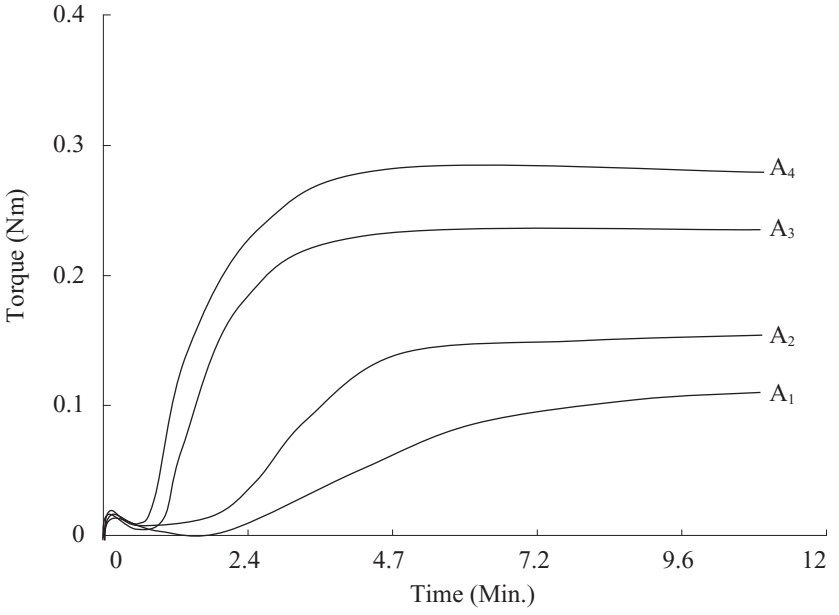


Figure 1. Cure curves of unfilled mixes containing APT.

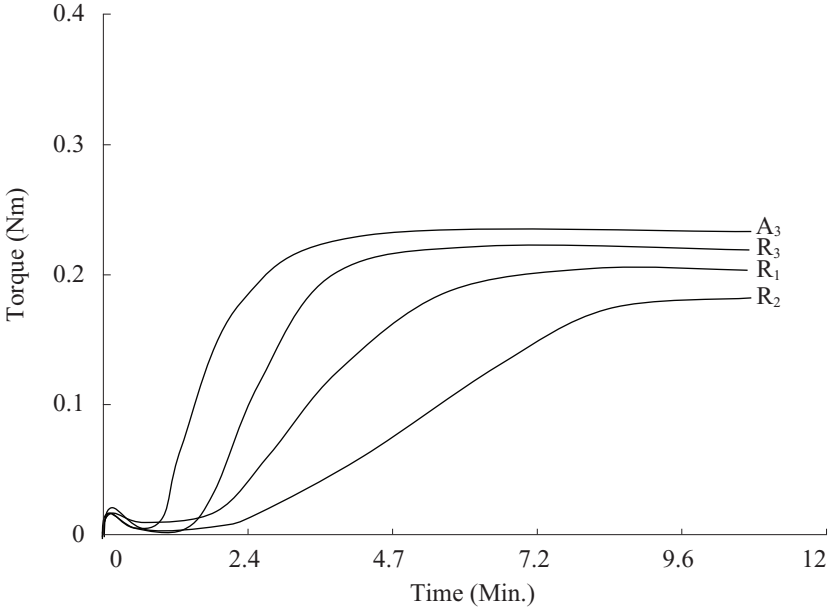


Figure 2. Cure curves of unfilled mixes containing optimum dosage of APT and control formulations.

TABLE 2. CURE CHARACTERISTICS OF NR-CR BLENDS (UNFILLED FORMULATIONS) AT 150ºC

	A1	A2	A3	A4	R1	R2	R3
Maximum torque (Nm)	0.112	0.153	0.236	0.277	0.205	0.185	0.227
Minimum torque (Nm)	0.004	0.004	0.005	0.008	0.010	0.004	0.006
Optimum cure time t_{90} (min)	7.76	4.96	3.08	2.88	5.44	7.88	3.96
Scorch time t_{10} (min)	2.44	1.88	1.12	0.84	2.20	2.84	1.76
Induction time t_5 (min)	2.04	1.64	1.04	0.80	1.96	2.48	1.60
Cure rate index	18.8	32.47	51.02	49.02	30.86	19.84	45.45

TABLE 3. CURE CHARACTERISTICS OF FILLED NR-CR BLENDS AT 150ºC

	Ac1	Ac2	Ac3	Ac4	As1	As2	As3	As4	Rc1	Rc2	Rc3	Rs1	Rs2	Rs3
Maximum torque (Nm)	0.5	0.5	0.6	0.6	0.5	0.5	0.4	0.4	0.6	0.5	0.6	0.3	0.8	0.6
Minimum torque (Nm)	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0
Optimum cure time t_{90} (min)	3.9	3.2	3.0	2.7	22.0	21.8	18.8	17.3	4.1	4.8	3.2	12.0	22.5	17.4
Scorch time t_{10} (min)	1.0	1.0	0.7	0.6	1.0	0.8	0.6	0.6	1.0	1.3	1.1	0.5	1.7	0.9
Induction time t_5 (min)	0.6	0.7	0.5	0.5	0.9	0.7	0.5	0.5	0.6	0.6	0.8	0.4	1.5	0.8
Cure rate index	32.3	45.6	43.9	48.1	4.8	4.8	5.5	6.0	31.9	28.7	46.3	8.7	4.8	6.1

and CR. When the tensile strength values of the blend vulcanisates are compared with those of individual elastomers containing equal amounts of APT, the blend systems show higher values than those of NR and CR[17,18]. As expected, 100% modulus values of carbon filled systems are found to increase manifold from those of unfilled vulcanisates (*Figure 5*). The system-containing APT shows better results in comparison with the control systems

Other physical properties of the vulcanisates such as tear strength, hardness, compression set, abrasion resistance; resilience and swelling index were evaluated and are reported in *Table 6*. In the unfilled formulations, tear strength values are found to increase with the increase in concentration of APT. Other properties like hardness and resilience values are also found to be satisfactory. Considering the case of black- filled vulcanisates, properties such as tear strength and hardness of APT system are comparable with the control mixes whereas compression set and abrasion resistance are better. In the case of silica-filled systems, the tear strength value of the optimum mix As3 is better and the

TABLE 4. COMPARISON OF CURE CHARACTERISTICS OF TMTD-APT SYSTEMS AT 150ºC

Parameter	Unfilled formulations			Carbon- filled systems			Silica filled-systems		
	NR	CR	NR-CR blend	NR	CR	NR-CR blend	NR	CR	NR-CR blend
Optimum cure time (min)	1.3	18.2	3.08	1.4	21.3	3	1.4	25.9	18.79
Scorch time (min)	0.5	3.4	1.12	0.8	1.5	0.72	0.7	3.7	0.60
Cure rate index	125	6.75	51.02	156.25	5.05	43.86	151.52	4.5	43.86

TABLE 5. TENSILE PROPERTIES OF NR-CR BLEND VULCANISATES

Mix No.	Tensile strength (MPa)			100% modulus (MPa)			Elongation at break (%)		
	Before ageing	After ageing 100ºC for 24 hours	Retention %	Before ageing	After ageing 100ºC for 24 hours	Retention %	Before ageing	After ageing 100ºC for 24 hours	Retention %
A1	16.4	13.2	80.3	0.8	0.7	90.1	411.0	480.8	116.7
A2	25.6	16.5	65.5	1.0	0.9	87.4	587.2	494.7	84.2
A3	27.6	19.6	71.2	1.0	1.0	99.0	629.7	608.0	96.5
A4	25.1	15.9	63.4	1.1	1.0	90.6	568.7	484.9	84.2
R1	19.8	12.7	64.2	0.8	0.7	85.9	481.0	529.7	110.2
R2	21.1	14.1	66.8	1.4	1.2	85.4	502.7	516.0	102.5
R3	22.2	21.5	96.8	0.7	0.8	108.2	611.2	516.2	94.3
Ac1	16.7	21.1	126.9	4.8	5.6	117.8	375.7	359.2	95.7
Ac2	23.5	21.2	89.9	5.2	5.0	96.2	386.8	316.9	81.9
Ac3	24.1	20.3	84.1	7.9	7.1	89.9	251.2	233.1	92.8
Ac4	23.6	23.9	101.1	5.7	5.6	99.1	286.9	332.4	116.1
As1	19.0	7.6	40.0	1.0	0.7	75.2	1420.6	992.5	69.9
As2	19.1	8.1	42.2	1.0	0.9	85.0	1421.6	1009.1	71.0
As3	20.6	9.7	47.2	0.8	0.8	97.6	1489.9	1059.1	71.1
As4	18.1	9.9	54.8	0.9	0.9	97.7	1331.0	1011.8	76.0
Rc1	21.1	18.1	85.6	6.7	7.2	107.8	239.8	208.2	87.0
Rc2	16.3	15.5	95.2	5.4	5.5	100.9	238.9	233.3	97.9
Rc3	18.2	17.9	96.2	5.0	4.7	94.6	213.5	263.0	123.4
Rs1	19.5	8.6	44.3	0.9	0.8	83.7	1398.7	1090.4	78.0
Rs2	18.8	12.7	67.6	1.3	1.2	88.1	1217.5	998.7	82.0
Rs3	19.9	8.0	40.2	1.0	0.9	91.9	1337.3	927.9	69.4

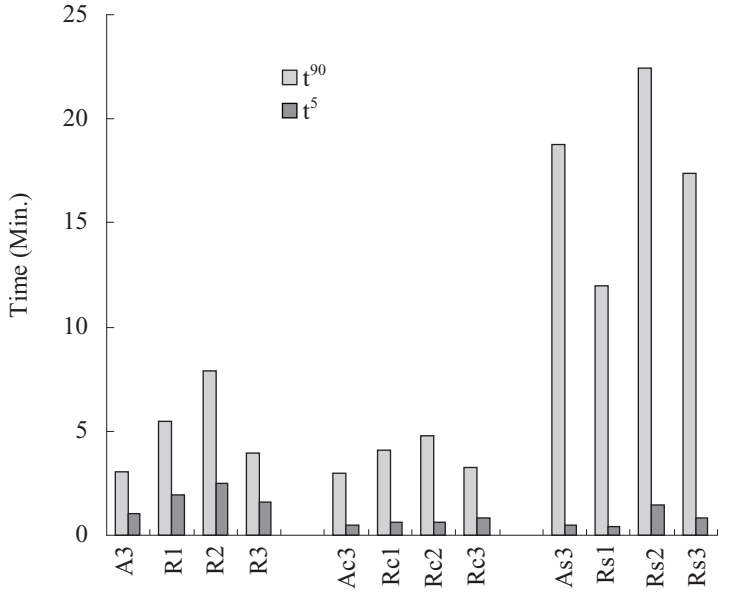


Figure 3. Comparative study of optimum cure time and induction time of mixes containing optimum dosage of APT with controls.

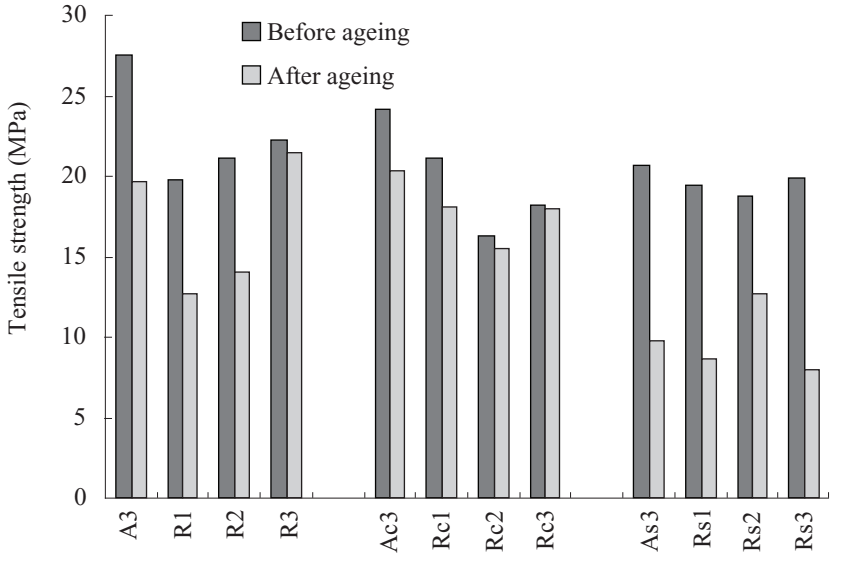


Figure 4. Comparative study of tensile strength of vulcanisates containing optimum dosage of APT with controls

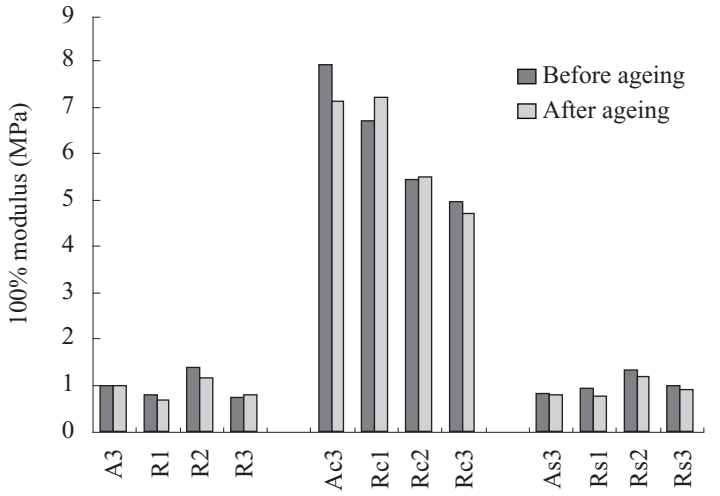


Figure 5. Comparative study of 100% modulus of vulcanisates containing optimum dosage of APT with controls

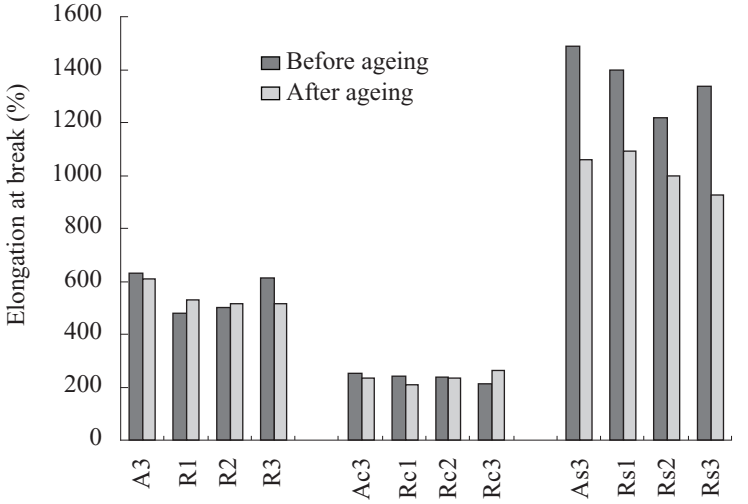


Figure 6. Comparative study of elongation at break (%)of Vulcanisates containing optimum dosage of APT with controls.

TABLE 6. OTHER PHYSICAL PROPERTIES OF NR-CR BLEND VULCANISATESS

Mix No.	Tear strength (N/mm)	Hardness (Shore A)	Resilience (%)	Compression set (%)	Abrasion loss (cm_3/hr)	Swelling index
A1	51.5	31.3	60.0	41.0	4.9	3.4
A2	55.4	35.7	66.3	48.4	5.3	3.6
A3	63.4	32.0	72.0	47.2	4.5	3.9
A4	72.3	34.3	70.6	53.4	5.3	3.5
R1	65.4	30.0	74.3	58.3	5.0	4.1
R2	58.9	38.3	73.0	52.5	4.7	3.7
R3	59.8	36.5	70.6	49.2	5.2	4.0
Ac1	59.0	46.0	47.5	30.4	3.9	1.3
Ac2	66.0	49.0	91.0	56.2	4.5	1.6
Ac3	72.3	53.0	98.9	21.5	4.3	2.4
Ac4	73.0	50.0	49.0	26.2	4.2	1.4
As1	63.2	42.0	40.0	66.4	12.2	3.0
As2	36.1	47.0	46.0	63.5	8.0	3.0
As3	57.1	48.0	46.0	66.2	9.1	3.0
As4	38.5	49.0	51.0	55.9	8.5	2.9
Rc1	74.0	44.0	66.0	36.4	4.2	1.4
Rc2	73.0	49.0	63.5	50.2	4.8	1.5
Rc3	69.0	58.0	62.5	48.9	5.3	1.5
Rs1	47.1	45.0	49.1	64.2	10.9	3.1
Rs2	42.9	55.0	46.0	59.7	6.6	2.9
Rs3	37.4	53.0	46.0	62.4	9.0	2.6

other properties *viz*. hardness, resilience, compression set and abrasion loss are comparable with the control formulations. The tensile properties reported for the unfilled and filled vulcanisates can in general be correlated to the observed swelling index values. Hence it can be reported that the system TMTD plus APT is an effective accelerator combination for vulcanisation of NR-CR blends in both unfilled and filled systems. Compared with the properties of vulcanisates obtained from the individual elastomers NR and CR there is general improvement in properties for the blend vulcanisates.

CONCLUSIONS

Studies on the effect of amidino phenyl thiourea in the vulcanisation of NR-CR blends showed that APT can be advantageously used as a secondary accelerator along with TMTD. The optimum cure time and scorch time of the TMTD-APT system is seen to be less

than for the corresponding TMTD-TU and TMTD-NA22 control mixes. Considering cure characteristics and tensile properties, the optimum dosage of APT required for a practical cure system for the unfilled and filled blends seem to be a 1:1 molar combination of TMTD and APT. The effect of APT as an accelerator is more noticeable in NR-CR blends than in the individual elastomers. It is also found that the different vulcanisates prepared with this non-toxic accelerator show comparable or better tensile and other physical properties compared with the control formulations used.

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