

## ***Influence of Flame Retardant Additives on the Flammability Behaviour of Natural Rubber (NR)***

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*A combination of decabromodiphenyl oxide (DBBO) and antimony trioxide ( $Sb_2O_3$ ) is a widely used flame retardant system for rubber compounds. In addition to cost effectiveness, thermal and mechanical performance, halogen content is responsible for its low flammability characteristics. Nevertheless, there are concerns on the corrosiveness and toxicity of smoke and other emission products generated during the combustion of rubbers utilising these materials. Fillers such as aluminium hydroxide (ATH), organoclay and zinc hydroxystannate (ZHS) have been used as alternative halogen-free flame retardants. This paper describes the effect of these flame retardants on flammability behaviour and tensile strength of natural rubber (NR). ZHS is an alternative to  $Sb_2O_3$  because of the former's smoke suppression properties. However, similar to  $Sb_2O_3$ , it does not have flame retarding properties on its own. ZHS loaded at 20 p.p.h.r. in combination with 40 p.p.h.r. chlorinated paraffin (CP) showed better flammability performance. Results from the National Bureau of Standard (NBS) smoke box showed that this compound gave lower smoke density compared to a similar compound with antimony trioxide in place of the ZHS. In general however, partial replacement of flame retardant (FR) additives in NR compounds by ZHS produced no synergistic improvement in fire retardant behaviour.*

**Key words:** flame retardant; natural rubber;  $Sb_2O_3$ ; aluminium hydroxide; zinc hydroxystannate; smoke density; limiting oxygen index; UL-94

Natural rubber (NR), in particular is widely used for belting and cables due to its outstanding properties such as tensile strength, abrasion and fatigue resistances. Nevertheless, it has its limitations due to its carbon and hydrogen structure and is flammable. In service, a flame retardancy requirement is essential, and this has created a marked change in the use of NR with its replacement by synthetic elastomers

in certain areas such as underground mining, insulations, subways and others.

There are several approaches to make rubbers flame retardant, which have been established since 1970, and the use of physical additives is favoured. The additives are incorporated at the compounding stage and must be stable at the processing conditions.

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The halogen type is normally preferred because of its efficiency at lower loadings but halogenated flame retardant and antimony trioxide produce toxic products and higher smoke density during combustion. This, therefore, is one of the main reasons for the demand for halogen free flame retardants. Non-halogenated flame retardants are phosphorus or nitrogen compounds, graphite, magnesium and aluminium, molybdenum, tin, zinc, silicon and boron. Some of these have been shown to be good smoke suppressants and effective FRs when used in combination with a halogen source<sup>1</sup>. The inclusion of organoclay to improve the flame retardancy of polymers has also been reported<sup>2</sup>.

It is well recognised that the addition of  $\text{Sb}_2\text{O}_3$  increased smoke production. Tin compounds such as zinc stannate (ZS) and zinc hydroxystannate (ZHS) were looked into by Tin Technology Ltd. (ITRI) as a possible replacement for  $\text{Sb}_2\text{O}_3$ . Cusack and co-workers<sup>3-6</sup> investigated extensively the effect of ZHS on the flammability and properties of several polymers such as unsaturated polyester resins, poly(vinylchloride), chlorosulfonated polyethylene, polyamides, epoxy resins and polychloroprene. The benefit of these tin based additives as flame retardants and smoke suppressants has been shown. However, very little work has been done on NR and synthetic elastomers.

The aim of this work was to investigate the flammability behaviour, cure characteristics and tensile strength of commercially important NR compounds with various flame retardants added. In particular the possible advantages to be gained from using tin compounds, as both flame retardants and smoke suppressants, in comparison with established systems.

It should be noted that this paper is not to provide a complete formulation for flame

retarded NR. The compounds employed are simple non-commercial sulphur based gum-stock formulations. Although such compounds are of little use in practical applications, they were chosen in order to eliminate complications arising from polymer filler interaction.

## MATERIALS AND METHODS

### Material

NR (SMR L) was supplied by the Tun Abdul Razak Research Centre (TARRC), Hertford, England. The chemical additives comprised an activator, accelerator, anti-degradants and a curing agent. The additives were supplied by TARRC, Flexsys and AKM (Safic-Alcan).

Flame retardant additives were ZHS (Joseph Storey Ltd), aluminium trihydroxide (Alcan Chemicals, UK), decabromodiphenyl oxide (DBBO),  $\text{Sb}_2\text{O}_3$  (Great Lakes Chemical Corporation) and Chlorinated Paraffin, Cereclor 70 (Ellis & Everard). Clay grade was Cloisite 20A (CL20) from Southern Clay Products, Inc. They were used without any purification and were all commercial grades.

### Mixing

The rubber samples were prepared using a Farrel Bridge open swing-side 6 inches  $\times$  12 inches laboratory two-roll mill or in a Francis Shaw K1 Intermix Mark 4. The cure characteristics were determined using a Monsanto oscillating disc rheometer (ODR) according to the *BS 903-A60.2:1992*<sup>7</sup>. The samples were then vulcanised in a temperature controlled hydraulic press at  $160 \pm 2^\circ\text{C}$  according to their respective cure times,  $t_{95}$ .

### Flammability Study

Evaluation of the flame retardancy was carried out by a limiting oxygen index (LOI) and Underwriters Laboratory (UL-94) tests<sup>8</sup>. The LOI test is based on the determination of minimum percentage of oxygen in a gas mixture ( $O_2$  and  $N_2$ ), which will sustain the burning of either three minutes or burning within a 50 mm reference mark below the top of the samples (*BS 2782 Part 1:Method 141*)<sup>9</sup>. The higher the LOI, the less likely the material will burn.

UL-94 test provides only a qualitative classification. The three vertical ratings, V2, V1 and V0 indicate that the material was tested in a vertical position and self-extinguished within a specified time after the ignition source was removed. V0 is the best rating and V2 is the lowest rating. The specimens used for the test are of dimensions  $127 \times 12.7 \times 3$  mm.

### Tensile Strength

Three samples were cut from the vulcanised rubber using a dumb bell cutter. Tests were run on a Lloyds mechanical testing machine at room temperature with a crosshead speed of 500 mm/min.

### SEM Analysis

A Cambridge/Leica stereoscan 360 scanning electron microscope (SEM) was used to examine the fracture surfaces of the samples. Each sample was gold-coated prior to analysis.

### Thermal Analyses

Thermogravimetric analysis (TGA) was carried out in air at a heating rate of  $10^\circ\text{C}/\text{min}$

using a TA Instruments TGA 2950 thermogravimetric analyser. A sample size of approximately 5 mg – 15 mg was used, which was heated from room temperature to  $700^\circ\text{C}$ .

### Smoke Density Determinations

Smoke emission properties were determined using a smoke chamber conforming to NBS specification in the flaming condition according to *BS 6401*. In this study, rubber samples  $75 \times 75$  mm with a thickness of 3 mm were prepared. Maximum specific smoke density (Dmc) values were corrected for soot deposition on the optical windows and the data expressed as Ds (specific smoke density)/g and Dmc/g in order to normalise for weight of sample lost during the tests.

## RESULTS AND DISCUSSIONS

### Cure Characteristics

The trends in the cure time were identified from the test results as shown in *Table 1*. It was found that the chlorinated paraffin (CP) has a more pronounced effect on cure time as compared to other flame retardant additives. CP retarded the cure time due to its acidic nature. As for ZHS and DBBO, they had little effect on the cure parameters. The higher loading of aluminium trihydroxide (ATH) accelerated the cure time whereas ATH-organoclay combination resulted in a significantly shorter cure time. Such an accelerating effect has already been reported for different rubbers<sup>10</sup>, and is probably attributed to the reaction of sulphur-containing compounds and the amine groups in the nanoclay structure.

### Flammability Behaviour of NR Compounds

The flammability behaviour of NR containing various flame retardant additives and several combined effects is shown in *Table 1*. It can be seen that the addition of up to 20 p.p.h.r. of  $\text{Sb}_2\text{O}_3$  alone did not have a significant effect on both the LOI and UL-94 test. The samples were considered highly flammable compounds since they had an LOI value under 20%, which indicates that the sample will burn readily in an atmosphere containing 19% oxygen or more. The result was expected with  $\text{Sb}_2\text{O}_3$  as it has no fire retardant effect when used on its own and is in agreement with other studies<sup>11</sup>.

Similar addition of ZHS or ZS, behaved in a similar way to the  $\text{Sb}_2\text{O}_3$ . Halogen type, DBBO at 20 p.p.h.r. increased the LOI value slightly but was not sufficiently effective in suppressing the flame from spreading. As a result it gave a 'FAIL' rating in the UL-94 test. The addition of 20 p.p.h.r. of CP also gave a similar result (compound 5).

The common established system used for flame retardant applications is a synergistic effect of DBBO and  $\text{Sb}_2\text{O}_3$  at a ratio of 3:1. In this work, a compound with the addition of 22.5 p.p.h.r. of DBBO and 7.5 p.p.h.r.  $\text{Sb}_2\text{O}_3$  was able to achieve 22.6% oxygen index and V1 rating for the UL-94 test.

The influence of CP at higher loading (compound 9) was also investigated. When 40 p.p.h.r. of CP was incorporated, the LOI value gave 20.8% compared to 18.6% for the control compound. Higher concentrations did not seem to produce a large improvement in the LOI value. This was as a result of dripping which was observed during the test, leading to flame spread. This can be attributed to the

plasticising effect of CP, leading to a significant reduction in viscosity as measured by the Mooney Viscometer (*Table 2*).

### Combined Effect of Zinc Hydroxystannate (ZHS)

The inclusion of 4 p.p.h.r. of ZHS in combination with CP and DBBO did not have a significant effect on the LOI value (*Table 1*). Therefore, there was no degree of FR synergism up to 4 p.p.h.r. loading exhibited by the tin additives in both the NR containing CP and those containing aromatic bromine compounds (DBBO). This result is the opposite of that obtained with polyester resins<sup>12</sup>. In the resins containing additive-type halogen compounds, the author concluded that ZHS are effective FR synergists when used at levels of up to 5 p.p.h.r. This suggests that the effectiveness of ZHS is strongly dependent on the nature of the polymer/elastomer structure.

Since there is no effect of ZHS at low loadings (4 p.p.h.r.), the influence of 20 p.p.h.r. ZHS in combination with 40 p.p.h.r. CP was carried out. The combined effect of 20 p.p.h.r. of ZHS with 40 p.p.h.r. of CP (compound 13) lowered the flammability of NR achieving the V0 classification. In addition, the LOI results were significantly higher than the results of the two materials added separately. This could be explained partly by a dilution effect. In comparison, NR with  $\text{Sb}_2\text{O}_3$  and CP loading (compound 14) was classified as V2 due to the presence of flaming drips. The lower minimum torque value was observed in compound 14 compared to compound 13 (*Table 2*). The lower minimum torque value is an indication of a lower viscosity of the compound which probably increases the tendency to drip.

TABLE 1. LOI, UL-94 AND  $T_{95}$  DATA FOR NR COMPOUNDS

Compound IDs	Additives (parts per hundred rubber, p.p.h.r.)	$t_{95}$ ,min	LOI (%)	UL-94 Rating	UL-94 Total Burn Time (s)
1	None	12.4	18.2	FAIL	BTC
2	20 ZHS	14.2	18.2	FAIL	BTC
3	20 ZS	11.3	18.2	FAIL	BTC
4	20 $Sb_2O_3$	11.3	18.4	FAIL	BTC
5	20 CP	16.1	20.2	FAIL	BTC
6	20 DBBO	12.8	19.4	FAIL	BTC
7	5 $Sb_2O_3$ + 15 DBBO	10.8	20.2	FAIL	> 315
8	7.5 $Sb_2O_3$ + 22.5 DBBO	10.5	22.6	VI	133
9	40 CP	19.1	20.8	FAIL	BTC
10	4 ZHS + 20 CP	16.7	20.4	FAIL	BTC
11	4 ZHS + 40 CP	19.9	22.4	FAIL	BTC
12	4 ZHS + 20 DBBO	11.8	20.2	FAIL	BTC
13	20 ZHS + 40 CP	18.6	24.5	V0	30
14	20 $Sb_2O_3$ + 40 CP	17.5	25.6	V2	25
15	60 ATH	9.4	20.8	FAIL	>470
16	100 ATH	8.6	23.8	VI	185
17	140 ATH	7.1	26.2	VI	54
18	130 ATH + 10 ZHS	8.4	26.6	VI	52
19	125 ATH + 15 ZHS	8.9	26.4	VI	70
20	100 ATH + 40 CP	13.8	26.0	V0	44
21	90 ATH + 40 CP + 10 ZHS	14.0	25.6	V0	25
22	130 ATH + 10 CL20	5.2	28.0	V0	47
23	120 ATH + 10 CL20 + 10 ZHS	5.5	27.4	VI	60

Base formulations (p.p.h.r.): NR:100; Zinc oxide:5; Stearic acid:2; Santoflex 13 (N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine):1; Sulphur 2.5; CBS (N-Cyclohexyl-2-benzothiazolesulphenamide):1. ZHS: Zinc Hydroxystannate; ZS: Zinc Stannate; CP: Chlorinated Paraffin; ATH: Aluminium trioxide; DBBO: Decabromodiphenyl oxide; CL20: organoclay, cloisite 20A;  $Sb_2O_3$ : Antimony trioxide. BTC: Burnt to clamp.

### Effect of ZHS in Halogen Free Formulations

Halogen free systems are generally well specified in terms of low smoke emission; therefore all efforts were directed towards improving both fire retardance and reducing the levels of heat release. In this section, halogenated compounds were not included in the compounding compositions.

As indicated in *Table 1* NR filled with 60 p.p.h.r. ATH (compound 15) was not

sufficient to achieve the V0 rating in the UL-94 test. Thus an increase in loading, up to 100 p.p.h.r. and even higher, was necessary. With the incorporation of 60 p.p.h.r. to 140 p.p.h.r., the rubber content in the compound formulation was reduced to between 58 wt% and 40 wt%. This reduced the amount of fuel and interrupted the burning cycle. Additionally, alumina (AlO) protects the underlying surface by forming a layer of char. The water vapour which is released works through cooling and will further assist in extinguishing the flame. From physical

TABLE 2. CURE CHARACTERISTICS OF SELECTED NR COMPOUNDS

Cure characteristics	Compound IDs											
	1	5	6	7	8	9	10	11	12	13	14	
Mooney viscosity ML (1+4) at 100°C	33.9	N/A	32.5	44.0	53.3	14.2	28.7	18.4	N/A	N/A	N/A	
Minimum torque (dNm)	7.8	6.4	8.1	5.3	5.2	4.8	6.5	5.2	7.9	7.8	3.8	
Maximum torque (dNm)	63.6	50.6	66.2	56.6	56.6	38.6	52.4	39.7	61.4	65.2	35.6	
Scorch time, t <sub>s2</sub> (min)	6.7	8.7	6.8	6.5	6.5	9.9	8.8	10.3	6.7	7.2	10.5	
Optimum cure time, t <sub>95</sub> (min)	Refer to <i>Table 1</i>											

observation, NR filled with ATH did not produce a dense smoke as was the case with FR-DBBO/Sb<sub>2</sub>O<sub>3</sub> mixtures, which is a major advantage of using this type of FR. In addition, spreading of the burning flame with ATH loading was quite slow. In this experiment, 140 p.p.h.r. ATH loading improved the UL-94 rating from 'FAIL' to 'V1'. This was achieved by a reduction in their burn time.

Partial replacement of ATH by ZHS seemed to have little effect on the LOI and the UL-94 results (*Table 1*). Further replacement of ATH with 15 p.p.h.r. of ZHS slightly decreased the LOI value and prolonged the burning time in the UL-94 (compound 19). The effect of having ZHS also had no influence in reducing smoke density (*Figure 1*). The opposite effect was found for ethylene-vinyl acetate copolymer<sup>13</sup>. These findings showed that partial replacement of ATH with ZHS gave a reduction in the smoke parameter as measured in the Cone Calorimeter method. Although a different method was used to evaluate the smoke density, Cusack P.A.<sup>14</sup> has demonstrated that there is a correlation in the determination of smoke obscuration by Cone Calorimeter and NBS Smoke Box tests.

### ATH in Combination with Organoclay

The incorporation of organoclay filler as partial replacement of ATH (compound 22) produced a better flame retardant effect. Further replacement of ATH with ZHS, however, did not have any improvement in their flammability behaviour. The effects of ZHS when used in conjunction with ATH or CL20 are less pronounced in NR compounds. It is also less effective with regards to smoke suppressant (*Figure 1*).

### Tensile Strength

The addition of up to 20 p.p.h.r. ZHS did not have a significant effect on the tensile strength. The incorporation of CP in unfilled rubber acted as a plasticiser besides imparting flame resistance. A large amount incorporated (compound 9) resulted in a deterioration in tensile strength (*Table 3*) and gave no significant improvement in the LOI value. A significant decrease in the tensile strength of compounds 15 to 17 was also observed. The fact that higher loadings of ATH have a detrimental effect on the properties of the

TABLE 3. TENSILE STRENGTH<sup>a</sup> OF SELECTED NR COMPOUNDS

Sample	(p.p.h.r.)	Tensile Strength (MPa)	Sample	(p.p.h.r.)	Tensile Strength (MPa)
1	None	28.9	16	100 ATH	17.0
2	20 ZHS	26.7	17	140 ATH	15.7
3	20 ZS	27.6	18	130 ATH + 10 ZHS	14.7
4	20 Sb <sub>2</sub> O <sub>3</sub>	28.6	19	125 ATH + 15 ZHS	14.9
5	20 CP	25.6	20	100 ATH + 40 CP	19.9
9	40 CP	11.6	21	90 ATH + 40 CP + 10 ZHS	20.0
15	60 ATH	23.8	22	130 ATH + 10 CL20	14.6

<sup>a</sup>Values are median of 3 readings.

compounds tested has been reported by other authors<sup>15,16</sup>. Reduction of the properties is due to the fact that the amount of rubber in the matrix is considerably reduced and there is no intimate interaction between the ATH particles and the elastomer, which is essential for reinforcement to take place. The microscopy results shown in *Figures 3* and *4* demonstrate that the ATH particles are not well adhered to the NR matrix. This would act as an initial flaw and crack the initiator site in the rubber compounds, corresponding to a drop in tensile strength values.

The tensile strength of the combined system (compound 20) was higher than that of the single system (compound 17) at the same concentration. When compared with compound 16, the addition of CP clearly showed an improvement both in tensile strength and the UL-94 burning time.

The best balance of tensile properties and flame retardancy was achieved with compound filled with 90 p.p.h.r. of ATH, 40 p.p.h.r. CP and 10 p.p.h.r. of ZHS (compound 21), however, at the expense of smoke production.

### Smoke Density Test

NBS smoke tests were carried out on selected samples of the NR containing various combinations of FR additives/filler. Most of the samples in this study produced extremely high levels of smoke and tended to saturate the smoke test detector. Therefore, the samples were tested at one quarter normal size. ZHS is claimed as an excellent smoke suppressant compared to Sb<sub>2</sub>O<sub>3</sub><sup>17</sup>. Thus smoke density measurements were carried out to evaluate the effectiveness of both additives in NR compounds. *Figures 1* and *2* show the specific optical density ( $D_s$ )/g plotted as a function of time. From *Figure 1*, notably 20 p.p.h.r. of ZHS in combination with 40 p.p.h.r. of CP gave lower smoke density than Sb<sub>2</sub>O<sub>3</sub> at the same loading. This shows that ZHS could be a positive replacement for Sb<sub>2</sub>O<sub>3</sub>. ZHS is also regarded as a low toxic material in comparison to Sb<sub>2</sub>O<sub>3</sub>.

For NR filled with ATH in combination with ZHS or organoclay, at a continuous constant external radiant flux, several smoke density peaks were observed as shown in *Figure 2*. These peaks could be a result of the

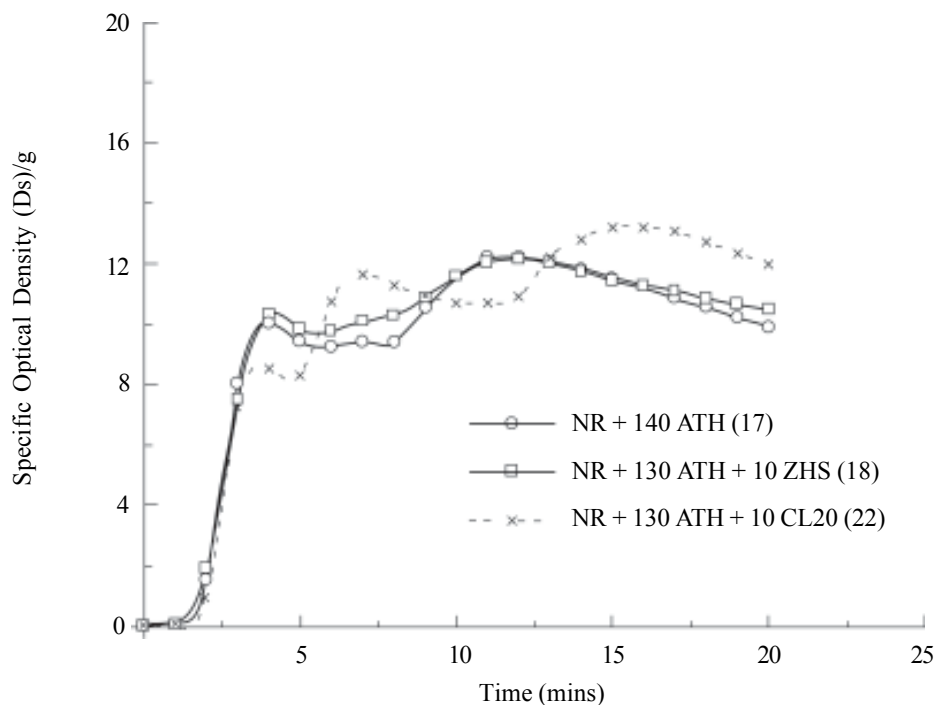


Figure 1. Specific optical density of NR in halogen free formulations.

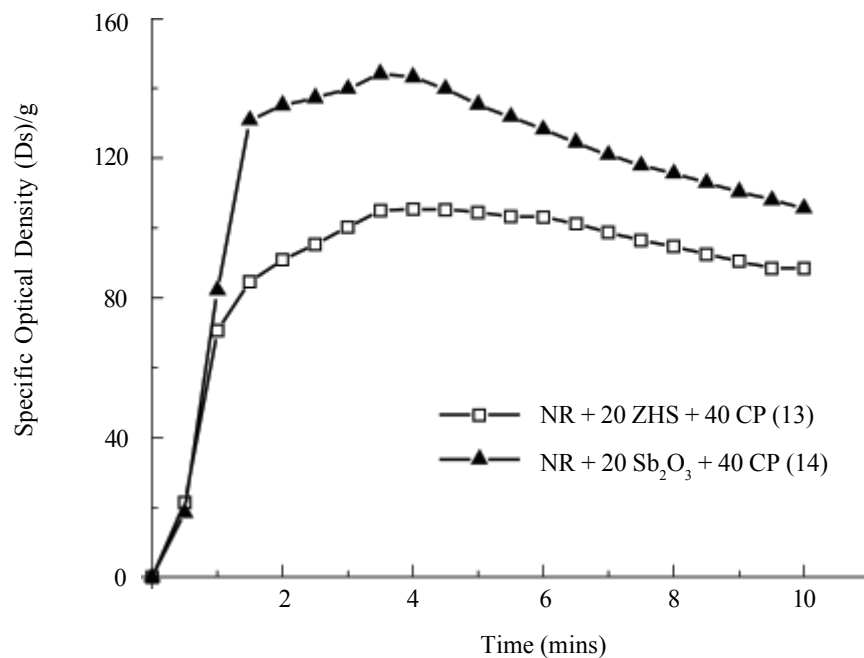


Figure 2. Comparison of smoke density for  $Sb_2O_3$  and ZHS in halogenated NR compounds.



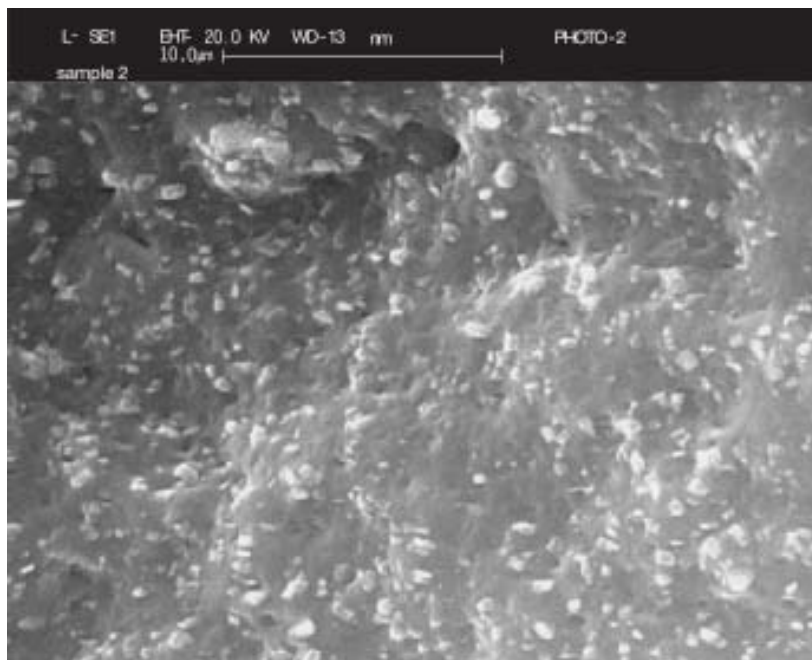


Figure 3. Sample of rubber compound containing 100 p.h.r. ATH (virgin sample from freeze fracture sample).

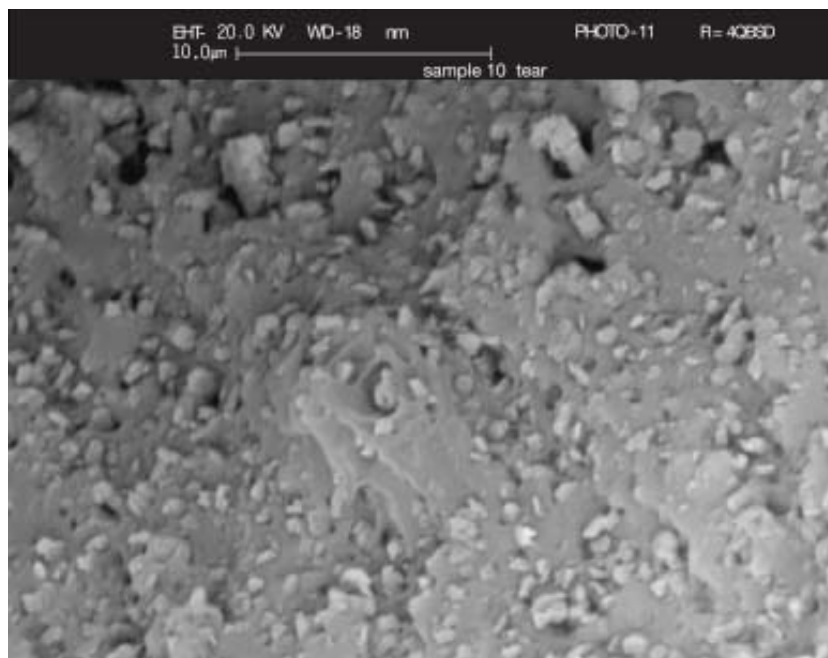


Figure 4. Sample of rubber compound containing 100 p.h.r. ATH (tear strength specimen).

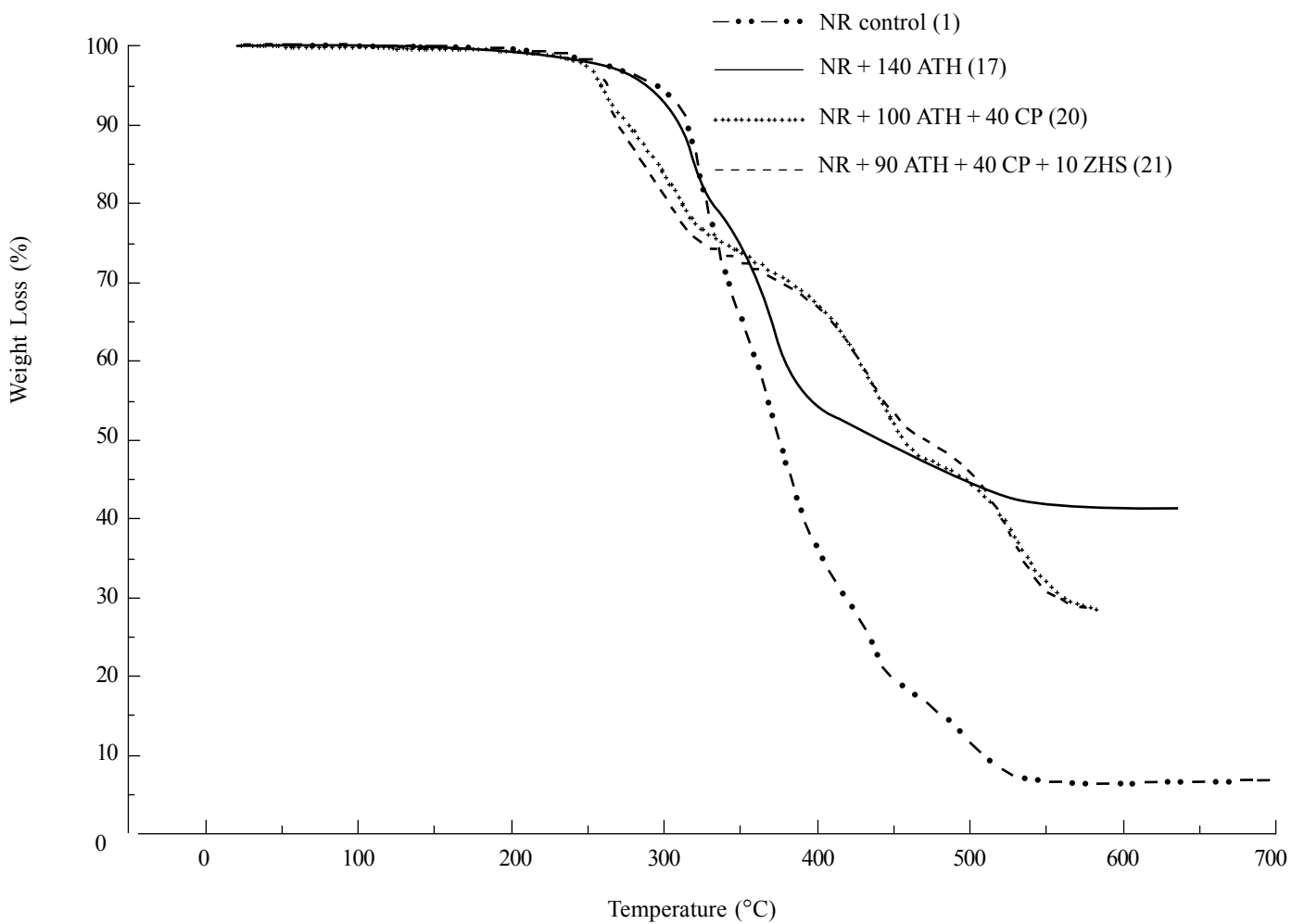


Figure 5. Thermal degradation of NR compounds.

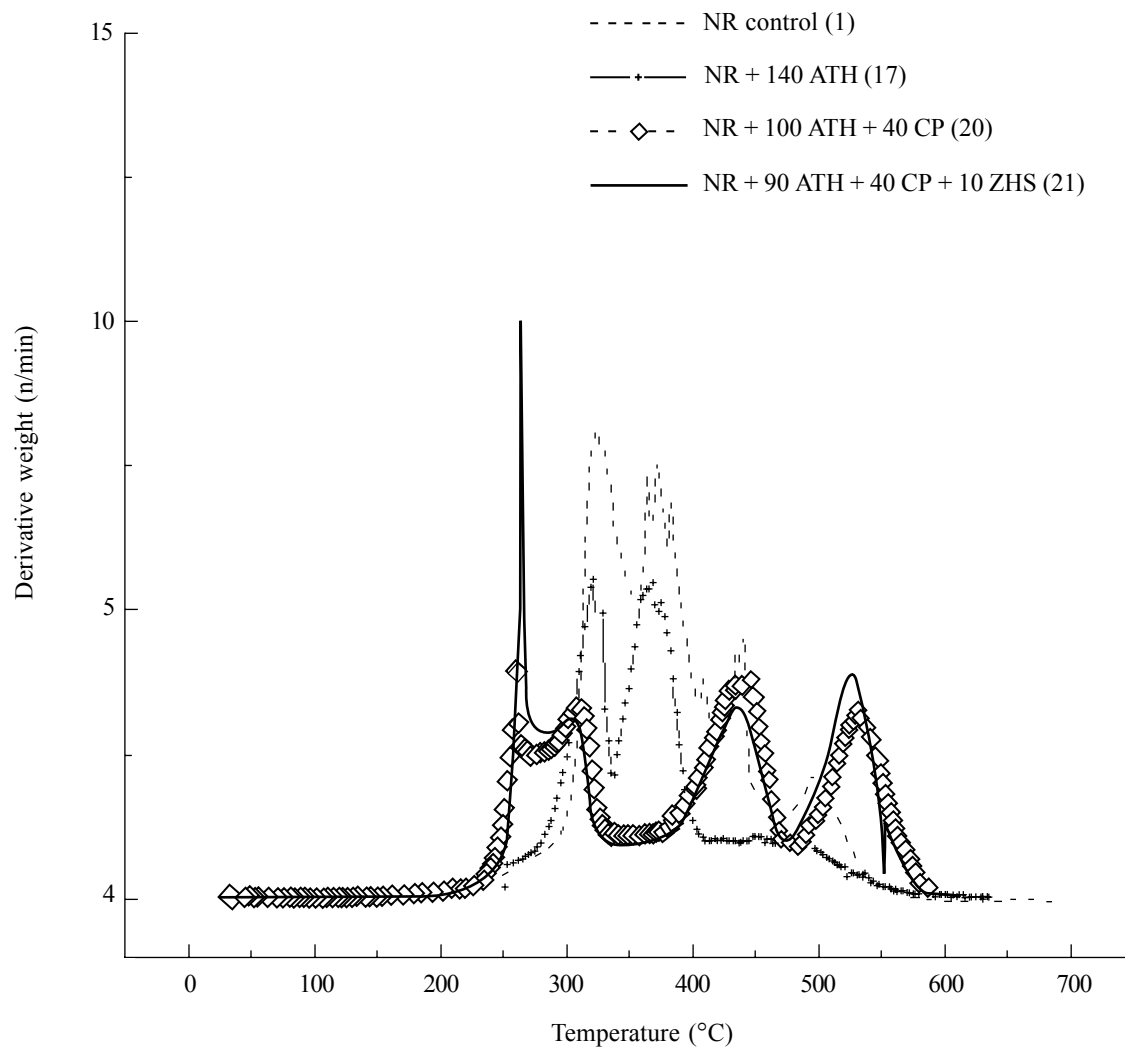


Figure 6. DTG curves of NR compounds.

following: Once the samples were burned, a protective layer was formed. The smoke density decreased rapidly with time due to the formation of a heat insulating char layer near the sample surface. At some stage, when the sample absorbs more heat, the char layer was physically broken and the burning continues. It is generally accepted that one of the key attributes necessary to improve fire performance of polymer materials is the enhancement of the char stability. Thus, it is believed that the instability of the char layer was responsible for several peaks observed in the smoke density curve.

### Thermal Behaviour of NR Compounds

*Figure 5* shows the TGA curves of NR containing ATH and compounds with ATH partially replaced by CP and ZHS. Compounds filled with 140 p.p.h.r. ATH gave the highest residues compared to other compounds tested. This behaviour was expected since more ATH was incorporated, it would provide both incomplete dehydration and solid-phase charring. This supports the improvement seen in the LOI tests (*Table 1*). The two-stage weight losses in compound 17 are probably attributable to water released by the decomposition of ATH and the main breakdown of the hydrocarbon chain. The thermal stability of NR was reduced with the partial replacement of 40 p.p.h.r. of CP, resulting in less residue. This indicates less solid phase charring and eventually leads to the formation of larger amounts of carbon rich solids, which are the major constituent of smoke. From the DTG curves (*Figure 6*), it can be seen that the pyrolysis peaks shifted to a lower temperature. Further replacement by ZHS produced no pronounced change in the TGA. However, there is a significantly higher peak in the weight loss derivative curve at 260°C in comparison with the compound without ZHS (compound 20). Further evaluations are

needed to explain all the differences in these curves.

### CONCLUSION

- The addition of up to 20 p.p.h.r. ZHS/ ZS or  $\text{Sb}_2\text{O}_3$  was not effective as a single flame retardant in NR compounds.
- From the trials conducted in this work with ZHS in combination with halogenated compounds, compounds containing 10 p.p.h.r. of ZHS with 90 p.p.h.r. of ATH and 40 p.p.h.r. of CP has the best balance of fire retardant behaviour and mechanical properties.
- ATH produced good fire retardancy if a sufficient amount was added. A loading of 140 p.p.h.r. was required to achieve a V1 rating. SEM micrographs revealed that there was poor adhesion between the ATH particles and the rubber matrix. This had an adverse effect on the tensile strength of NR.
- ZHS in combination with ATH, in halogen free formulations, did not produce any synergistic effect in the flammability behaviour and no degree of smoke suppressant.

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