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Low Temperature Curing of NBR for Property Improvement

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ABSTRACT: Zinc salts of ethyl, isopropyl, and butyl xanthates are prepared in the laboratory, and the effect of these xanthates with zinc diethyl dithiocarbamate (ZDC) on the vulcanization of HAF-filled nitrile butadiene rubber (NBR) compounds has been studied at different temperatures. The cure times of these compounds have been compared with that of NBR compounds containing TMTD/MBTS. The rubber compounds with the three xanthate accelerators and ZDC are cured at various temperatures from 60 to 150°C. The sheets are molded and properties such as tensile strength, tear strength, cross-link density, elongation at break, compression set, abrasion resistance, flex resistance, etc. have been evaluated. The properties show that zinc salt of the xanthate/ZDC accelerator system has a positive synergistic effect on the cure rate and mechanical properties of NBR compounds.

KEY WORDS: low temperature curing, nitrile rubber, mechanical properties, xanthate accelerators, synergism.

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INTRODUCTION

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

Nitrile butadiene 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].

The NBR shows no self-reinforcing effect, as there is no crystallinity. So the unfilled vulcanizates have very low tensile strength [5] but when used in combination with reinforcing fillers, vulcanizates with excellent mechanical properties can be obtained from NBR [6]. The dynamic properties, which are important for applications like tires, are altered tremendously by the addition of carbon black [7]. There have been a number of studies on the reinforcement mechanism of fillers involving vulcanizates [8–11]. Studies on filled systems have also been reviewed by Kraus [12] and Voet [13]. It is generally agreed that strong links exist between rubber chains and reinforcing filler particles [14,15]. Zinc salt of xanthate/zinc diethyldithiocarbamate (ZDC) combination is found to produce a positive synergistic effect on the mechanical properties of HAF-filled NR compounds [16].

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

EXPERIMENTAL

Materials

The NBR having [acrylonitrile content–33%, Mooney viscosity (ML(1 + 4) at 100°C–40.9)] was supplied by Apar Polymers Pvt. Ltd., Gujarat. Compounding ingredients, i.e., zinc oxide, stearic acid, ZDC, dioctyl phthalate (DOP), carbon black (HAF N 330), vulcanox 40-20, HS, and sulfur were of commercial grade. Denatured spirit, isopropyl alcohol, *n*-butyl alcohol, potassium hydroxide, carbon disulfide, and toluene 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 as per the procedure described earlier [17]. HAF-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. In order 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 1 and the concentration of ZDC was changed from 1 to 1.75 phr as shown in Table 2. The cure characteristics of the mixes were determined using a Goettfert elastograph model 67.85 as per ASTM D1646 (1981) at 150°C. The minimum torque, maximum torque, scorch time, optimum cure time, and cure rate of the aforesaid mixes were determined.

Table 1. Formulation of mixes (in phr).

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

Table 2. Formulation of mixes (in phr).

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

The NBR was compounded on a (6 × 12″) mixing mill in a laboratory according to formulations given in Table 4. The optimum cure times of the compounds were determined. NBR compounds were molded in an electrically heated hydraulic press at various temperatures from 60 to 150°C up to their optimum cure times at a pressure of 200 kg/cm^2. Dumbbell-shaped tensile 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 crosshead speed of 500 mm/min according to ASTM D2240. Cross-link density values of the samples were determined by equilibrium swelling methods using chloroform as the solvent. The degree of cross-linking was calculated using the Florey–Rehner equation [18]. Abrasion resistance was tested using a DIN abrader according to DIN 53516. The flex resistance of the samples was determined by using a Wallace De Mattia flexing machine as per ASTM D340-57 T. Compression (for a set of 6.25 mm thick and 18 mm diameter samples) was determined by compressing to a constant deflection (25%) and kept for 22 h in an air oven at 70°C (ASTM D395-61, method B). The mechanical properties of NBR vulcanizate containing MBTS/TMTD cured at 150 and 125°C were determined.

RESULTS AND DISCUSSIONS

Table 5 shows the cure times of the mixes given in Table 4 at different temperatures. It is seen that at 150 and 125°C, the curing of the NBR compound containing MBTS/TMTD is slow compared to the corresponding compound containing ZDC/xanthate. Below 125°C, MBTS/TMTD combination cannot cure NBR.

Zinc alkyl xanthates and ZDC are ultrafast accelerators and both ensure low temperature vulcanization. It is known that ZDC contains very small amounts of thiuram, which can initiate the sulfur exchange reactions during vulcanization [19,20]. Xanthates are much more effective accelerators compared to dithiocarbomates because of the presence of the oxygen atom. The O–C_2H_5 bond in xanthates is more polar than the N–C_2H_5 bond in dithiocarbomates. When two ultraaccelerators are combined, a synergistic effect may appear. Minatoya and Aoe [21,22] explained the higher activity by the formation of either eutectic mixture or salt forming compounds having better solubility in rubber and greater chemical reactivity.

Table 3. Cure characteristics of the mixes given in Table 1 and Table 2.

Mix	Min torque (Nm)	Max torque (Nm)	Scorch time (min)	Optimum cure time (min)	Cure rate index (Nm/min)
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

Table 4. Formulation of mixes (in phr).

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
HAF N330	40	40	40	40
DOP	6.0	6.0	6.0	6.0
Vulcanox 40-20	1.0	1.0	1.0	1.0
HS	0.5	0.5	0.5	0.5
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

The cure characteristics given in Table 3 show that the maximum torque and cure rate index are maximum and the optimum cure time is minimum for compounds containing 1.25 phr ZDC and 1.75 phr xanthate. This compound requires ample scorch time if processing problems are to be avoided. So, 1.25 phr ZDC and 1.75 phr xanthate are taken as the optimum dosage for NBR compounds.

Table 5 shows that the optimum cure times of NBR compounds containing $Zn(ext)_2$/ZDC, $Zn(ipxt)_2$/ZDC, and $Zn(bxt)_2$/ZDC increases as the temperature of curing is changed from 150 to 60°C. Again, it is clear that at a particular temperature the cure times of

Table 5. Cure times of the mixes given in Table 4 (in min).

Temperature (°C)	A	B	C	D
150	3.1	2.5	1.91	1.78
125	9.8	6.7	5.7	4.9
100	No curing	17.1	15.6	14.1
80	No curing	45.1	40.2	36.56
60	No curing	72.6	69.38	67.58

Table 6. Mechanical properties of compound A given in Table 4.

Temperature (°C)	Tensile strength (N/mm^2)	Tear strength (N/mm)	E.B. (%)	Crosslink density ($g/mol/cm^3$)	Abrasion loss (cc/h)	Flex resistance (kcycles)	Compression set (%)
150°C	24.3	72.4	790	4.326×10^{-5}	5.162	79.2	22.36
125°C	22.6	69.9	792	4.125×10^{-5}	5.879	75.4	25.3

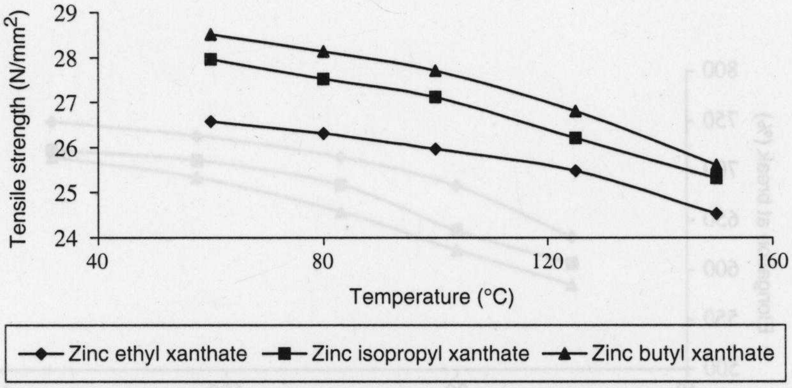

FIGURE 1. Effect of temperature on the tensile strength of compounds B, C, and D given in Table 4.

NBR compounds containing xanthate accelerators decrease in the following order:

$$\mathrm{Zn(ext)_2/ZDC} \rightarrow \mathrm{Zn(ipxt)_2/ZDC} \rightarrow \mathrm{Zn(bxt)_2/ZDC}.$$

Table 6 shows the mechanical properties of compound A cured at 150 and 125°C. Figures 1–3 show the tensile properties of mixes B, C,

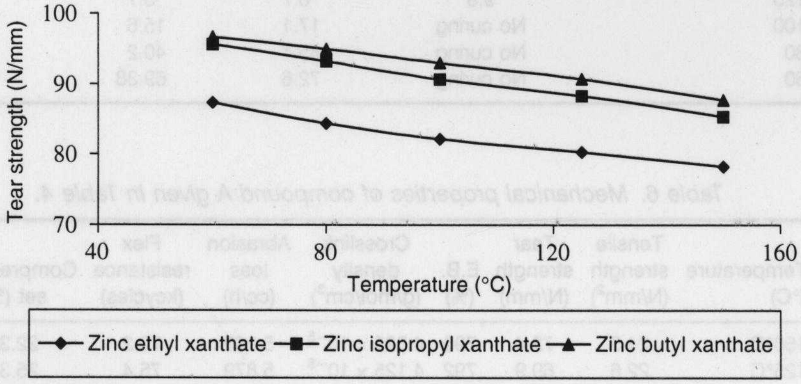

FIGURE 2. Effect of temperature on the tear strength of compounds B, C, and D given in Table 4.

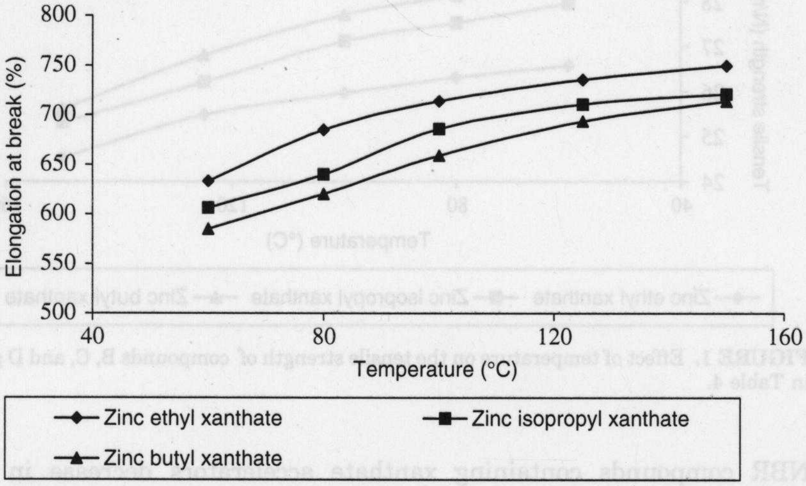

FIGURE 3. Effect of temperature on the elongation at break of compounds B, C, and D given in Table 4.

and D given in Table 4. At all the temperatures, NBR compounds show considerable tensile properties. At 150 and 125°C, tensile properties of the zinc xanthate/ZDC system are superior compared to those of the MBTS/TMTD cured system. When the temperature of curing is changed from 150 to 60°C, tensile and tear strengths increase and elongation at break decreases. This is because of the lesser degradation of rubber at lower temperatures. Figure 4 shows the cross-link density of mixes B, C,

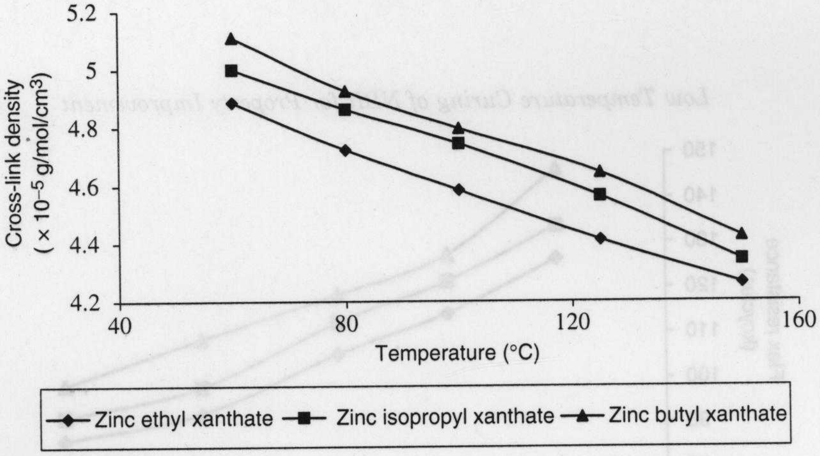

FIGURE 4. Effect of temperature on the cross-link density of compounds B, C, and D given in Table 4.

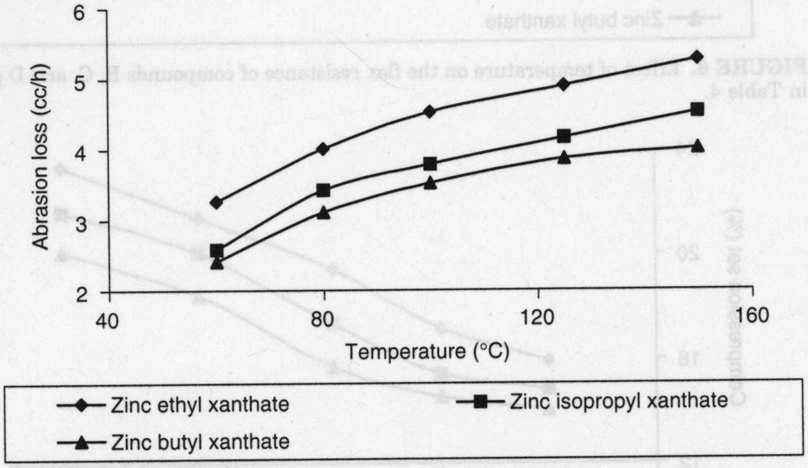

FIGURE 5. Effect of temperature on the abrasion loss of compounds B, C, and D given in Table 4.

and D. Cross-link 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. Figures 5–7 show the abrasion loss, flex resistance, and compression set respectively. At all the temperatures, the NBR compounds show considerable

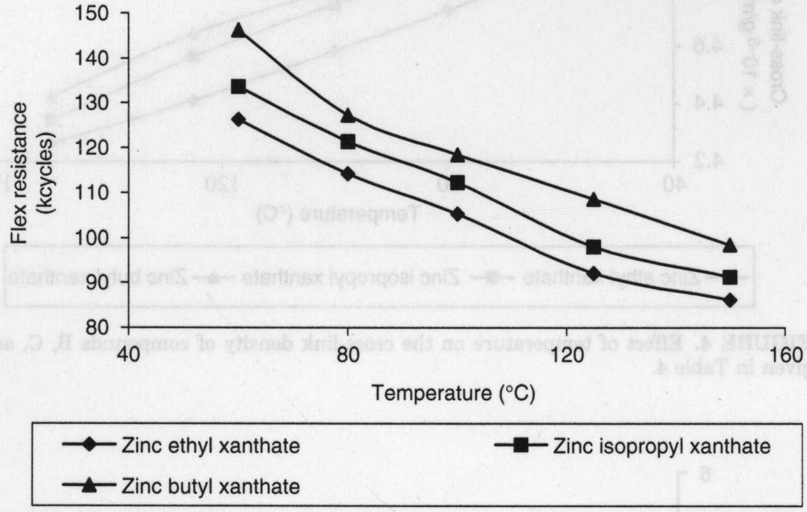

FIGURE 6. Effect of temperature on the flex resistance of compounds B, C, and D given in Table 4.

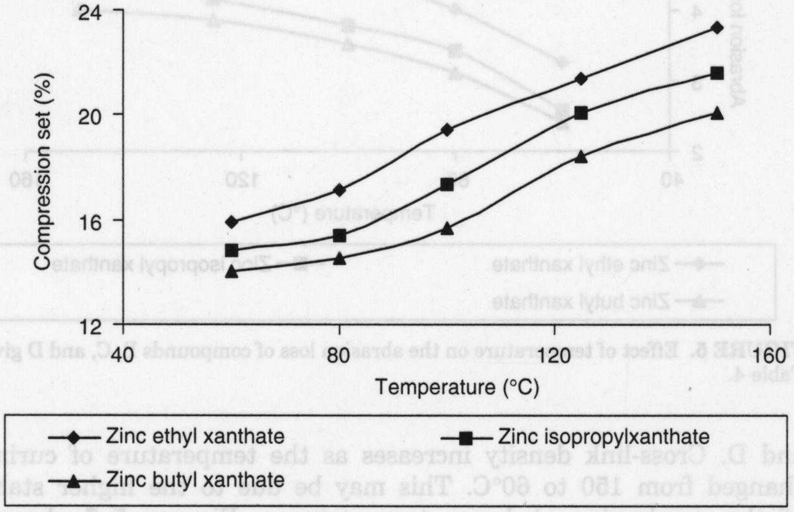

FIGURE 7. Effect of temperature on the compression set of compounds B, C, and D given in Table 4.

mechanical properties. These values are superior to those of compound A cured at 150 and 125°C. 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 cross-linking at lower temperatures.

CONCLUSIONS

Zinc salts of xanthate/ZDC combination can be used to vulcanize HAF filled NBR compounds at temperatures varying from 60 to 150°C. The nitrile butadiene rubber (NBR) compound using MBTS/TMTD combination cures slower compared to zinc salt of the xanthate/ZDC combination at 150 and 125°C. Below 125°C, MBTS/TMTD combination cannot cure NBR compounds. As the temperature of vulcanization decreases from 150 to 60°C, all the mechanical properties of NBR vulcanizate improve. At a particular temperature, the cure time is minimum for the compound containing $Zn(bxt)_2$/ZDC compared to the other two xanthates.

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