

A Novel Accelerator Combination for the Low Temperature Curing of Silica-Filled NBR Compounds

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ABSTRACT: Zinc salts of ethyl, isopropyl, and butyl xanthates were prepared in the laboratory. The effect of these xanthates in combination with zinc diethyldithiocarbamate (ZDC) on the vulcanization of silica-filled NBR compounds has been studied at different temperatures. The cure times of these compounds were compared with that of NBR compounds containing tetramethylthiuram disulphide/dibenzothiazyl disulphide. The rubber compounds with the xanthates and ZDC were cured at various temperatures from 60 to 150°C. The sheets were molded and properties such as

tensile strength, tear strength, crosslink density, elongation at break, compression set, abrasion resistance, flex resistance, heat buildup, etc. were evaluated. The properties showed that zinc salt of xanthate/ZDC combination has a positive synergistic effect on the cure rate and mechanical properties of NBR compounds. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5680–5683, 2006

Key words: nitrile rubber; zinc xanthate; low temperature vulcanization; mechanical properties

INTRODUCTION

Natural rubbers (NRs) and synthetic rubbers differ in vulcanization characteristics and vulcanizate properties. Compared to NR, synthetic rubbers are vulcanized with higher concentration of accelerators with a corresponding reduction in sulfur. Synthetic rubbers do not stress crystallize as much as NR and hence the green strength and tensile properties of the gum vulcanizates of synthetic rubbers are inferior to those of NR.

Nitrile rubber (NBR) is a copolymer of butadiene and acrylonitrile and it comes under “special purpose synthetic rubbers.”¹ It has excellent oil resistance but is subject to degradation at very high temperatures.^{2,3} It is widely used in products like oil seals, water pump seals, blow out preventors, fuel lines, hoses, fuel pump diaphragms, etc. because of its high oil, solvent, and fuel resistance and gas impermeability.⁴

NBR shows no self-reinforcing effect, as there is no crystallinity. So the unfilled vulcanizates have very low tensile strength.⁵ When used in combination with reinforcing fillers, vulcanizates with excellent mechanical properties can be obtained from NBR.⁶ There have been a number of studies on the reinforcement mechanism of fillers involving vulcanizates.^{7–10} Studies on filled systems have also been reviewed by Kraus¹¹ and Voet.¹² It is generally agreed that strong links exist between rubber chains and reinforcing fil-

ler particles.^{13,14} Zinc salt of xanthate/zinc diethyldithiocarbamate (ZDC) combination is found to produce a positive synergistic effect on the mechanical properties of gum and filled NR compounds.^{15,16}

Vulcanization temperature is very important in determining the quality of the rubber product. Optimum properties are obtained when curing is done at the lowest possible temperature. In the rubber industries, the rubber products are molded at very high temperatures. In addition to the high energy consumption, high temperature vulcanization will also affect the quality and lifetime of the product. Zn(bxt)₂/ZDC accelerator combination is found to vulcanize NR at lower temperatures, even at room temperature.¹⁷ It is found that the mechanical properties of the NR vulcanizate is improved with decrease in vulcanization temperature and is reported to be maximum when the vulcanization temperature is 60°C. The low temperature curing property of xanthate/ZDC accelerator combination is investigated through this work.

This article reports the vulcanization of silica-filled NBR using zinc salt of xanthate/ZDC accelerator combination at various temperatures and the effect of temperature of curing on the mechanical properties of the vulcanizates.

EXPERIMENTAL

Materials used

NBR [acrylonitrile content: 33%, Mooney viscosity (ML(1 + 4) at 100°C: 40.9)] was supplied by Apar

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TABLE I
Formulation of Mixes Containing Varying Amounts of Zn(ipxt)₂

| Mix | A1 | A2 | A3 | A4 | A5 | A5 |
|-----------------------|-----|-----|------|-----|------|-----|
| NBR | 100 | 100 | 100 | 100 | 100 | 100 |
| ZnO | 4 | 4 | 4 | 4 | 4 | 4 |
| Stearic acid | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Zn(ipxt) ₂ | 0 | 1.0 | 1.25 | 1.5 | 1.75 | 2.0 |
| ZDC | 3 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Sulfur | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |

Polymers, Gujarat. Compounding ingredients, i.e., zinc oxide, stearic acid, ZDC, dioctyl phthalate (DOP), silica, and sulfur, were commercial grade. Denatured spirit, isopropyl alcohol, *n*-butyl alcohol, potassium hydroxide, carbon disulphide, diethylene glycol (DEG), styrenated phenol (SP), and methyl ethyl ketone (MEK) used for swelling studies were of reagent grade. Zinc sulfate used for precipitation was of commercial grade.

Zinc salts of ethyl, isopropyl, and butyl xanthates were prepared in the laboratory according to the procedure reported earlier.¹⁸ Silica-filled NBR compounds were prepared using zinc ethyl xanthate [Zn(ext)₂]/ZDC, zinc isopropyl xanthate [Zn(ipxt)₂]/ZDC, and zinc butyl xanthate [Zn(bxt)₂]/ZDC accelerator systems. A reference NBR compound containing TMTD/MBTS was also prepared. To optimize the amount of accelerator for vulcanization, the concentration of Zn(ipxt)₂ was changed from 0 to 2 phr as shown in Table I and the concentration of ZDC was changed from 1 to 1.75 phr as shown in Table II. The cure characteristics of the mixes were determined using a Goettfert elastograph model 67.85 as per ASTM D 1646 (1981) at 150°C. The minimum torque, maximum torque, scorch time, optimum cure time, and the cure rate of the above mixes were reported in Table III.

NBR was compounded on a (6 × 12") laboratory-mixing mill according to the formulations given in Table IV. The optimum cure times of the compounds were determined and are reported in Table V. NBR compounds were molded in an electrically heated laboratory hydraulic press at various temperatures from 60 to 150°C upto their optimum cure times at a pressure of 200 kg cm⁻². Dumbbell-shaped tensile

TABLE II
Formulation of Mixes Containing Varying Amounts of ZDC

| Mix | B1 | B2 | B3 | B4 |
|-----------------------|------|------|------|------|
| NBR | 100 | 100 | 100 | 100 |
| ZnO | 4 | 4 | 4 | 4 |
| Stearic acid | 1.5 | 1.5 | 1.5 | 1.5 |
| Zn(ipxt) ₂ | 1.75 | 1.75 | 1.75 | 1.75 |
| ZDC | 1.0 | 1.25 | 1.50 | 1.75 |
| Sulfur | 1.50 | 1.50 | 1.50 | 1.50 |

TABLE III
Formulation of Mixes

| Mix | Min torque (N m) | Max torque (N m) | Scorch time (min) | Optimum cure time (min) | Cure rate index (N m min ⁻¹) |
|-----|------------------|------------------|-------------------|-------------------------|--|
| A1 | 0.024 | 0.285 | 1.40 | 2.82 | 0.14 |
| A2 | 0.027 | 0.264 | 1.11 | 2.41 | 0.16 |
| A3 | 0.034 | 0.272 | 1.02 | 2.20 | 0.19 |
| A4 | 0.039 | 0.279 | 0.84 | 2.12 | 0.21 |
| A5 | 0.040 | 0.291 | 0.75 | 1.99 | 0.24 |
| A6 | 0.041 | 0.290 | 0.74 | 1.99 | 0.23 |
| B1 | 0.035 | 0.258 | 0.83 | 2.16 | 0.22 |
| B2 | 0.039 | 0.315 | 0.81 | 1.91 | 0.27 |
| B3 | 0.040 | 0.291 | 0.75 | 1.99 | 0.24 |
| B4 | 0.039 | 0.290 | 0.73 | 2.02 | 0.24 |

test pieces were punched out of these compression-molded sheets along the mill grain direction. The tensile properties of the vulcanizates were evaluated on a Zwick universal testing machine using a cross head speed of 500 mm min⁻¹ according to ASTM D 2240 and are reported in Table VI. Crosslink density of the samples were determined by equilibrium swelling methods using MEK as the solvent. The degree of crosslinking was calculated using the Florey-Rehner equation¹⁹ and are given in Table VI. Abrasion resistance was tested using DIN abrader according to DIN 53516 and are given in Table VII. The flex resistance of the samples was determined by using a Wallace De Mattia flexing machine as per ASTM D 340-57 T and are given in Table VII. Compression set of 6.25 mm thick and 18 mm diameter samples was determined by compressing to constant deflection (25%) and were kept for 22 h in an air oven at 70°C (ASTM D 395-61, method B) and are given in Table VII. The heat buildup was measured using the Good rich flexometer conforming to ASTM D 623. 78 (method A) and is given in Table VII. SEM studies of the fractured tensile surfaces of the NBR vulcanizates containing

TABLE IV
Formulation of Mixes

| | Mixes | | | |
|-----------------------|-------|------|------|-----|
| | A | B | C | D |
| NBR | 100 | 100 | 100 | 100 |
| ZnO | 4.0 | 4.0 | 4.0 | 4.0 |
| Stearic acid | 1.5 | 1.5 | 1.5 | 1.5 |
| Silica | 40 | 40 | 40 | 40 |
| DOP | 6.0 | 6.0 | 6.0 | 6.0 |
| DEG | 2.0 | 2.0 | 2.0 | 2.0 |
| SP | 1.5 | 1.5 | 1.5 | 1.5 |
| MBTS | - | - | - | 1.5 |
| TMTD | - | - | - | 0.5 |
| ZDC | 1.25 | 1.25 | 1.25 | - |
| Zn(ext) ₂ | 1.75 | - | - | - |
| Zn(ipxt) ₂ | - | 1.75 | - | - |
| Zn(bxt) ₂ | - | - | 1.75 | - |
| Sulfur | 1.5 | 1.5 | 1.5 | 1.5 |

TABLE V
Cure Times (min) of the Mixes Given in Table IV

| Temp (°C) | A | B | C | D |
|-----------|-------|-------|-------|-----------|
| 150 | 1.31 | 1.12 | 0.98 | 2.1 |
| 125 | 4.20 | 3.94 | 3.16 | 7.9 |
| 100 | 12.32 | 10.61 | 10.36 | No curing |
| 80 | 33.96 | 31.07 | 29.65 | No curing |
| 60 | 62.54 | 59.38 | 56.04 | No curing |

Zn(bxt)₂/ZDC molded at 150 and 80°C were taken using a SEM model Hitachi-H.6010 A scanning system. The SEM photographs are given in Figures 1 and 2.

RESULTS AND DISCUSSIONS

The cure characteristics given in Table III show that the maximum torque and cure rate index are maximum and the optimum cure time is minimum for the compound containing 1.25 phr ZDC and 1.75 phr xanthate. This compound is having enough scorch time as not to cause processing problems. So 1.25 phr ZDC and 1.75 phr xanthate are taken as the optimum dosage for NBR compounds.

Table V shows the cure times of the mixes given in Table IV at different temperatures. It is seen that at 150 and 125°C, the curing of NBR compound containing MBTS/TMTD is slow compared to the corresponding compound containing ZDC/xanthate. Below 125°C, MBTS/TMTD combination cannot cure NBR. ZDC and zinc alkyl xanthates are ultrafast accelerators and both ensure low temperature vulcanization. Xanthates are much more effective accelerators compared to dithiocarbamates because of the presence of oxygen atom. The mechanism of the syn-

TABLE VI
Tensile Properties of the Silica-Filled NBR Vulcanizates

| Mix | Temperature (°C) | Crosslink density (10 ⁻⁵) (g mol ⁻¹ cm ⁻³) | Tensile strength (N mm ⁻²) | Tear strength (N mm ⁻¹) | Elongation at break (%) |
|-----|------------------|---|--|-------------------------------------|-------------------------|
| A | 150 | 3.986 | 23.51 | 68.35 | 760 |
| | 125 | 4.123 | 24.80 | 72.47 | 744 |
| | 100 | 4.865 | 25.79 | 81.06 | 713 |
| | 80 | 4.983 | 26.08 | 88.59 | 661 |
| | 60 | 5.164 | 27.01 | 90.34 | 610 |
| B | 150 | 4.222 | 24.16 | 77.34 | 749 |
| | 125 | 4.501 | 24.94 | 81.97 | 711 |
| | 100 | 4.985 | 25.57 | 88.01 | 654 |
| | 80 | 5.099 | 27.65 | 95.97 | 612 |
| C | 60 | 5.424 | 28.93 | 98.78 | 576 |
| | 150 | 4.326 | 24.89 | 79.15 | 732 |
| | 125 | 4.917 | 25.06 | 83.90 | 698 |
| | 100 | 5.206 | 26.73 | 88.71 | 619 |
| | 80 | 5.425 | 28.97 | 96.36 | 590 |
| | 60 | 5.653 | 29.35 | 100.51 | 552 |

TABLE VII
Mechanical Properties of Silica-Filled NBR Vulcanizates

| Mix | Temperature (°C) | Abrasion loss (cm ³ h ⁻¹) | Compression set (%) | Heat build up (ΔT) | Flex resistance (1000 cycles) |
|-----|------------------|--|---------------------|--------------------|-------------------------------|
| A | 150 | 6.35 | 25.32 | 61 | 80.34 |
| | 125 | 5.01 | 22.41 | 53 | 87.56 |
| | 100 | 4.51 | 19.24 | 49 | 107.43 |
| | 80 | 3.85 | 16.89 | 44 | 120.59 |
| | 60 | 3.01 | 14.82 | 39 | 131.02 |
| B | 150 | 5.07 | 22.15 | 55 | 89.93 |
| | 125 | 4.56 | 19.05 | 50 | 97.42 |
| | 100 | 3.69 | 16.14 | 44 | 115.10 |
| | 80 | 3.10 | 14.07 | 41 | 128.43 |
| | 60 | 2.42 | 13.23 | 35 | 136.35 |
| C | 150 | 4.81 | 21.24 | 52 | 101.90 |
| | 125 | 4.17 | 17.36 | 46 | 107.76 |
| | 100 | 3.55 | 15.19 | 41 | 120.87 |
| | 80 | 3.01 | 12.80 | 37 | 134.43 |
| | 60 | 2.28 | 12.13 | 33 | 153.50 |

ergistic effect of zinc xanthate/ZDC is reported in our earlier study.¹⁵ The O—C₂H₅ bond in xanthates is more polar than the N—C₂H₅ bond in dithiocarbamates. When two ultraaccelerators are combined together, a synergistic effect may appear. Minatoya 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.^{20,21}

Table V shows that the optimum cure times of the NBR compounds containing Zn(ext)₂/ZDC, Zn(ipxt)₂/ZDC, and Zn(bxt)₂/ZDC increases as the temperature

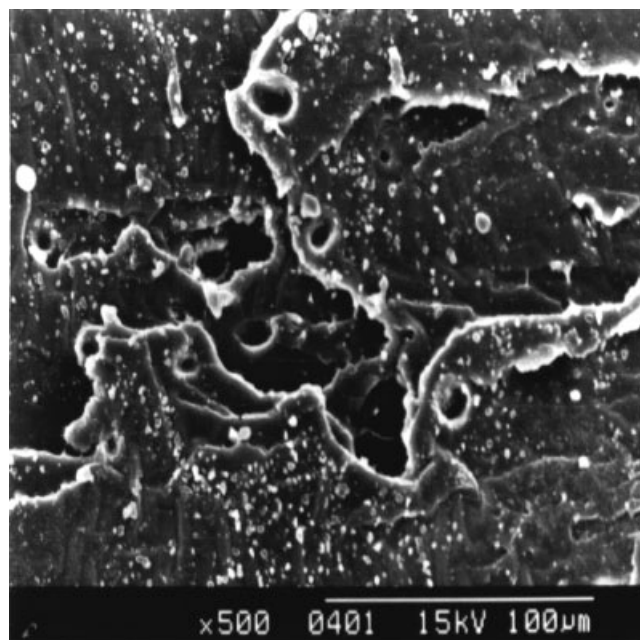


Figure 1 SEM photograph of the fractured tensile surfaces of the NBR vulcanizates containing Zn(bxt)₂/ZDC, molded at 150°C.

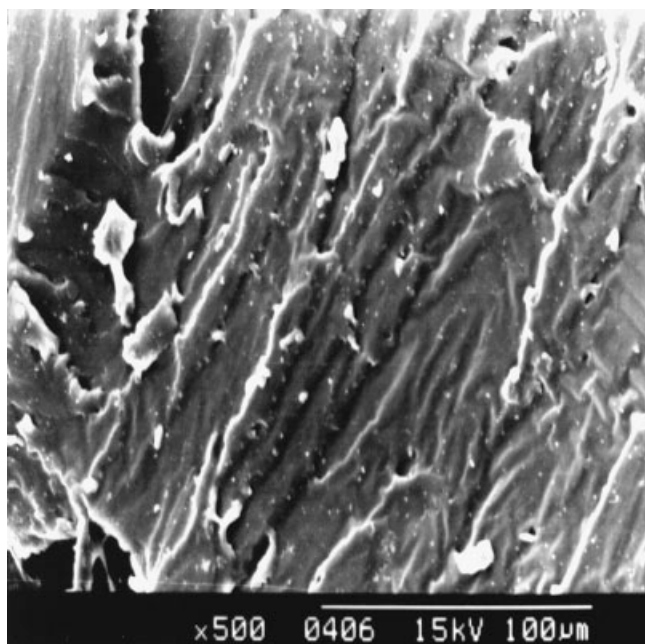


Figure 2 SEM photograph of the fractured tensile surfaces of the NBR vulcanizates containing $\text{Zn}(\text{bxt})_2/\text{ZDC}$, molded at 80°C .

of curing is changed from 150 to 60°C . Again, it is clear that, at a particular temperature the cure times of the NBR compounds containing the xanthate accelerators decreases in the following order: $\text{Zn}(\text{ext})_2/\text{ZDC} \rightarrow \text{Zn}(\text{ipxt})_2/\text{ZDC} \rightarrow \text{Zn}(\text{bxt})_2/\text{ZDC}$. This is due to the better solubility of the accelerator in NBR when the size of the alkyl group in the accelerator increases.

Table VI gives the tensile properties of the mixes A, B, and C given in Table IV. At all temperatures, the NBR compounds show considerable tensile properties. But, when the temperature of curing is changed from 150 to 60°C , tensile strength and tear strength increase and elongation at break decreases. This is because of the lesser degradation of rubber at lower temperatures. When silica is used as filler in rubber compounds, the hydroxy groups in silanols on the surface of silica can interact with basic accelerators. Xanthates are found to be basic with a pH of 10.6. Figures 1 and 2 show the SEM photographs of the tensile fracture surface of the NBR vulcanizates molded at 150 and 80°C , respectively. More tear marks are present in the vulcanizates molded at 80°C . From the nature of the stretch marks, it is clear that the polymer is existing in a high molecular state when it is vulcanized at a lower temperature, which clearly indicates that the degradation of rubber is prevented at low temperatures.

The crosslink densities of the mixes A, B, and C are also given in Table VI. Crosslink density increases as the temperature of curing is changed from 150 to 60°C . This may be due to the higher stability of the accelerator at lower temperatures. So more crosslinks

are formed at lower temperatures. Table VII gives the abrasion loss, flex resistance, heat buildup, and compression set at different temperatures. At all temperatures, NBR compounds show considerable mechanical properties. But when the temperature of curing is changed from 150 to 60°C , all the mechanical properties are found to be increased. This is due to the higher crosslinking at lower temperatures.

CONCLUSIONS

1. Zinc salts of xanthate/ZDC combination can be used to vulcanize silica-filled NBR compounds at temperatures varying from 60 to 150°C .
2. NBR compounds using MBTS/TMTD combination cures slowly compared to zinc salt of xanthate/ZDC combination at 150 and 125°C and below 125°C , MBTS/TMTD combination cannot cure NBR compounds.
3. As the temperature of vulcanization decreases from 150 to 60°C , all the mechanical properties of the NBR vulcanizate increased.
4. At a particular temperature, the cure time is minimum for the compound containing $\text{Zn}(\text{bxt})_2/\text{ZDC}$ compared to the other two combinations.

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