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Safe Vulcanisation System for Heat Resistant Natural Rubber Products for Engineering Applications

Abhitha K., Thomas Kurian

Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi – 682022, India

Abstract: - Natural rubber is a very versatile material that has been successfully used in engineering applications for over a century. The rubber articles that are vulcanised using conventional accelerators such as tetra methyl thiuram disulphide (TMTD) are carcinogenic because of the production of nitrosamines (NA) during heating for the vulcanisation reaction. The nitrosamine producing TMTD has to be replaced with a safe accelerator. Tetrabenzyl thiuramdisulphide (TBzTD) is reported to be a safe (non-carcinogenic) accelerator. An efficient vulcanization system has been selected to get heat and reversion resistance to the natural rubber vulcanisates during the long service life in engineering applications. Safe natural rubber vulcanisates have been prepared using TBzTD in an efficient vulcanisation system. The vulcanisates prepared using the safe vulcanisation system shows properties comparable to the vulcanisate prepared using TMTD. The compound containing TBzTD shows better scorch safety. The novel safe vulcanisate shows comparable crosslink density and improved aging resistance. The test results indicate that the TBzTD can be used as a safe accelarator for the manufacture of rubber products for general engineering functions such as shock, noise and vibration control.

Keywords: - *binary accelerator, cross linking, mechanical properties, natural rubber, nitrosamine.*

I.   INTRODUCTION

Vulcanisation or curing is the insertion of a relatively small number of chemical cross links, by the addition of vulcanizing agents along the polymer chains to enable the strength and elastic properties inherent in raw rubber to be fully realized [1]. This is achieved when the compounded rubber is heated to an appropriate temperature. The first commercial method of cross linking has been attributed to Charles Goodyear in 1839 [2] who could improve the mechanical properties of natural rubber by heating after mixing with sulphur. Over the year's three special types of sulphur vulcanisation systems such as efficient vulcanisation (EV) systems, semi efficient vulcanisation (SEV) systems, and conventional vulcanisation (CV) systems have been developed.

EV systems are those where a low level of sulphur (0.3 – 0.8 phr) and a correspondingly high level of accelerator (6.0 – 2.0 phr) are used for achieving an extremely high heat and reversion resistance in the rubber vulcanisates [1, 2, 3]. In the CV systems, the sulphur dosage is high (2 – 3.5 phr) and correspondingly the accelerator level is low (1.0 - 0.4 phr). The CV systems provide better flex and dynamic properties but thermal and reversion resistance are poor. For optimum levels of mechanical and dynamic properties of vulcanisates with intermediate heat and reversion resistance SEV systems with an intermediate level of accelerator (2.5 – 1.0 phr) and sulphur (1.0 – 1.8 phr) are employed [1, 2]. In the vulcanisation reaction of elastomers, accelerators perform the important function of bringing down the time needed for vulcanisation.

Over the last century or so, a large number of basic and specialty elastomers have been developed to meet a wide range of applications and operating environments. Their properties vary widely in terms of their elasticity, temperature range, strength, hardness, compatibility, environmental resistance, etc. Natural rubber is preferred in many products because of its superior building tack, green stock strength, and better processability, high strength in non-black formulations, hot tear resistance, retention of strength at elevated temperatures, better resilience, low heat build-up, fatigue resistance, and better dynamic properties [4]. Anti-vibration mountings,

flexible couplings, bridge bearings, rail pads, power transmission and conveyer belts, rubber covered rollers, cable covering, automobile components, hoses, tubing, lining of tanks, extruded products, and components for domestic and industrial machinery are some of the industrial and engineering rubber products. Flooring, gloves, adhesive for pressure sensitive tapes, door/barrier mats and footwear are the familiar examples of household rubber products.

Nitrosamines are found in rubber articles that are vulcanised with very common traditional accelerators such as tetra methyl thiuram disulphide (TMTD) [5]. These vulcanisates have been tested positive as mutagens and are carcinogenic [5, 6]. Other accelerators and sulphur donors that form hazardous nitrosamines are tetra methyl thiuram monosulphide (TMTM), N- oxydiethylene dithiocarbamyl N^I- oxydiethylene sulphenamide (OTOS) and N- oxydiethylene – 2- benzothiazole sulphenamide (MBS) [7]. Nitrosamines are produced mostly during curing and post curing process of rubber. Nitrosamines are formed by the reaction of secondary amines with nitrogen oxides [8] as shown in the equation:

$$RR^INH + N_2O_3 \longrightarrow RR^INNO + HNO_2$$
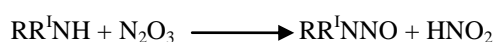
Binary accelerator formulations involve the use of two different accelerators in the system, often leading to improved properties. In many cases a synergistic behaviour is observed leading to better vulcanisate properties in the combined system than expected by the rule of mixtures [9]. Tetra benzyl thiuramdisulphide (TBzTD) which is not carcinogenic has been developed as a non-regulated or safe nitrosamine producing accelerator [10] to replace thiurams such as TMTD. TBzTD is a fast curing accelerator in natural rubber and provides longer scorch times than TMTD [11].

This paper reports the preliminary investigations on the effect of combinations of TBzTD and a primary amine based sulfenamide (tertiary butyl benzothiazole sulfenamide (TBBS)) as non – regulated safe binary accelerating system for the efficient vulcanisation of natural rubber.

II. EXPERIMENTAL SECTION

2.1 Materials used

Natural rubber (ISNR-5) used in this study was obtained from the Rubber Research Institute of India (Kottayam, Kerala). The antioxidant N-(1,3-Dimethyl butyl)-N^I-phenyl-p-phenylene diamine i.e. 6PPD (Mernox 6C), the accelerators TBBS (Mercure TBBS), TMTD (Mercure TMT) and TBzTD (Mercure TBzTD) were supplied by Merchem Ltd , Kochi, Kerala. The structure of TBzTD is:
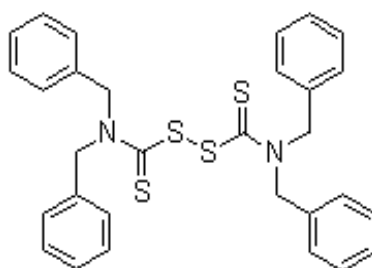
Zinc oxide, stearic acid and sulphur were supplied from Associated Rubber Chemicals, Kochi.

2.2 Compounding and testing

The formulations employed for the study are shown in Table 1. The compounding of NR was done on a two roll open mill as per ASTM D 3184-89.The rheographs of the mixes and their cure characteristics were obtained using Rubber Processing Analyser.The test specimens were prepared by molding in an electrically heated hydraulic press at 150 ^{o}C for the optimum cure time. Tensile and tear strength were measured according to ASTM D 412 and ASTM D 624 respectively using a Shimadzu Universal Testing Machine, at a cross head speed of 500 mm/min. The ageing of the samples were done in a hot air oven at 70 ^{o}C and 100 ^{o}C for 24 hours according to ASTM D 572-99 to determine the influences of elevated temperature and time on tensile properties. The hardness (Shore A) of the samples was determined using Mitutoyo hardmatic hardness tester according to ASTM D 2240-03. Compression set at constant strain was measured according to ASTM D 395. The flex resistances of the vulcanisates were determined using De Mattia flexing machine as per ASTM D 813-95. Rebound resilience was determined by vertical rebound method according to ASTM D 2632-01.The cross link densities of the vulcanisates were determined by the Flory- Rehner equation using the equilibrium swelling data [12-16].

Table1. Formulation of mixes

Ingredients	C	C_1	C_2	C_3
NR (g)	100	100	100	100
ZnO (phr)	5.0	5.0	5.0	5.0
Stearic acid (phr)	2.0	2.0	2.0	2.0
6PPD (phr)	1.0	1.0	1.0	1.0
TBBS (phr)	1.5	1.5	1.5	1.5
TMTD (phr)	2.0	-	-	-
TBzTD (phr)	-	2.0	2.2	2.4
Sulphur (phr)	0.3	0.3	0.3	0.3

III.   RESULTS AND DISCUSSION

3.1 Cure characteristics

The rheographs of the mixes cured at 150 ^{o}C are shown in Fig. 1 and the optimum cure time and scorch time are shown in Table 2.The value of the scorch time of the compound containing 2.2 phr TBzTD (mix C_2) is almost the same as that of compound containing 2.0 phr TMTD (mix C). As the concentration of TBzTD increases from 2.0 (mix C_1) to 2.4 (mix C_3) the optimum cure time is reduced considerably. The optimum cure time of the mix C_2 is low; therefore, more cross links are formed in shorter time [17]. The Cure Rate Index (CRI) which is a measure of the speed with which the cure reaction is taking place, is given by the equation:

$$CRI = 100 \div (t_{90} - t_{10})$$

where t_{90} and t_{10} are the optimum cure time and scorch time respectively. The CRI values increases with increasing concentration of TBzTD and shows high value for the mix C_2.

Table 2. Optimum cure time and scorch time of mixes cured at 150 o C

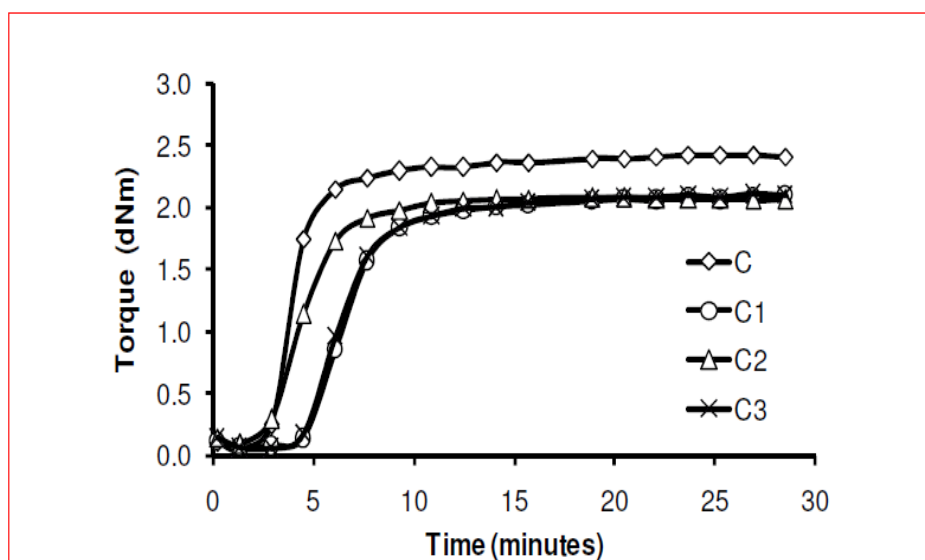| Properties	C	C_1	C_2	C_3
Scorch Time t_{10} (min)	2.96	5.10	2.89	4.95
Optimum Cure Time t_{90} (min)	6.82	10.41	7.17	9.83
Cure Rate Index (CRI)	25.91	18.83	23.36	20.49

Fig 1. Rheographs of the mixes cured at 150°C

3.2 Mechanical properties

The stress - strain curves of the vulcanisate samples are shown in Fig. 2. Tensile properties of the samples are tabulated in Table 3. Tensile strength of the control vulcanisate C was found to be 17.43 MPa. The tensile strength values are in the order $C_1 < C < C_3 < C_2$ in agreement with the aim of this work, i.e. developing

a non carcinogenic, nitrosamine – safe vulcanisate with properties comparable to that of the control vulcanisate. The tensile strength values are in exact correlation with the chemical cross link density values shown later in this article. It could be seen that the modulus values increases with increase in concentration of TBzTD and it shows a maximum at a dosage of 2.2 phr. This is in accordance with the cross link density values.

The tear strength of the samples C, C_1, C_2 and C_3 are shown in Table 3. Tear strength indicates the capacity of the vulcanisates to resist cutting, chipping and tearing actions during service. From the result it was observed that the samples C_1 and C_3 have almost the same tear strength and that for C_2 is high. Hardness (Shore A) of the samples C, C_1, C_2 and C_3 are shown in Table 3. Hardness is a measure of modulus of elasticity at low strain [18]. The hardness value remains practically unchanged. This indicates that the hardness is not adversely affected by the addition of the safe accelerator.
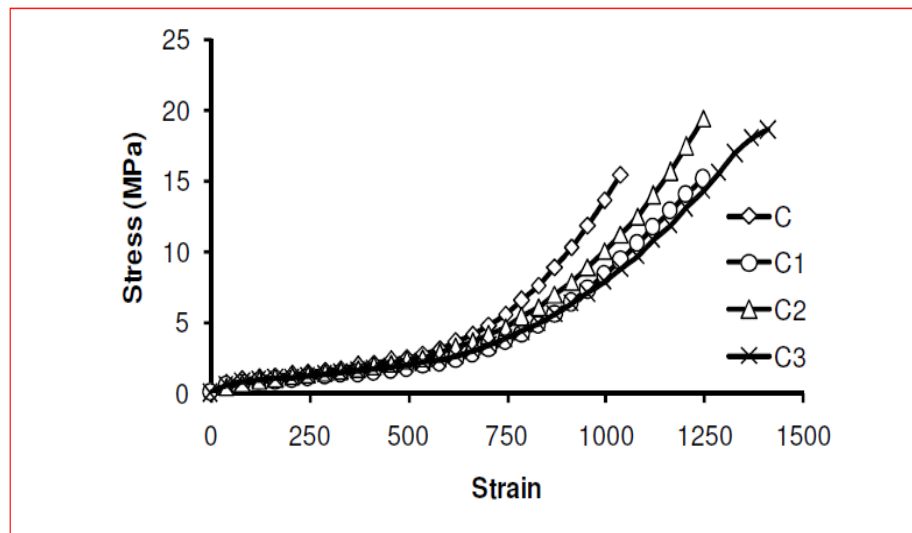

Figure 2: Stress-Strain curves of the samples

Compression set of rubber vulcanisates results from rearrangement of the network structure, degradation of polymer chains, debonding of polymer- filler attachments, etc. It is dependent on the type of the polymer, nature of cross links, type of filler and its quantity [19 – 21]**.** Measurement of set under compression provides a practical evaluation of either the creep or the stress relaxation of rubber. A high state of cure is found to reduce set. Compressions set value of the vulcanisate containing TMTD is 14%. The compression set of the vulcanisates prepared from the compounds containing TBzTD are almost similar to that of the control vulcanisate containing TMTD.

Table 3. Properties of the rubber vulcanisates

Properties	C	C_1	C_2	C_3
Tensile strength(MPa)	17.43	14.52	19.55	18.97
Modulus at 300% elongation (MPa)	1.61	1.32	1.46	1.39
Elongation at break(%)	1071	1084	1230	1354
Tear strength (N/mm)	25.37	24.13	26.71	24.96
Hardness (Shore A)	29	28	31	31
Rebound resilience (%)	65	62	65	66
Crosslink density $x10^5$ (moles/g rubber hydrocarbon)	3.93	3.64	7.09	6.10

Flex crack resistance of elastomer vulcanisates is the ability to sustain numerous flexing cycles without the occurrence of cracks in the surface from stress and ozone attack [22]. The number of test cycles required for the control sample for the initiation of crack growth was found to be about 2 lakhs. In the case of the samples C_1, C_2 and C_3 containing TBzTD crack growth initiation was not observed even after 2 lakhs flexing cycles. Rebound resilience of the samples C, C_1, C_2 and C_3 are shown in Table 3.The values are in the order $C_3 > C > C_1$ with marginal difference. The Control sample C and C_2 have the same rebound resilience values.

The stress –strain properties of the vulcanisates after aging for 24 hours at 70 ^{o}C and 100 ^{o}C are shown in Table 4. In all the cases the stress – strain properties improved marginally after aging at 70 ^{o}C. After aging at 100 ^{o}C the vulcanisate C, C_2 and C_3 shows marginal improvement in the properties. The improvement in properties on thermal aging may be due to the conversion of the small percentage of the polysulphidic crosslinks formed initially in the vulcanisate to monosulphidic and disulphidic linkages [3, 9,23].

Table 4. Tensile properties of the rubber vulcanisates after ageing

Sample	Tensile strength (MPa)		Modulus at 300% elongation (MPa)		Elongation at break (%)	
	70^{0}C	100^{0}C	70^{0}C	100^{0}C	70^{0}C	100^{0}C
C	17.54	17.75	1.62	2.12	995	863
C_1	14.95	14.8	1.44	1.73	1084	967
C_2	20.64	19.19	1.62	2.04	1082	906
C_3	19.08	19.46	1.55	1.95	1069	1016

The cross link densities of the vulcanisates calculated from the equilibrium swelling measurements in toluene are shown in Table 3. The crosslink densities are in the order $C_1 < C < C_3 < C_2$. Cross link density is an important parameter, which can be related to the physical properties of rubber vulcanisate [24]. The results of the study cited above show that the mechanical properties of the samples such as tensile strength, hardness and rebound resilience are in accordance with the cross link density. The study establishes that in natural rubber vulcanisates it is possible to develop equivalent and even superior crosslink densities and the mechanical properties by replacing TMTD which is known to be carcinogenic with marginally high dosage of TBzTD which is non-regulated and safe.

IV.   CONCLUSION

The use of TBzTD instead of TMTD in a natural rubber compound for engineering applications containing an efficient vulcanization system results in better scorch safety. The dosage of TBzTD in a vulcanisate equivalent to that of the dosage of TMTD in the cure system in the control vulcanisate shows marginally inferior mechanical properties and cross link density. However the vulcanisate containing 10% higher dosage of TBzTD shows mechanical properties, aging resistance and cross link density comparable to that of the control. TBzTD is a safe (non-carcinogenic) substitute for TMTD in the compounds for the manufacture of rubber engineering components ranging from small automotive mounts and bushes through anti-seismic devices to large marine fenders

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