

New Binary Systems Containing TMTD-Amidino Phenyl Thiourea and CBS-Amidinophenyl Thiourea for the Vulcanization and Rheological Behavior of Natural Rubber Latex

A. P. Susamma,¹ N. M. Claramma,² Ajalesh B. Nair,¹ A. P. Kuriakose³

¹Department of Chemistry, Maharaja's college, Ernakulam, Kerala 682 011, India

²Rubber Technology Division, Rubber Research Institute of India, Kottayam, Kerala, India

³Department of Polymer Science and Rubber Technology, Cochin University of Science & Technology, Kochi, Kerala 682 022, India

Received 5 July 2009; accepted 25 August 2009

DOI 10.1002/app.31360

Published online 7 October 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The use of accelerators in rubber latex is basically different from their use in dry rubber. In the present study, N amidino N'phenyl thiourea (APT) which is more nucleophilic than thiourea was studied as a secondary accelerator along with tetra methyl thiuram disulphide (TMTD) and N-cyclohexylbenzothiazyl sulphenamide (CBS) in the vulcanization of natural rubber latex. These binary systems were found to be very effective in reducing the

vulcanization time. The optimum dosages for this non-toxic secondary accelerator required were derived. Rheological studies of the compounded latex show that the introduction of APT in these systems does not have adverse effect in processing in comparison with the thiourea systems. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2310–2316, 2010

Key words: rheology; vulcanization; rubber

INTRODUCTION

Natural rubber latex obtained from *Hevea brasiliensis* is a colloidal dispersion of negatively charged rubber particles suspended in an aqueous medium having density between 0.975 and 0.98 gm cm⁻³ and has a variable viscosity. Its pH ranges from 6.5 to 7. It has a rubber content of 25–40% by weight, which depends on the type of tree, the tapping intensity, soil condition, season, etc. The rubber hydrocarbon in latex is 1,4 cis-poly isoprene and it occurs as molecular aggregates with an average diameter ranging from 0.025 to 0.3 microns.¹

Vulcanization of latex

Vulcanization of latex is the result of colloidal chemical reactions taking place in the heterogeneous system. The conversion of NR latex into a product can be accomplished in many ways. Until it is converted into a solid product, the colloidal system should be maintained stable.² The different ingredients used in

a latex compound are (i) surface active agents, (ii) curing agents, (iii) accelerators, (iv) activators, (v) antioxidants, (vi) fillers, and (vii) special additives. The water-soluble materials are added as solutions, insoluble solids as dispersions and immiscible liquids as emulsions.³ The universal vulcanizing agent for natural rubber latex is sulphur.

Accelerator Systems in NR latex

The use of organic accelerators in latex compounding is basically different from their use in dry rubber compounding.^{4,5} The accelerators introduced into the latex mixture should become evenly distributed without causing the mixture to coagulate or to thicken.^{6,7} Philpott⁸ showed that certain sulphur containing nucleophiles like thiourea are able to activate vulcanization of NR latex with TMTD, so that well cured natural rubber vulcanisates may be prepared rapidly around 100°C. He suggested a nucleophilic reactivity in these vulcanization reactions, even though no conclusive evidence is given. It is suggested that accelerators like TMTD, CBS etc. in which sulphur is combined as S–C, C–S–C, or S–N, are inactive below 100°C because of the high thermal stability of the sulphur bonds. Sulphur containing nucleophiles enable such accelerators to operate at lower vulcanization temperatures. He

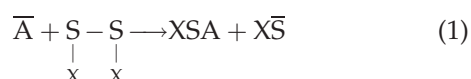
Correspondence to: A. P. Susamma (malayil1@sify.com).

Contract grant sponsor: Kerala State Council for Science Technology & Environment (KSCSTE), Kerala, India.

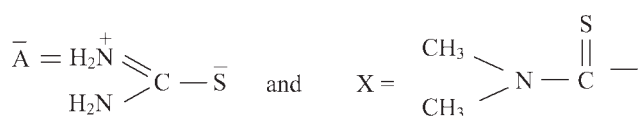
TABLE I
Formulations of the Mixes

Ingredients	Wet weight in gm											
	T ₁	T ₂	T ₃	T ₄	C ₁	C ₂	C ₃	C ₄	TR ₁	TR ₂	CR ₁	CR ₂
60% centrifuged NR Latex	167	167	167	167	167	167	167	167	167	167	167	167
10% KOH solution	1	1	1	1	1	1	1	1	1	1	1	1
10% Potassium oleate solution	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
50% ZnO dispersion	1	1	1	1	1	1	1	1	1	1	1	1
33% TMTD dispersion	3.6	3.6	3.6	3.6	—	—	—	—	7.2	3.6	—	—
33% CBS dispersion	—	—	—	—	4	4	4	4	—	—	8	4
10% TU solution	—	—	—	—	—	—	—	—	—	3.8	—	3.8
10% APT dispersion	2.24	4.85	9.70	14.55	2.24	4.85	9.70	14.55	—	—	—	—
50% sulphur dispersion	3	3	3	3	3	3	3	3	3	3	3	3

suggested an ionic mechanism for vulcanization reactions (1) where S—S bond in TMTD is cleaved by the nucleophile produced from thiourea as:



where



Kuriakose and coworkers⁹⁻¹² investigated this further and found that the higher the nucleophilicity of the thiourea derivative the greater is the rate of vulcanization of the systems under review. Studies on dry natural rubber^{13,14} indicate that the thiourea derivative *viz.* *N*-amidino *N'*-phenyl thiourea (APT) functions effectively in binary accelerator combinations for vulcanization. One of the aims of this study is to see whether the theory of nucleophilic reaction in such binary systems is applicable to the latex systems as well. Control formulations containing thiourea were also prepared to see the effectiveness of a

nucleophilic reaction mechanism in these latex systems. This study was undertaken in view of the fact that natural rubber latex requires special combination of accelerators compared to dry rubber and because latex vulcanization temperature is comparatively lower than that of dry rubber. The nontoxic nature of this amidino thiourea derivative was considered to be an added advantage. In this part of study, APT is used along with TMTD/CBS and latex compounds were prepared using standard formulations. Different mixes with varying concentration of APT were prepared and the optimum concentration of APT required is derived based on the cure characteristics and tensile properties obtained. Mixes containing thiourea were taken as control. Latex films prepared from the matured compounds were vulcanized under standard conditions. To study the effect of temperature on cure of these latex compounds, they were cured at two different temperatures *viz.* 120 and 100°C. Tensile properties of the vulcanisates like tensile strength, elongation at break, tear strength, *etc.* were also evaluated and compared with those of reference mixes. Chemical characterization of vulcanisates was also carried out using standard procedures.

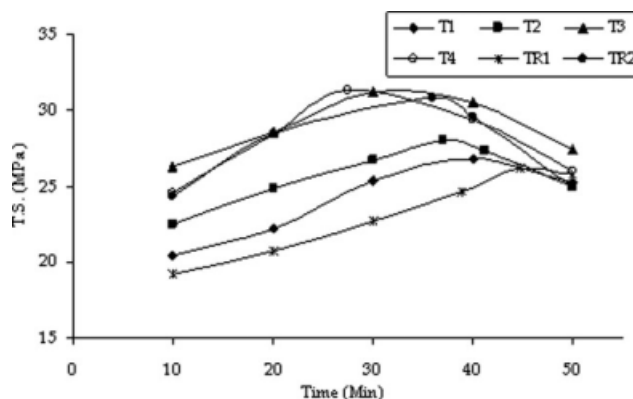


Figure 1 Variation of tensile strength with cure time of TMTD mixes at 120°C.

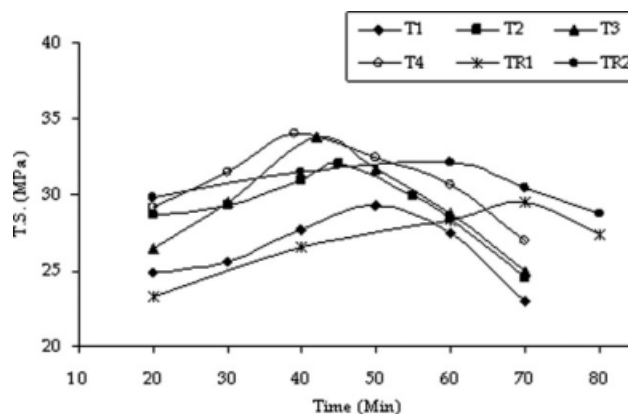


Figure 2 Variation of tensile strength with cure time of TMTD mixes at 100°C.

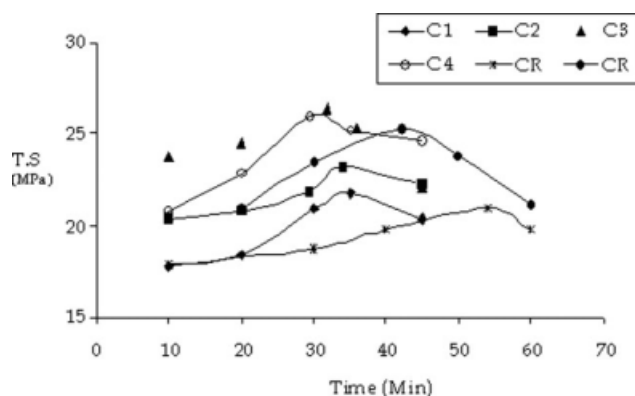


Figure 3 Variation of tensile strength with cure time of CBS mixes at 120°C.

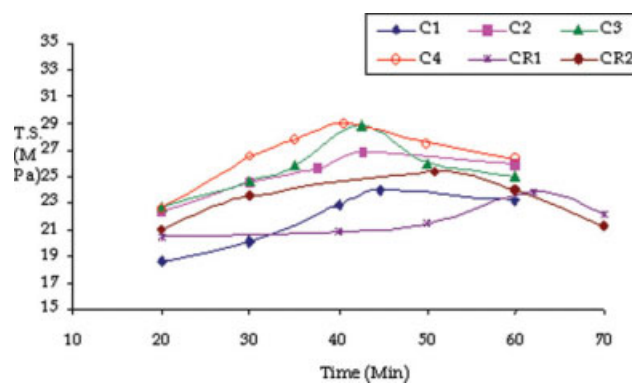


Figure 4 Variation of tensile strength with cure time of CBS mixes at 100°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

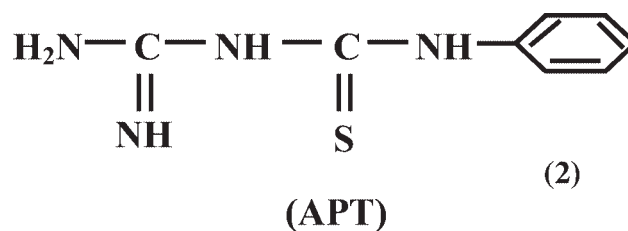
Rheology of latex

The flow properties of latex are of vital importance in the manufacture of latex products. Natural rubber latex is a non-Newtonian fluid that exhibits pseudo-plastic flow pattern. At rest, the rubber particles in latex are in random movement and when sheared the particles are progressively aligned and offers less resistance to flow.¹⁵ Under processing conditions, latex is subjected to different forms of stress and undergoes flow and other deformations. Hence, study of rheology is significant and very much relevant for understanding and evaluating the scope and limitations of its use and applications. Viscosity is the most important physico-chemical property, which influences the processing characteristics of the latex. Owing to the non-Newtonian behavior, a single viscosity measurement of latex at a particular temperature is not enough to understand its flow behavior. The important factors affecting rheological behavior of latex are shear rate, particle size distribution, and presence of electrolytes. Temperature has got a tremendous effect on the viscosity of latex. On the basis of the fact that rheology of latex is of utmost importance in latex product manufacture, a detailed study on the effect of shear rate and temperature on the viscosity of these latex compounds were carried out.

EXPERIMENTAL

Synthesis of *N*-amidino *N'*-phenyl thiourea (APT)

APT was synthesized according to Furukawa et al.¹⁶ as follows: 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 drop wise with stirring till 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 (MP 174°C) to obtain APT (2)



To study the effect of APT as secondary accelerator for the vulcanization we selected TMTD and CBS as the primary accelerators. High ammonia Type 60% centrifuged latex was used. Compounding ingredients were added to latex as aqueous solutions

TABLE II
Properties of Vulcanisates Containing TMTD (Cured at 120°C)

Mix no	Tensile strength (MPa)			Elongation at break (%)	Tear strength (N/mm)	Total crosslink density $\times 10^5$ (g mol cm ⁻³)
	Before aging	After aging	Retention %			
T ₃	31.4	30.96	97.36	825	55.4	5.03
TR ₁	26.2	23.46	89.54	1004	53.2	4.95
TR ₂	30.6	29.98	97.97	985	51	4.76

TABLE III
Properties of Vulcanisates Containing CBS (Cured at 120°C)

Mix no	Tensile strength (MPa)			Elongation at break (%)	Tear strength (N/mm)	Total crosslink density $\times 10^5$ (g mol cm ⁻³)
	Before aging	After aging	Retention %			
C ₃	26.4	24.8	93.93	565.0	48.7	4.88
CR ₁	21.0	20.1	95.71	451.5	46	4.37
CR ₂	25.4	22.56	88.81	590.8	47.9	4.5

or dispersions and compounding was done in a glass vessel, which is chemically resistant to ammoniated latex and the compounding ingredients. The ingredients were added to the continuously stirred latex in a slow and steady stream with minimum of splashing. Dispersions of sulphur, ZnO, TMTD, CBS, and APT were prepared using a ball mill. Potassium hydroxide, potassium oleate, and thiourea were added as 10% aqueous solutions. The latex was deammoniated to ammonia content of 0.2%. Ingredients were added according to the following order: Stabilizing agent, sulphur, accelerator, and zinc oxide.² Mixing was done in a glass vessel and stirred well for homogenization using a laboratory stirrer at 20–30 rpm. This was then occasionally stirred during storage in order to prevent settling of the ingredients. After compounding the mixes were kept for maturation at room temperature (35°C) for 24 hrs.

Latex films were prepared by casting the matured compound in shallow glass dishes. About 30–35 mL of the latex compound was poured and distributed evenly so that a film of thickness 1–1.25 mm was obtained upon drying. The films were then vulcanized at 120 and at 100°C for specific time periods ranging from 10 to 80 min in an air oven. The tensile properties of these latex films were determined and a tensile–time graph was generated. The optimum cure time was found out from the tensile strength–time graph. This is calculated as the time for attaining maximum tensile strength. The samples were

then vulcanized to the optimum cure time and their physical properties evaluated. The aging resistance was evaluated by keeping the specimens in an air oven at 70°C for 7 days. The tear strength of the vulcanisates was determined as per ASTM D 624–86. The total crosslink density of samples containing optimum concentration of APT was also determined by swelling the samples in toluene. Formulations of the different mixes used in the present study are given in Table I. The weight of various ingredients given is wet weight in gram calculated on dry rubber content. Mixes T_1 – T_4 contain varying amounts of APT *viz* 0.25, 0.5, 1, and 1.5 molar equivalents with 1 molar equivalent of TMTD. Mix TR₁ contains TMTD alone and TR₂ is the control mix with TMTD and TU in 1 : 1 molar ratio. Similarly C series are mixes with CBS as the primary accelerator.

Rheological study of the compounded latex was made by taking compounds matured for 24 h. The experimental systems containing optimum dosage of APT and the corresponding references were only used for the rheological studies. Haake viscometer VT 550 was used for these investigations. The functional units of this instrument consist of viscotester VT 550, power supply unit, temperature control vessel, sensor system and Pt 100 temperature sensor. The equipment operates over a temperature range from –30 to 150°C. Thirty different sensor systems are available. Sensor system NV was used for this study. Latex was located in the measuring gap of the sensor system. Rotational speed, measuring time,

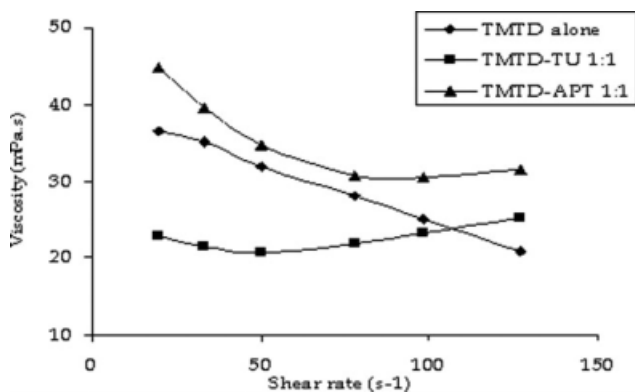


Figure 5 Variation of viscosity with shear rate at 25°C (TMTD Mixes).

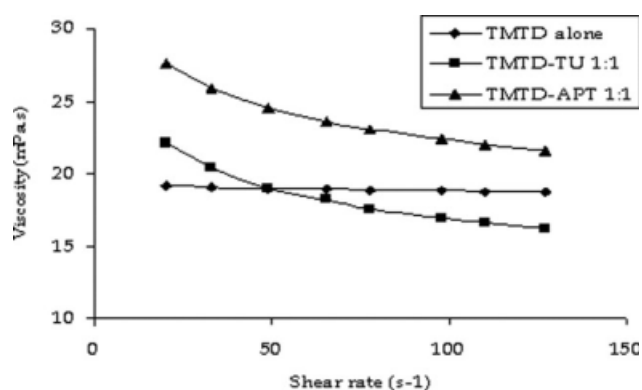


Figure 6 Variation of viscosity with shear rate at 35°C (TMTD Mixes).

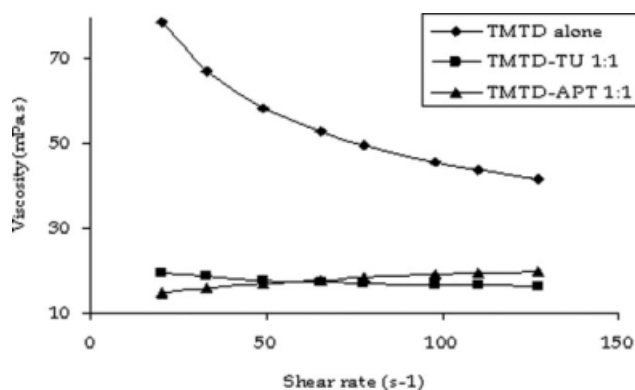


Figure 7 Variation of viscosity with shear rate at 45°C (TMTD Mixes).

number of measuring points and measuring temperature were preset. The rotor was rotated at the preset speed range. The latex exerts a resistance to the rotational movement due to its viscosity, which becomes apparent as a torque value applied on the measuring shaft of the viscometer. The computer attached to the system calculates the relevant values like viscosity η in mPa.s, shear rate γ in s^{-1} and shear stress τ in Pa from the measured variables of speed, torque and sensor geometry. The temperature T was measured in °C. This study was conducted at three different temperatures *viz.* 25, 35, and 45°C, which are the normal range of temperature encountered during compounding/processing of NR latex. Shear rate employed ranged from 1 to 150 s^{-1} .

RESULTS AND DISCUSSION

Cure characteristics and tensile properties

The tensile strength–cure time graph for the samples from TMTD-APT systems at 120 and 100°C are given in Figures 1 and 2, respectively. Optimum cure time of different mixes is estimated as the time to reach maximum tensile strength. It can be seen that the optimum cure time values decrease as the

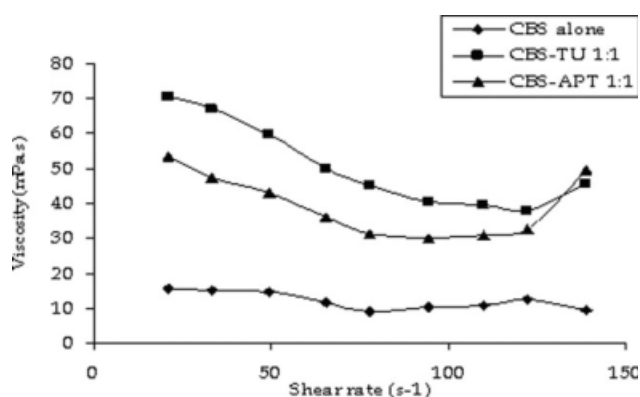


Figure 8 Variation of viscosity with shear rate at 25°C (CBS Mixes).

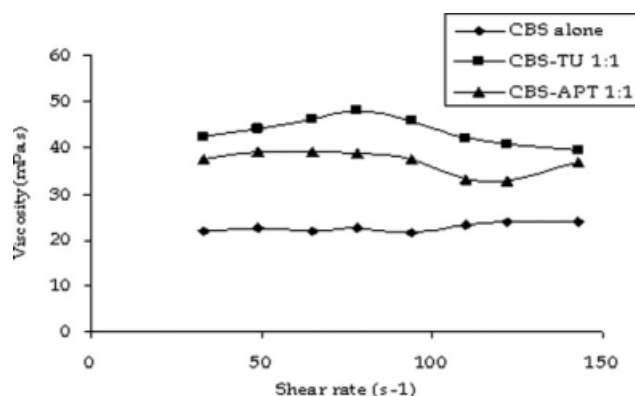


Figure 9 Variation of viscosity with shear rate at 35°C (CBS Mixes).

concentration of APT increases. Considering systems containing equivalent accelerator combinations at 120°C, TMTD – APT mix in 1 : 1 molar ratio (T_3) shows an optimum cure time of 30 min to attain optimum tensile strength, while system containing TMTD and TU (mix TR_2) takes 36 min and TMTD alone takes 44.8 min. At 100°C also the optimum cure time for TMTD – APT (42 min) is much lower than for TMTD-TU (60 min) and TMTD alone (70 min). There is definite decrease in cure time with increase in concentration of APT at 100°C also.

The optimum cure time values evaluated for the CBS systems at 120 and 100°C. The corresponding cure curves are given in Figures 3 and 4, respectively.

In CBS systems also as the dosage of APT increases the optimum cure time is found to decrease. The cure time for the mix containing 1 : 1 molar equivalents of CBS and APT (C_3) is considerably less than that for the reference mix CR_2 containing CBS and TU. This is true for vulcanization at 120° and at 100°C. The CBS-APT mixes take 32 min and 42.5 min at 120°C and 100°C, respectively. The control systems containing CBS with TU show values of 42.1 min and 51 min at similar temperatures.

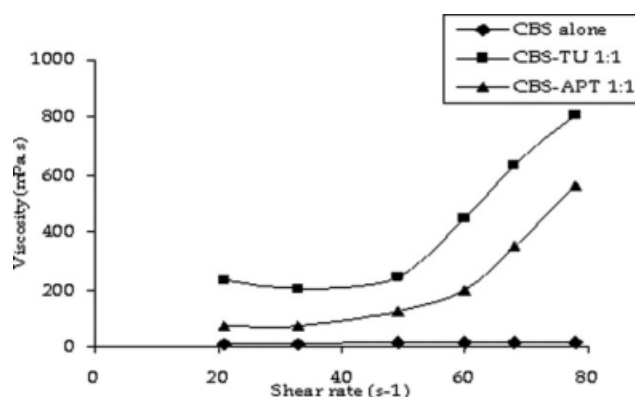


Figure 10 Variation of viscosity with shear rate at 45°C (CBS Mixes).

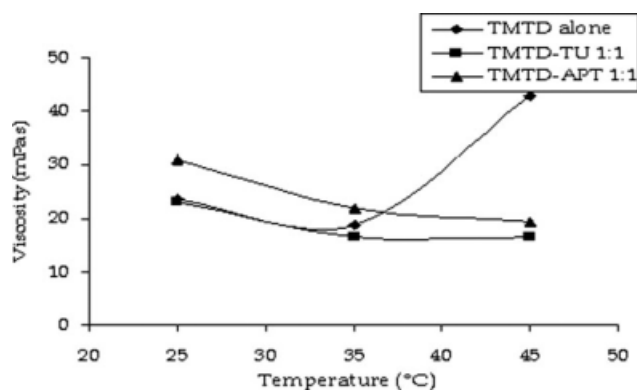


Figure 11 Variation of viscosity with temperature at shear rate 110 s^{-1} (TMTD mixes).

These results indicate that *N*-amidino *N'*-phenyl thiourea can be used as a secondary accelerator in the vulcanization of natural rubber latex containing TMTD or CBS advantageously. There is substantial reduction in optimum cure time for the binary systems containing APT. Also considering the nucleophilic character of APT and comparing it with TU, the reduction in optimum cure time for APT systems gives supporting evidence for the nucleophilic reaction mechanism for such binary systems suggested by Philpott⁸ and by Moore.¹⁷ Considering the cure time and tensile strength values mixes T_3 and C_3 containing TMTD/CBS and APT in 1 : 1 molar ratio can be taken to be the optimum concentrations. The physical properties of these vulcanisates cured at 120°C were further investigated.

Tensile properties of the vulcanisates containing optimum concentration of APT and of references prepared using the optimum cure time calculated as before are given in Tables II and III. It can be seen that properties like tensile strength of APT systems show slightly better values compared to the reference mixes. Heat aging studies show that the aging resistance of APT systems are comparable with that of reference systems containing TU. The tear

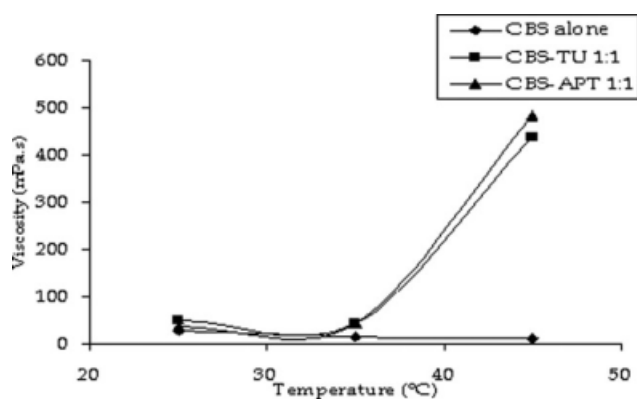


Figure 12 Variation of viscosity with temperature at shear rate 110 s^{-1} (CBS mixes).

TABLE IV
Zero Shear Viscosity at Various Temperatures

Mix No.	Zero shear viscosity (mPa.s)		
	25°C	35°C	45°C
T_3	50.3	30.0	10
TR_1	38.0	18.2	92
TR_2	27.5	25.1	26
C_3	63.0	36.7	48
CR_1	17.5	22.0	5
CR_2	75.4	37.5	37.5

strength values of these experimental systems are also comparable to those of control mixes.

Chemical characterization of the vulcanisate samples was carried out using the equilibrium swelling method. The results obtained for the various systems are reported in Tables II and III. Mixes T_3 and C_3 containing optimum dosage of APT with TMTD/CBS showed higher values for crosslink density. This can be correlated to the better tensile properties observed with these vulcanisates. It may be noted that at 100°C also these systems cure in a reasonable time period and this may be attributed to the nucleophilic reactivity of the secondary accelerator. The overall cure and vulcanisate properties of these formulations studied indicate that APT can advantageously be used as a non-toxic accelerator for the preparation of natural rubber latex products.

Flow behavior

The effect of shear rate on compounded latex for various TMTD formulations at 25, 35, and 45°C are shown in Figures 5–7. On increasing the shear rate, viscosity is found to be decreasing confirming the pseudoplastic behavior of these latex compounds. As the temperature is raised to 45°C the APT and TU systems do not show much variation in viscosity with shear rate whereas mix-containing TMTD alone shows higher viscosity values. APT and thiourea are seen to stabilize the systems at this temperature. In the case of CBS the effect of shear rate on viscosity is different from that of TMTD mixes. Here APT systems show a tendency of increase in viscosity at high shear rate region. Similar trend is shown by thiourea systems also (Figs. 8–10). At higher temperature (45°C) this tendency is more prominent. The effect of temperature on viscosity of latex compounds (at constant shear rate) is shown in Figures 11 and 12. Taking the case of TMTD mixes, as the temperature is increased from 25 to 35°C viscosity is found to be decreasing in all the three systems under review. But as the temperature is increased to 45°C mix TR_1 (containing TMTD alone) shows a sharp increase in viscosity indicating destabilization of the compound. The presence of amidino thiourea

and thiourea is found to stabilize the mix. The addition of APT to CBS mix also is found to change the flow characteristics of this binary system as temperature varies. At about 45°C CBS-APT mix show a sudden tendency to thicken as indicated by the sharp increase in the viscosity value. Similar is the behavior of the control mix containing thiourea. This indicates that when CBS systems are used APT and thiourea are not useful especially when processing temperature is above 35°C.

The zero shear viscosity values of the various systems at different temperatures are given in Table IV. The system with higher zero shear viscosity exhibits more pseudoplastic behavior. The experimental mix containing optimum dosage of APT with TMTD behaves as a typical pseudoplastic fluid, considering the change in viscosity with temperature. Compared with the control mix (TMTD-TU) the viscosity value is higher for the APT mix at lower temperatures. In the case of the CBS systems variation of zero shear rate viscosity values with temperature of the CBS-APT and CBS-TU systems is more or less similar and is more than that of the CBS mix.

CONCLUSIONS

From the results obtained in this study, it is clear that *N*-amidino *N'*- phenyl thiourea can be used as an effective secondary accelerator in NR latex especially with TMTD, which is a very popular accelerator for latex systems. The disadvantage of APT in dry rubber processing is its scorchiness at high concentrations. But in latex systems as there is no problem of scorching APT can be used safe. On the basis of cure time values at 120 and 100°C, it can be stated that APT being more nucleophilic than TU, the results support a nucleophilic reaction mechanism in these binary combinations. The systems containing optimum dosages of APT give satisfactory values for mechanical properties like tensile strength and tear strength. Nontoxic nature of APT is especially bene-

ficial in these latex formulations. The rheological studies of the compounded latex show that the introduction of APT in the systems do not have adverse effect in processing especially in comparison to the control mixes. At higher temperature, APT stabilizes the TMTD mix where as the CBS-APT shows a tendency to thicken, as is the case with control mixes containing thiourea.

References

1. Archer, B. L.; Banard, D.; Cockbain, E. G.; Dukenson, P. B.; McMullen, A. I. In *The Chemistry and Physics of Rubber-Like Substances*; Bateman, L., Ed.; McLaren & Sons Ltd.: London, 1963; Chapter 3.
2. Gazeley, K. F.; Gorton, A. D. T.; Pendle, T. D. In *Natural Rubber Science and Technology*; Roberts, A. D., Ed.; Oxford University Press: Oxford, England, 1988; pp 99–137.
3. Flory, P. J.; Rehner, J. *J Chem Phys* 1943, 11, 512.
4. Clavert, K. O. *Polymer Lattices and their Applications*; Applied Science Publishers Ltd.: London, 1982; p 187.
5. Blokh, G. A. *Organic Accelerators in the Vulcanisation of Rubber*; IPST: Jerusalem, 1968; 17–68.
6. Brown, H. Corp. Brit. Pat. 564,232 (1944).
7. Coleman, C. Brit. Pat. 410,454 (1934).
8. Philpott, M. W. *Proceedings of Rubber Technology Conference*; Institute of Rubber Industry (IRI): London, 1962; p 470.
9. Mathew, G.; Kuriakose, B.; Kuriakose, A. P. *Kautsch Gummi Kunst* 1992, 45, 161.
10. Mathew, C.; Mini, V. T. E.; Kuriakose, A. P.; Francis, D. J.; Geethakumariam, L. *J Appl Polym Sci* 1996, 59, 365.
11. Mathew, G.; Pillai, P. V.; Kuriakose, A. P. *Rubb Chem Technol* 1992, 65, 277.
12. Mini, V. T. E.; Mathew, C.; Francis, D. J.; Kuriakose, A. P. *J Mater Sci* 1995, 30, 2049.
13. Susamma, A. P.; Mini, V. T. E.; Kuriakose, A. P. *J Appl Polym Sci* 2001, 79, 1.
14. Susamma, A. P.; Kurian, M.ary; Kuriakose, A. P. *Iranian Polym Jr* 2002, 11, 311.
15. Wilkinson, W. L. *Non-Newtonian Fluids*; Pergamon: London, 1960.
16. Furukawa, G. M.; Hayashi, S. *Bull Chem Soc Jap* 1977, 47, 1974.
17. Moore, C. G.; Saville, B.; Watson, A. A. *Rubb Chem Technol* 1961, 34, 795.