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Xanthate Accelerators for Low Temperature Curing of Natural Rubber

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ABSTRACT: Zinc salts of ethyl, isopropyl, and butyl xanthates were prepared in the laboratory. They were purified by reprecipitation and were characterized by IR, NMR, and thermogravimetric analysis techniques. The melting points were also determined. The rubber compounds with different xanthate accelerators were cured at temperatures from 30 to 150°C. The sheets were molded and properties such as tensile strength, tear strength, crosslink density, elongation at break, and modulus at 300% elongation were evaluated. The properties showed that all three xanthate accelerators are effective for room temperature curing. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1769–1775, 2000

Key words: natural rubber; low temperature curing; xanthate accelerators; mechanical properties; crosslink density

INTRODUCTION

Sulfur vulcanization of natural rubber (NR) has been studied by many researchers since the initial discovery of Charles Goodyear and Thomas Hancock. Today, sulfur still predominates over other vulcanizing agents (organic peroxides, polyfunctional coupling agents, etc.) because it gives the best vulcanizate properties for the least cost and with the greatest degree of control.[1] When accelerators are used in the vulcanization of NR, crosslinking precursors precede the formation of crosslinks.[2–4] The mechanical, elastic, and dynamic properties of the final products are influenced by the compound recipe, (including carbon black and fillers), the curing system, the reaction temperature, and the reaction time.[5] In 1906 the use of organic accelerators by Fritz Hoffman and colleagues reduced the vulcanization time, as well as the vulcanization temperature.[6] In ultraaccelerated compounds, smaller quantities of sulfur can be used to produce optimum physical properties in a shorter curing time than can be obtained with other classes of accelerators.[7] Low temperature curing can result in products of good quality and fine appearance.

Room temperature vulcanization of NR is feasible by highly reactive accelerators such as xanthate derivatives. A 1 : 1 mixture of a zinc(II) bis-(isopropylxanthate) [Zn(ipxt)$_2$] and bis-(pentamethylene dithiocarbamato)piperidine Zn(II) [Zn(pmtc)$_2$•(pip)] accelerator system can vulcanize rubber at room temperature.[8]

This article presents the results of a study on the use of xanthate accelerators for vulcanization of NR at various temperatures and the effect of the temperature of curing on the mechanical properties of the vulcanizates.

EXPERIMENTAL

Materials

The NR [ISNR-5, Mooney viscosity ML (1 + 4) 100°C value of 82] was supplied by the Rubber

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Table I NR Formulations

Mix	A	B	C	D	E	F
NR	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
HAF N330	—	—	—	25	25	25
Aromatic oil	—	—	—	3	3	3
Butyl xanthate	2.5	—	—	2.5	—	—
Isopropyl xanthate	—	2.5	—	—	2.5	—
Ethyl xanthate	—	—	2.5	—	—	2.5
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5

Research Institute of India (Kottayam). The compounding ingredients [i.e., zinc oxide, stearic acid, aromatic oil, and carbon black (HAF N330)] were commercial grade. The *n*-butyl alcohol, isopropyl alcohol, denatured spirits, potassium hydroxide, carbon disulfide, and zinc chloride were reagent grade and were used as supplied.

Preparation

Potassium ethyl, potassium isopropyl, and potassium butyl xanthates were prepared in the laboratory by mixing equimolar amounts of the corresponding alcohol, potassium hydroxide, and carbon disulfide. These xanthates were then precipitated as their zinc salts by adding zinc chloride solution. They were purified by reprecipitation using methanol as the solvent.

Analysis of Xanthates

Analysis of the zinc salts of xanthates were carried out by using IR spectroscopy, proton magnetic resonance spectroscopy (^{1}H-NMR), and thermogravimetric analysis (TGA). IR spectra of the samples were taken on a Perkin–Elmer model 377 IR spectrometer. The proton NMR spectra of the samples were recorded from a solution of $CDCl_3$ using a dpx300 model spectrometer. The TGA was carried out using a V5. IA Du Pont 2000 model in air.

The melting points of the xanthates were also determined using capillary melting point apparatus.

In order to optimize the amount of accelerator for vulcanization, the concentrations of the xanthates were varied from 0.5 to 2.5 phr.

The NR was compounded on a 6 × 12 in. laboratory mixing mill according to the formulations given in Table I.

The gum compounds and the carbon black filled compound were prepared. The optimum cure times (time to reach 90% of the maximum torque) of the compounds were determined on a Göttfert elastograph (model 67.85) per ASTM D-1646 (1981).

The rubber compounds were molded in an electrically heated laboratory hydraulic press at tem-

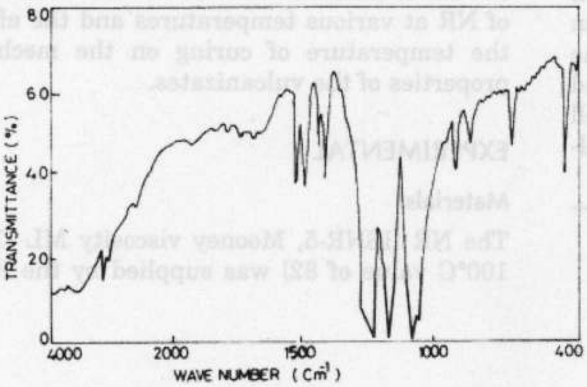


Figure 1 An IR spectrum of zinc ethyl xanthate.

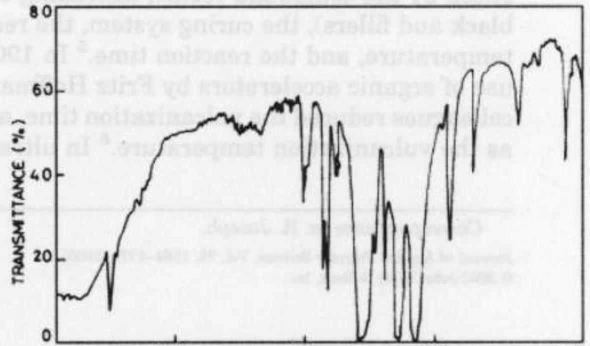


Figure 2 An IR spectrum of zinc isopropyl xanthate.

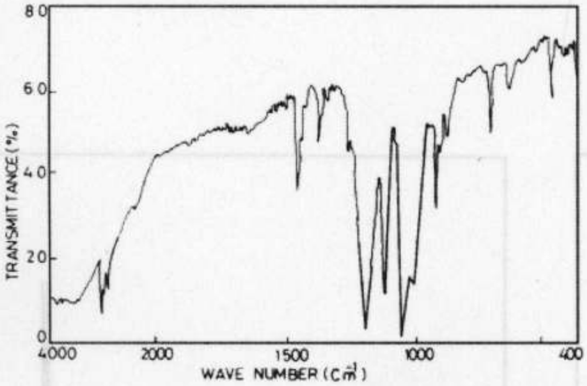


Figure 3 An IR spectrum of zinc butyl xanthate.

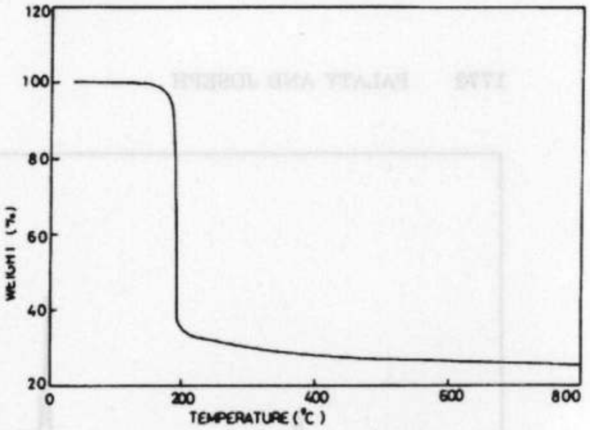
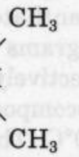


Figure 5 A thermogram of zinc isopropyl xanthate.

peratures from 30 to 150°C up to their optimum cure times at a pressure of 200 kg/cm^2. Dumbbell shaped tensile test pieces was 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 (model 1445) using a crosshead speed of 500 mm/min according to ASTM D-2240. The crosslink density of the samples was determined by the equilibrium swelling method using toluene as the solvent. The swelling ratio was corrected for the nonnetwork ingredients. The degree of crosslinking was calculated by using the Florey–Rehner equation.[9]

RESULTS AND DISCUSSION

Figures 1–3 show the IR spectra of zinc ethyl xanthate [$Zn(ext)_2$], zinc isopropyl xanthate [$Zn(ipxt)_2$], and zinc butyl xanthate [$Zn(bxt)_2$], respectively.

The IR spectrum of $Zn(ext)_2$ shows sharp peaks at 1385.1 cm^{-1}, corresponding to —C═S stretching, at 868.1 cm^{-1} corresponding to C—C stretching in *n*-alkanes, and at 657.8 cm^{-1} corresponding to C—S stretching. The IR spectrum of $Zn(ipxt)_2$ shows peaks at 1385.1 cm^{-1} corresponding to —C═S stretching, at 1371 cm^{-1} due to the  $-\mathrm{CH}\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}$ group, and at 652 cm^{-1} due to C—S stretching. The IR spectrum of $Zn(bxt)_2$ shows sharp peaks at 1385.1 cm^{-1} corresponding to —C═S stretching, at 902.8 cm^{-1} corresponding to C—C stretching

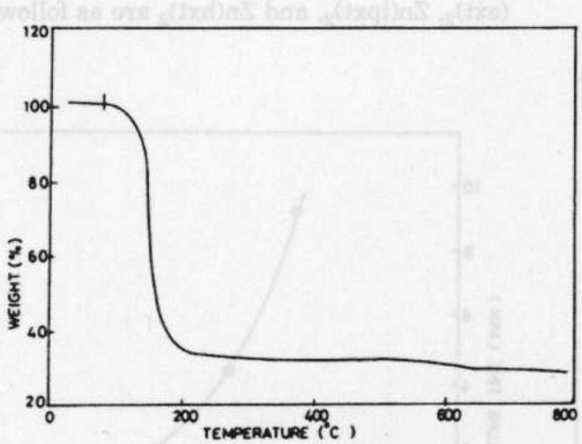


Figure 4 A thermogram of zinc ethyl xanthate.

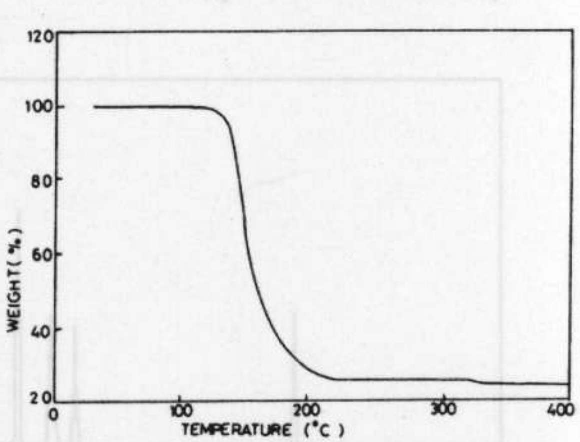


Figure 6 A thermogram of zinc butyl xanthate.

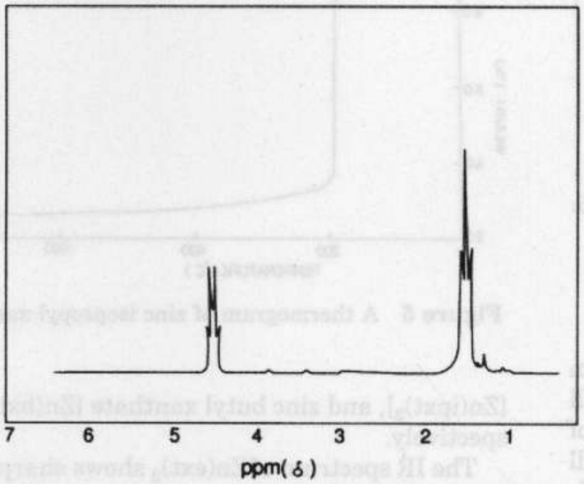


Figure 7 An H-NMR spectrum of zinc ethyl xanthate.

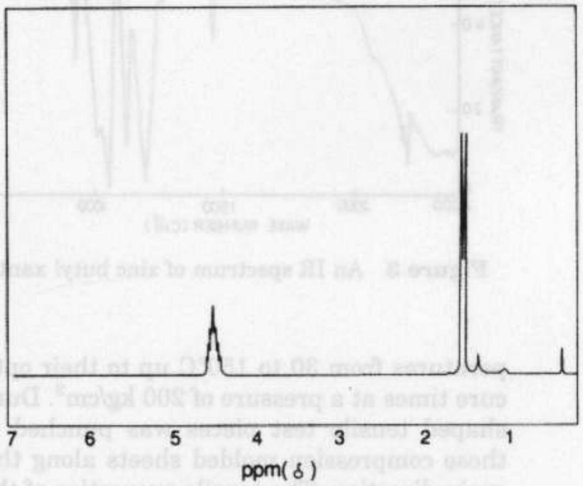


Figure 8 An H-NMR spectrum of zinc isopropyl xanthate.

in *n*-alkanes, and at 663.6 cm $^{-1}$ corresponding to C—S stretching. These show the presence of C═S and C—S bonds in all three xanthates.[10]

Figures 4–6 show thermograms of $Zn(ext)_2$, $Zn(ipxt)_2$, and $Zn(bxt)_2$, respectively. From the figures it is clear that the decomposition of the xanthates starts at about 150°C. The change in the weight percentages suggests that the xanthates finally decompose to zinc oxide.[11]

Figures 7–9 show the ^{1}H-NMR spectra of $Zn(ext)_2$, $Zn(ipxt)_2$, and $Zn(bxt)_2$, respectively.

There is a triplet at $\delta = 1.6$ (CH_3) and a quartet at $\delta = 4.5$ (CH_2), which shows the presence of the $—CH_2—CH_3$ group in ethyl xanthate. Figure 8 shows the ^{1}H-NMR spectrum of isopropyl xanthate. There is a six proton doublet (upfield) and a one proton septet (downfield), which shows the presence of a $C^{CH_3}_{CH_3}$ group in isopropyl xanthate. Figure 9 shows the ^{1}H-NMR spectrum of butyl xanthate. There is a three proton triplet at $\delta = 1$, a two proton sextet at $\delta = 1.5$, a two proton pentet at $\delta = 2$, and a two proton triplet at $\delta = 4.5$ that show the presence of the $CH_3—CH_2—CH_2—CH_2—$ group in butyl xanthate.[12]

From the above data, the structures of $Zn(ext)_2$, $Zn(ipxt)_2$, and $Zn(bxt)_2$ are as follows:

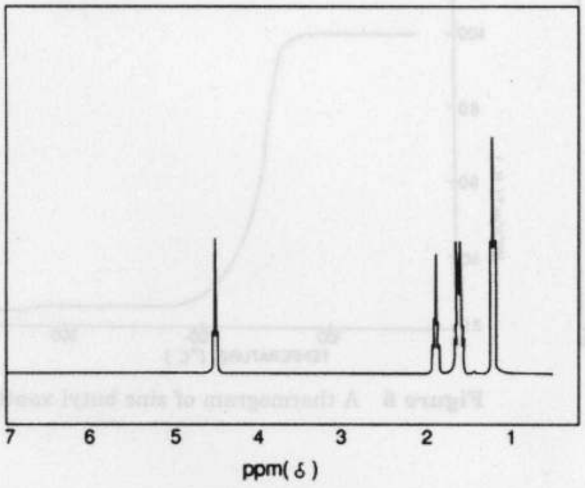


Figure 9 An H-NMR spectrum of zinc butyl xanthate.

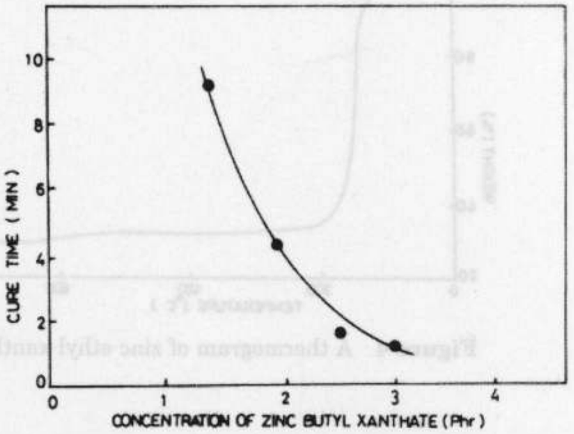
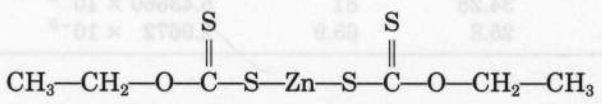


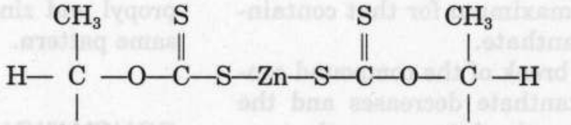
Figure 10 The variation of cure time of the NR compound with the concentration of zinc butyl xanthate.

Table II Properties of NR Compound with Zn(ext)$_2$

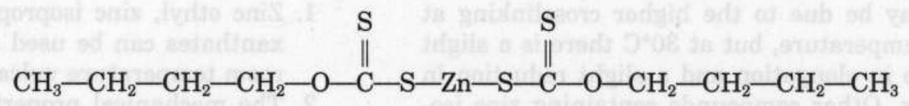
Temp. (°C)	Cure Time	Tensile Strength (N/mm^2)	Tear Strength (N/mm)	Crosslink Density (g/mol/mL)	Elongation at Break (%)	Modulus at 300% Elongation (N/mm^2)
Gum Compound						
150	0.76 min	10.63	27.01	1.2940×10^{-5}	750	4.06
100	5.00 min	20.90	56.23	3.26401×10^{-5}	673	6.38
80	21.2 min	23.12	62.62	4.48206×10^{-5}	647	7.88
60	50.1 min	24.72	68.6	5.62462×10^{-5}	533	8.24
30	18 h	21.00	55.2	3.18015×10^{-5}	651	4.68
Black Filled Compound						
150	0.92 min	12.8	29.32	0.082416×10^{-5}	702	2.60
100	7.48 min	24.26	58.1	2.05253×10^{-5}	639	6.78
80	25.6 min	29.72	69.2	3.6450×10^{-5}	528	7.37
60	53.1 min	30.6	75.6	4.51624×10^{-5}	483	7.84
30	18 h	24.43	59.01	1.96154×10^{-5}	625	6.75



$$CH_3{-}CH_2{-}O{-}\overset{\overset{S}{\parallel}}{C}{-}S{-}Zn{-}S{-}\overset{\overset{S}{\parallel}}{C}{-}O{-}CH_2{-}CH_3$$



$$H{-}\underset{\underset{CH_3}{|}}{\overset{CH_3}{C}}{-}O{-}\overset{\overset{S}{\parallel}}{C}{-}S{-}Zn{-}S{-}\overset{\overset{S}{\parallel}}{C}{-}O{-}\underset{\underset{CH_3}{|}}{\overset{CH_3}{C}}{-}H$$



$$CH_3{-}CH_2{-}CH_2{-}CH_2{-}O{-}\overset{\overset{S}{\parallel}}{C}{-}S{-}Zn{-}S{-}\overset{\overset{S}{\parallel}}{C}{-}O{-}CH_2{-}CH_2{-}CH_2{-}CH_3$$

The melting points of Zn(ext)$_2$, Zn(ipxt)$_2$, and Zn(bxt)$_2$ were found to be 120, 148, and 107°C, respectively.

Figure 10 shows the variation in cure time of the NR compounds with the change in the amount of butyl xanthate at 150°C. At concentrations of 0.5, 1.0, and 1.5 the compound does not undergo curing, even after 1 h. At 2 phr there is curing, but there is a good reduction in the cure time when the concentration of zinc butyl xanthate is increased to 2.5 phr.

Table II shows the cure time, tensile strength, tear strength, crosslink density, elongation at break, and 300% modulus of the NR compound containing zinc ethyl xanthate cured at different temperatures.

Tables III and IV shows the properties of the NR compounds containing zinc isopropyl xanthate and zinc butyl xanthate, respectively.

The above results show that the xanthate accelerators can bring about vulcanization, even at room temperature. But at 150°C the properties are very low. This may be due to the decomposition of the xanthates at high temperature. The properties are found to increase with a decrease in temperature and are maximum at 60°C. Again, it is clear that at a particular temperature the cure time is maximum for zinc isopropyl xanthate and minimum for zinc ethyl xanthate; the cure times of zinc butyl xanthate lie in between. But the tensile properties are minimum for the vulcanizate containing zinc

Table III Properties of NR Compound with $Zn(ipxt)_2$

Temp. (°C)	Cure Time	Tensile Strength (N/mm^2)	Tear Strength (N/mm)	Crosslink Density (g/mol/mL)	Elongation at Break (%)	Modulus at 300% Elongation (N/mm^2)
			Gum Compound			
150	0.9 min	12.82	31.2	2.70479×10^{-5}	671	5.07
100	9.24 min	24	59.7	5.83714×10^{-5}	635	6.66
80	24.2 min	26.3	68.8	6.40959×10^{-5}	541	9.20
60	54 min	28	78.47	6.80493×10^{-5}	471	9.68
30	18 h	23.1	58.9	5.45332×10^{-5}	661	6.20
			Black Filled Compound			
150	1.32 min	15.2	36.89	1.76943×10^{-5}	651	4.63
100	10.08 min	26.2	67.9	3.29875×10^{-5}	583	7.08
80	27.1 min	32	78.2	4.9002×10^{-5}	512	9.99
60	56.2 min	34.28	81	5.43660×10^{-5}	448	10.58
30	18 h	25.8	65.9	2.9672×10^{-5}	548	6.99

ethyl xanthate and maximum for that containing zinc isopropyl xanthate.

The elongation at break of the compound containing zinc ethyl xanthate decreases and the modulus at 300% elongation increases as the temperature of curing is changed from 150 to 60°C. This may be due to the higher crosslinking at lower temperature, but at 30°C there is a slight increase in elongation and a slight reduction in modulus. Other compounds containing zinc isopropyl and zinc butyl xanthates also follow the same pattern.

CONCLUSIONS

1. Zinc ethyl, zinc isopropyl, and zinc butyl xanthates can be used as accelerators for room temperature vulcanization of NR.
2. The mechanical properties are maximum

Table IV Properties of NR Compound with $Zn(bxt)_2$

Temp. (°C)	Cure Time	Tensile Strength (N/mm^2)	Tear Strength (N/mm)	Crosslink Density (g/mol/mL)	Elongation at Break (%)	Modulus at 300% Elongation (N/mm^2)
			Gum Compound			
150	0.84 min	12.01	29.3	1.62326×10^{-5}	695	4.02
100	7.24 min	21.3	58.67	4.64182×10^{-5}	645	6.76
80	23.9 min	25.00	65.86	5.26324×10^{-5}	585	8.08
60	52.9 min	26.7	74.38	6.13245×10^{-5}	496	9.72
30	18 h	21.32	57.10	4.43261×10^{-5}	598	7.01
			Black Filled Compound			
150	1.16 min	14.7	34.32	1.13246×10^{-5}	670	3.95
100	8.84 min	25.68	61.00	2.32162×10^{-5}	635	6.98
80	26.8 min	31.00	73.86	3.8008×10^{-5}	521	8.36
60	54.2 min	32.01	79.10	5.1002×10^{-5}	461	9.88
30	18 h	24.1	61.26	2.2306×10^{-5}	562	6.75

when the temperature of vulcanization is 60°C.

3. The vulcanizate containing zinc isopropyl xanthate shows maximum tensile properties compared to zinc ethyl and zinc butyl xanthates.

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