

Synergism of Xanthate/Dithiocarbamate Accelerator in Carbon Black Filled NR Compounds

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ABSTRACT

Zinc salts of ethyl, isopropyl and butyl xanthates were prepared in the laboratory. The effect of these xanthates with zinc diethyldithiocarbamate (ZDC) on the vulcanization of HAF filled NR compound has been studied at different temperatures. The rubber compounds with the three xanthate accelerators and ZDC were cured at various temperatures from 60°C to 150°C. The sheets were moulded and properties such as tensile strength, tear strength, cross-link density, elongation-at-break, compression set, heat build up, abrasion resistance, flex resistance, etc. were evaluated. The properties showed that zinc xanthate/ZDC accelerator combination has a positive synergistic effect on the mechanical properties of NR compounds. The curing of HAF filled NR compound containing zinc xanthate/ZDC is slightly slower than the curing of the corresponding gum compounds. It is observed that, by gradually increasing the amount of the accelerator, the cure time of black filled NR compound can be made equal to that of the gum compound.

Key Words:

natural rubber;
low temperature curing;
mechanical properties;
xanthate accelerators; synergism.

INTRODUCTION

Even though gum natural rubber vulcanizate has high tensile strength, it is not suitable for many commercial applications. Fillers are generally incorporated for improved processability, reinforcement or for cost reduction. Reinforcement by a filler

is the enhancement of one or more properties of elastomer by filler, thus making it more suitable for a given application [1,2]. The effect of a filler on rubber vulcanizates depends on its physical properties such as particle size, surface area, surface

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reactivity, electrical charge on the particle and chemical properties such as pH and reactivity with accelerators. The fundamental aspects of polymer filler interaction has been studied in detail in a number of polymers [3,6]. Studies on filled systems have also been reviewed by Kraus [7] and Voet [8]. In general, the best reinforcing fillers are those having the smallest particle size. Carbon blacks are the most effective reinforcing fillers used in rubber industry. It is known that carbon black contains active functional groups such as phenolic, ketonic and carboxylic together with lactones [9,10].

During vulcanization, carbon black enters a chemical reaction with sulphur, accelerations, etc., participating in the formation of vulcanized network. It is generally agreed that strong links exist between rubber chains and reinforcing filler particles [11,12]. The nature of polymer-filler attachments in vulcanizates has been investigated in great detail by Rehner [13]. The introduction of carbon black in the rubber mixture results in an additional consumption of accelerators because of the adsorption of accelerators on the surface of the carbon black particles [1,2]. So more accelerators or a combination of more active accelerators has to be employed in the compounds containing carbon black.

This paper reports the synergistic effect shown by zinc salt of xanthate /ZDC accelerator combination on the vulcanization of HAF filled NR compounds at various temperatures and the effect of temperature of curing on the mechanical properties of the vulcanizates and also it shows the effect of accelerator concentration on the cure time of HAF filled NR compounds.

EXPERIMENTAL

Materials

Natural rubber (NR) [ISNR- 5, Mooney viscosity ML (1+4) 100°C value of 82] was supplied by the Rubber Research Institute of India, Kottayam. Compounding ingredients, i.e., zinc oxide, stearic acid, ZDC, sulphur, aromatic oil, HS, vulcanox 40,20 and carbon black (HAF N330) were commercial grades. Denatured spirit, isopropyl alcohol, n-butyl alcohol, potassium hydroxide, carbon disulphide and toluene used for swelling studies were of reagent grade and they were used as supplied. Zinc sulphate used for precipitation

Table 1. Formulation of mixes.

Mix	A	B	C
Natural rubber	100	100	100
Zinc oxide	5	5	5
Stearic acid	2	2	2
HAF, N 330	40	40	40
Aromatic oil	5	5	5
HS	0.5	0.5	0.5
Vulcanox 40-20	1.0	1.0	1.0
ZDC	0.75	0.75	0.75
Zn (ext) ₂	-	1.0	-
Zn (ipxt) ₂	1.0	-	-
Zn (bxt) ₂	-	-	1.0
Sulphur	2.5	2.5	2.5

Table 2. Optimum cure time in minutes.

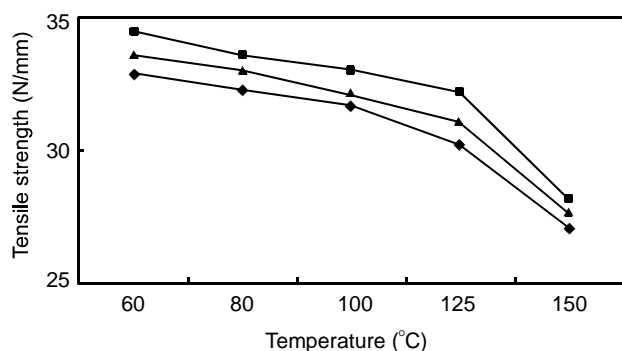
Temperature (°C)	A	B	C
150	1.81	1.42	1.26
125	8.01	7.20	7.11
100	30.12	25.31	21.24
80	78.16	72.41	63.62
60	92.65	90.42	88.31

was commercial grade.

Zinc salts of ethyl, isopropyl, and butyl xanthates were prepared in the laboratory [14]. Black filled NR

Table 3. Formulation of mixes.

Mix	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆
Natural rubber	100	100	100	100	100	100
ZnO	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
HAF	-	5	10	20	30	40
Aromatic oil	-	-	-	2	4	5
HS	0.5	0.5	0.5	0.5	0.5	0.5
Vulcanox 40.20	1.0	1.0	1.0	1.0	1.0	1.0
Zn (bxt) ₂	1.0	1.0	1.0	1.0	1.0	1.0
ZDC	0.75	0.75	0.75	0.75	0.75	0.75
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5



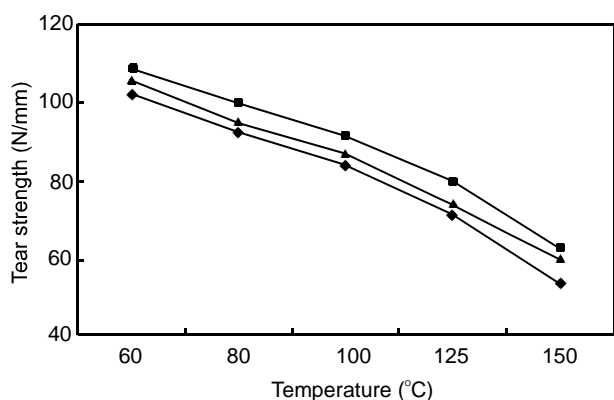
(—◆—)Zn ethyl xanthate;(—■—)Zn Isopropyl xanthate;(—▲—) Zn butyl xanthate.

Figure 1. Variation of tensile strength with temperature.

compounds were prepared using zinc butyl xanthate[Zn (bxt)₂]/ZDC, zinc isopropyl xanthate [Zn (ipxt)₂]/ZDC, zinc ethyl xanthate[Zn (ext)₂]/ZDC accelerator systems.

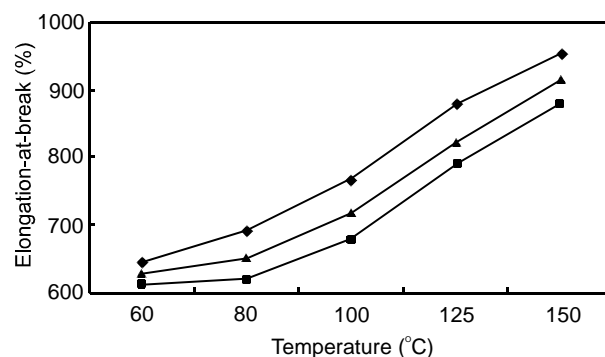
The optimum amounts of ZDC and zinc xanthate were determined to be 0.75 and 1.0 phr, respectively in NR gum compounds [15].

Natural Rubber was compounded on a (6 × 12) laboratory mixing mill as per the formulations given in Table 1. The optimum cure times of the compounds were determined using a Goettfert elastograph model 67.85 as per ASTM.D.1646 (1981) and are reported in Table 2. NR Compounds were moulded in an electrically heated laboratory hydraulic press at various temperatures from 60°C-150°C up to their optimum cure time at a pressure of 200 kg/cm². Dumb-bell shaped tensile test pieces were punched out of these compression-moulded sheets along the mill grain direction. The tensile properties of the vulcanizates were evaluated on



(—◆—)Zn ethyl xanthate;(—■—)Zn Isopropyl xanthate;(—▲—) Zn butyl xanthate.

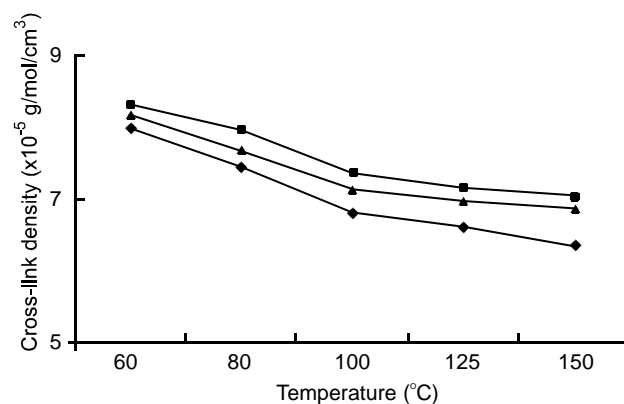
Figure 2. Variation of tear strength with temperature.



(—◆—)Zn ethyl xanthate;(—■—)Zn Isopropyl xanthate;(—▲—) Zn butyl xanthate.

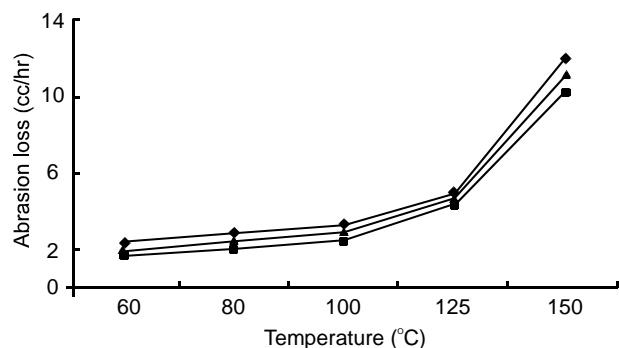
Figure 3. Variation of elongation at break with temperature.

a Zwick universal testing machine using a cross-head speed of 500 mm/min according to ASTM.D-2240. A graphical comparison of the tensile properties of the above mixes is given in Figures 1-3. Cross-link density of the samples was determined by equilibrium swelling methods using toluene as the solvent. The degree of cross-linking was calculated using the Flory-Rehner equation [16] and are shown in Figure 4. Abrasion resistance was tested using a DIN abrader according to DIN 53516 and is shown in Figure 5. The heat build up was measured using the Goodrich flexometer conforming to ASTM D 623.78 (method A) and is given in Figure 6. Flex resistance of the samples was determined by using a Wallace De Mattia flexing machine as per ASTM D 430-57T and are shown in Figures 7 and 8. Compression set (6.25 mm thick and 18 mm diameter samples) was determined by compressing to constant deflection (25%) and were kept for 23 h in an air over



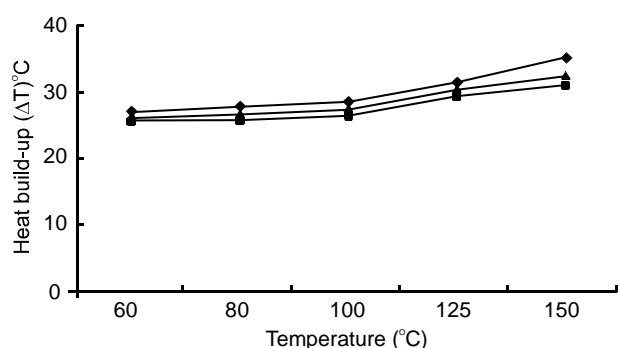
(—◆—)Zn ethyl xanthate;(—■—)Zn Isopropyl xanthate;(—▲—) Zn butyl xanthate.

Figure 4. Variation of cross-link density with temperature.



(—◆—) Zn ethyl xanthate; (—■—) Zn Isopropyl xanthate; (—▲—) Zn butyl xanthate.

Figure 5. Variation of abrasion loss with temperature.



(—◆—) Zn ethyl xanthate; (—■—) Zn Isopropyl xanthate; (—▲—) Zn butyl xanthate.

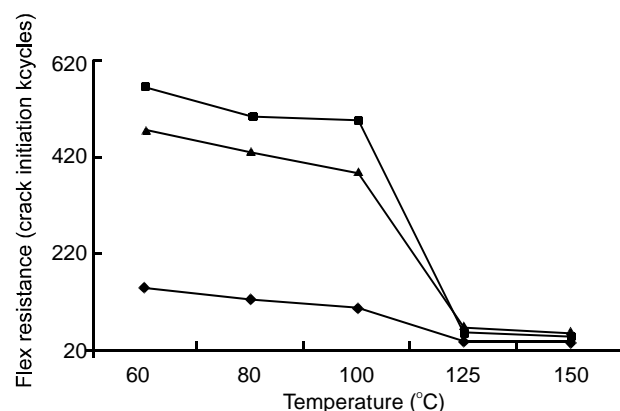
Figure 6. Variation of heat build up with temperature.

at 70°C (ASTM D 395-61, method B) and is given in Figure 9.

When the cure times of the mixes given in Table 1 were determined, it was seen that curing slowed down in black filled NR compounds compared to the curing of NR gum compounds. It is made clear by gradually increasing the concentrations of HAF from 5 phr to 40 phr as shown in Table 3. It can be seen that the cure time of HAF filled NR compounds, containing different amounts of carbon black can be made equal to the cure times of NR gum compounds by gradually increasing the concentration of the accelerator as shown in Table 4.

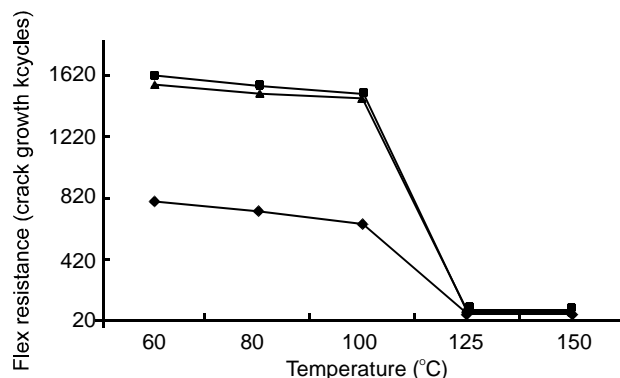
RESULTS AND DISCUSSION

Zinc diethyldithiocarbamate and zinc alkyl xanthates are ultrafast accelerators and both ensure low tempera-



(—◆—) Zn ethyl xanthate; (—■—) Zn Isopropyl xanthate; (—▲—) Zn butyl xanthate.

Figure 7. Variation of heat build up with temperature.



(—◆—) Zn ethyl xanthate; (—■—) Zn Isopropyl xanthate; (—▲—) Zn butyl xanthate.

Figure 8. Variation of flex resistance (crack growth) with temperature.

ture vulcanization. The effective commencing temperature (T_{ea}) of zinc xanthate is very low and hence it needs very little activation energy. So curing will be achieved in a shorter length of time. When two ultra accelerators are combined together, a synergistic effect may appear. Misatoya and Aoe explained the higher activity by the formation of either eutectic mixture or salt forming compounds having better solubility in rubber and greater chemical reactivity [17].

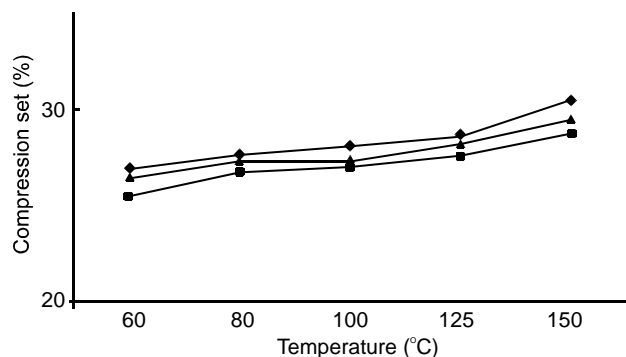
Table 2 shows the optimum cure time of the mixes given is Table 1 at different temperatures. The results show that the optimum cure time increases as the temperature of curing is decreased from 150°C to 60°C. At a particular temperature, cure time is minimum for the compound containing Zn (bxt)₂/ZDC.

Table 4. Formulation of mixes.

Mix	B ₁	B ₂	B ₃	B ₄	B ₅	B ₆
NR	100	100	100	100	100	100
ZnO	5	5	5	5	5	5
Stearic Acid	2	2	2	2	2	2
HAF	-	5	10	20	30	40
Aromatic oil	-	-	-	2	4	5
HS	0.5	0.5	0.5	0.5	0.5	0.5
40.20	1.0	1.0	1.0	1.0	1.0	1.0
ZDC	0.75	0.85	0.95	1.15	1.35	1.55
Zn (bxt) ₂	1	1.1	1.2	1.4	1.6	1.8
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5

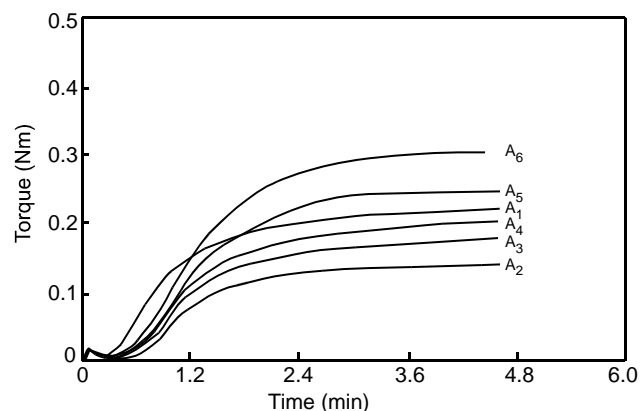
The cure time is found to be related to the bulkiness of the alkyl group present is zinc alkyl xanthate. As the bulkiness of the alkyl group increases, cure time decreases. It may be due to the better solubility of the accelerator in NR as the size of the alkyl group increases.

Figures 1-3 show the tensile properties of the mixes given in Table 1. The results show that the tensile strength and tear strength increase and elongation-at-break decreases as the temperature of curing is decreased from 150°C to 60°C. The increase in tensile properties is due to the lesser degradation of the rubber at lower temperatures and also due to the higher stability of the accelerator at lower temperatures. So more cross-link densities are observed at lower temperatures. Figure 4 shows the cross-link density of the mixes given in Table 1. Cross-link density increases as the



(—◆—)Zn ethyl xanthate;(—■—)Zn Isopropyl xanthate;(—▲—) Zn butyl xanthate.

Figure 9. Variation of compression with temperature.

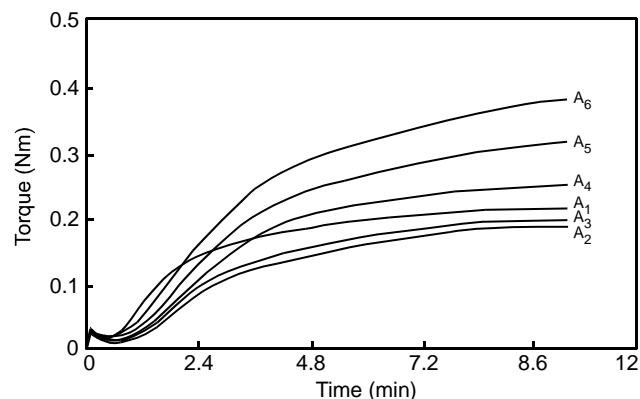


(—◆—)Zn ethyl xanthate;(—■—)Zn Isopropyl xanthate;(—▲—) Zn butyl xanthate.

Figure 10. Variation of torque with time.

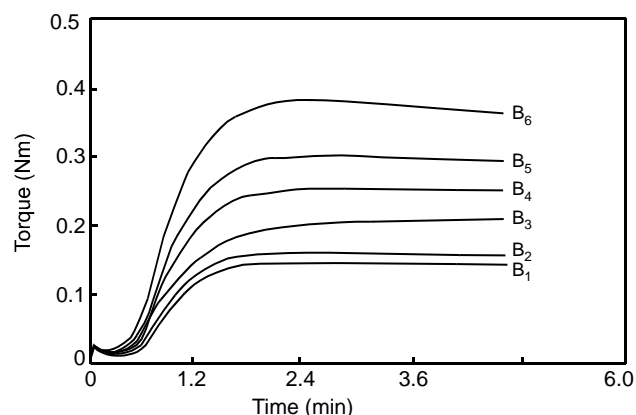
temperature of curing is changed from 150°C to 60°C. Figures 5 and 6 show the abrasion loss and heat build-up, respectively. It is seen that both abrasion loss and heat build-up decrease as the temperature decreases. Figures 7 and 8, show the flex resistance-crack initiation and crack growth, respectively. The values show that the flex resistance increases as the temperature of curing decreases. Figure 9 shows the compression set values at different temperatures. It is seen that compression set decreases as the temperature decreases. So all the mechanical properties are found to be increased as the temperature of curing is decreased from 150°C to 60°C. This is due to the higher cross-linking at lower temperatures.

The cure times of the black filled compounds containing different amounts of carbon black are compared



(—◆—)Zn ethyl xanthate;(—■—)Zn Isopropyl xanthate;(—▲—) Zn butyl xanthate.

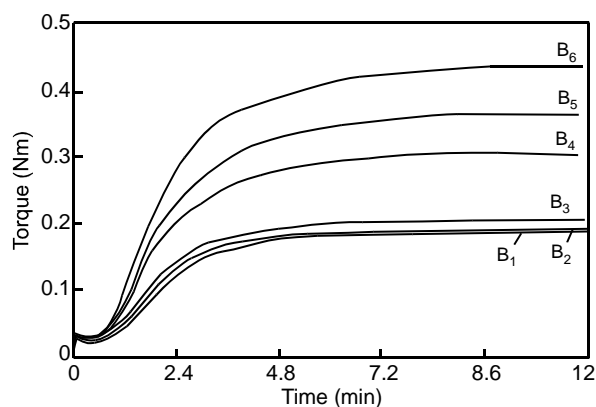
Figure 11. Variation of torque with time.



(—◆—) Zn ethyl xanthate; (—■—) Zn Isopropyl xanthate; (—▲—) Zn butyl xanthate.

Figure 12. Variation of torque with time.

with their corresponding gum compounds. It is done by gradually increasing the amount of carbon black from 0 to 40 phr as shown in Table 3. Figures 10 and 11 show the cure curves of the mixes given in Table 2 at 150°C and 125°C, respectively. It is seen that the increase in cure time is proportional to the amount of carbon black present in the compound. This may be due to the adsorption of accelerator on the surface of carbon black. It is reported that the functional groups of carbon black which enter into side reactions with the accelerator may reduce the accelerator concentration to a point where its residual amount is no longer sufficient to ensure a fast vulcanization [12]. But it can be shown that the cure times of HAF filled compounds, containing any amount of carbon black can be made equal to the corresponding gum compounds by gradually



(—◆—) Zn ethyl xanthate; (—■—) Zn Isopropyl xanthate; (—▲—) Zn butyl xanthate.

Figure 13. Variation of torque with time.

increasing the accelerator concentration as shown in Table 4. Figures 12 and 13 are the cure curves of the mixes given in Table 4 at 150°C and 125°C, respectively. Thus in HAF filled NR compounds, the cure time is influenced by the accelerator concentration.

Applications

The black filled natural rubber compounds containing xanthates can be applied in:

- Tyre repairing,
- Tyre retreading,
- Manufacture of solid tyres at lesser energy cost.

CONCLUSION

- Zinc salts of xanthate/ ZDC combination can be used to vulcanize HAF filled NR compounds at temperature varying from 60°C-150°C

- As the temperature of vulcanization decreases from 150°C to 60°C, all the mechanical properties of the NR vulcanizate improved.

- At a particular temperature, the cure time is minimum for the compound containing Zn (bxt)₂/ZDC compared to the other two combinations.

- At any temperature, the curing of the HAF filled NR compound containing zinc xanthate/ZDC is slow compared to the corresponding gum compound.

- By gradually increasing the accelerator concentration, the cure time of the HAF filled NR compound can be made equal to that of the NR gum compound.

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