Use of Sodium and Potassium Butyl Xanthate as Accelerator for Room Temperature Prevulcanization of Natural Rubber Latex

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ABSTRACT: Sodium and potassium butyl xanthates (Nabxt and Kbxt) were prepared in the laboratory. Characterization of these xanthates were done using Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (¹H NMR) spectroscopy, thermogravimetric analysis (TGA), and differential thermal analysis (DTA) techniques. These xanthates were used as accelerators for the prevulcanization of natural rubber latex (NRL) at room temperature. Optimization of prevulcanization time was done. Films were casted from these prevulcanized NRL. Tensile properties of latex vulcanisates were measured

INTRODUCTION

Xanthates are derivative of xanthic acids. They are prepared by the reaction of carbon disulphide (CS_2) with alcohols in the presence of alkali.¹ They can be prepared as their zinc, sodium, and potassium salts. Sodium and potassium butyl xanthates are used as two strong collectors in bulk flotation of various nonferrous metallic sulfide ores. They are mainly used in floting Cu, Pb, Zn etc sulfide ores, especially fit for the flotation of chalcopyrite, sphalerite, and pyrite. Under proper conditions, they can also be used in the selective flotation of copper sulfide minerals from iron sulfide minerals and in the flotation of sphalerite after activation with CuSO₄. They are also used as precipitant in the metallurgical industry. The strength of xanthate as a collector is based on the alcohol chain attached to the xanthate molecule, with ethyl being the weakest and amyl being the strongest. Potassium ethyl xanthate is very selective in nature and potassium N-amyl xanthate is a non selective collector. Potassium xanthates can also be used for the spectroscopic determination of metals. Platinum (IV) can be spectroscopically deterand potassium butyl xanthate gave superior properties to the NRL films compared with sodium butyl xanthate. Effect of thermal ageing on tensile properties of these prevulcanized NRL films was also investigated and these properties were found to be improved after thermal ageing. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 1325–1332, 2011

Key words: sodium butyl xanthate; potassium butyl xanthate; prevulcanization; natural rubber latex; tensile properties

mined using potassium butyl xanthate and iron (II) using potassium isobutyl xanthate.^{2,3}

In rubber industry, xanthates are used as vulcanization accelerators. Sodium and potassium xanthates being water soluble used in latex compounds while their zinc salts being water insoluble are used in dry rubber compounds. Zinc alkyl xanthates are known to be effective for the low temperature vulcanization of dry NR and NBR compounds.4-7 Xanthate can also be used for the room temperature prevulcanization of natural rubber latex (NRL).8 At present, sulfur prevulcanization of natural rubber latex is done by heating the compounded latex for 2-3 h at high temperature (55-60°C) using zinc diethyl dithiocarbamate (ZDC) alone as accelerator, which affects its colloidal stability. But room temperature prevulcanized NRL has many advantages including high colloidal stability, needs less sophisticated equipments and thus simplify the process, use of less thermal stable reinforcements and additives, eliminates the chance of premature vulcanization and scorching and saves a large amount of energy. Energy saving decreases pollution and thus enhancing the environment and decreases the production cost.

This article reports the details of preparation and characterization of sodium and potassium butyl xanthate. It also presents the use of these xanthates in combination with ZDC as accelerator systems for the room temperature prevulcanization of NRL.

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Figure 1 FTIR spectrum of sodium butyl xanthate.

EXPERIMENTAL

Equipments used

The equipments used in this study include Thermo Nicolet Avtar 370 FTIR Spectrometer using KBr pellet technique in the wave length range 400–4000 cm⁻¹, Bruker-Avence 400MHz Spectrometer, Perkin-Elmer TGA Q50 (TA), Universal Testing Machine Model 4411 (M/s Instron, Buckinghamshire, UK).

Materials used

Potassium hydroxide (KOH), sodium hydroxide (NaOH), *n*-butyl alcohol, and CS₂ (supplied by E. Merck, Mumbai, India) used for the preparation of sodium and potassium butyl xanthates and toluene used for swelling measurements were analytical grade. The compounding ingredients such as ZDC, zinc oxide (ZnO), sulfur (S), and dispersol F (M/s Standard Chemicals Co., Chennai, India) were commercial grade. High ammonia (HA) centrifuged NRL conforming to the specification BIS 5430-1981 was purchased from Njavallil Rubber Latex, Cochin, India and was used for the prevulcanization.

Experimental procedure

Sodium and potassium butyl xanthates were prepared by reacting equimolar amounts of *n*-butyl alcohol with CS₂ and corresponding alkali, such as NaOH or KOH. The prepared xanthates were characterized using Fourier transform infrared (FTIR) and nuclear magnetic resonance (¹H NMR) spectroscopic techniques. Thermal decomposition behavior of these xanthates was studied using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) techniques. FTIR spectrum was recorded using Thermo Nicolet Avtar 370 FTIR spectrometer using KBr pellet technique in the wave length range 400–4000 cm⁻¹. The results were reported in Figures 1 and 5. The ¹H NMR spectra of



Figure 2 ¹H NMR spectrum of sodium butyl xanthate.

sodium and potassium butyl xanthates were measured in deuterated water (D_2O) containing tetra methyl silane as an internal standard using Bruker-Avence 400 MHz Spectrometer. The results are reported in Figures 2 and 6.

The TGA was carried out in the temperature range of 30–900°C at a heating rate of 10°C per minute in an atmosphere of nitrogen using Perkin–Elmer TGA Q50 (TA). Sample weight is between 5 and 10 mg. The TGA curves are given in Figures 3 and 7. DTA curves show parallel peaks corresponding to weight losses in the TGA curves and Figures 4 and 8 represents the DTA curves of Nabxt and Kbxt, respectively. Nabxt and Kbxt in combination with ZDC were used as accelerator systems for the room temperature prevulcanization of NRL.

Fifty percent dispersions of the vulcanizing agents were prepared using the required amount of vulcanizing agents and distilled water by grinding in a ball mill under standard conditions. Dispersol F was used as the dispersing agent during ball milling to prevent the dispersed particles from reaggregation. Chemically, it



Figure 3 TGA curve of sodium butyl xanthate.



Figure 4 DTA curve of sodium butyl xanthate.

is sodium naphthalene formaldehyde sulfonate. NRL was deammoniated to 0.2% before compounding to avoid ZnO thickening. NRL was compounded as per the formulations given in Table I.

After compounding, the latex mixes were kept for maturation at room temperature for 3 h with occasional stirring. Latex films of thickness 1 mm were prepared by casting approximately 50 g of sieved compounded latex onto glass plates (15×15 cm) according to ASTM D 1076-88 and air-dried at room temperature. Equilibrium swelling index, apparent cross-link density and chemical cross-link density measurements of the latex films were done at an interval of one day for 9 days to determine the optimum time for prevulcanization. The tensile properties of these latex films were measured after optimum prevulcanization.

Equilibrium swelling experiments

Accurately weighed samples (0.1 g) which were die-cut from latex vulcanisates were immersed in toluene (20–30 mL) in stoppered bottles at room temperature for 24 h. At the end of the period, surface solvent was removed with filter paper and the sample weighed in stoppered weighing bottle. Toluene was removed by drying at room temperature, for a period not less than 3 days to a constant weight.

The equilibrium swell index was calculated as

Swell index(Q) =
$$\frac{W_2 - W_1}{W_1}$$

where W_1 is the initial weight and W_2 is the swollen weight. The value of Q gives an idea about crosslink density. Q > 15, unvulcanized state; Q = 7-15, lightly vulcanized state; Q = 5-7, moderately vulcanized state; Q < 5, fully vulcanized state. The results are given in Figure 9. The reciprocal of swell index (1/Q) was reported as the apparent cross-link density in Figure 10. The volume fraction of rubber (V_r) in the swollen vulcanisate was calculated by the method reported by Ellis and Welding from the following equation⁹

$$V_r = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_0\rho_s^{-1}}$$

where D = weight of the deswollen test specimen, F = weight fraction of insoluble components, T = weight of the test specimen, A_0 = weight of the absorbed solvent corrected for the swelling increment, ρ_r = density of the rubber; for NR, ρ_r = 0.92 g cm⁻³, ρ_s = density of the solvent; for toluene, ρ_s = 0.886 g cm⁻³

Knowing the value of V_r , the cross-link density $[1/2M_c]$, which represents the moles of cross-linked basic units per weight unit of the cross-linked polymer was calculated using Flory-Rehner equation.¹⁰

$$\frac{1}{2M_c} = \frac{-[\ln(1-V_r) + V_r + \chi V_r^2]}{2\rho_r V_s (V_r)^{1/3}}$$

where $\chi =$ interaction parameter; characteristic of the interaction between rubber and solvent; for NRtoluene, $\chi = 0.42$, $V_s =$ molar volume of solvent; V_s = 106.2 cm³ mol⁻¹ for toluene, M_c = number average molecular weight of the chains between crosslinks. It indicates the degree of cross-linking. The cross-linked polymers only swell in a nonreactive solvent and do not dissolve in a nonreactive solvent. Thus the degree of swelling in a nonreactive solvent determines the degree of cross-linking and the molecular weight between cross-links. The higher the value of M_{cr} lower the cross-link density. The results are given in Figure 11.

Dumb bell shaped tensile specimens were punched out of the casted films. Stress–strain measurements were carried out at a cross-head speed of 500 mm/min on a Universal Testing Machine, model 4411. Tensile strength was measured according to ASTM D 412-87 (method A). All these tests

TABLE I Formulation of Latex Mixes

Ingredients	Parts by weight (g)	
	А	В
NR latex	167	167
10% KOH	2.5	2.5
10% Potassium oleate	1.0	1.0
10% Vulcastabe VL	1.0	1.0
50% S	2.5	2.5
50% ZDC	1.0	1.0
50% ZnO	1.0	1.0
50% Kbxt	1.5	-
50% Nabxt	_	1.5

TABLE II Tensile Properties of Prevulcanized NRL films

Tensile properties	А	В
Tensile strength, MPa	20.19	17.02
Modulus (100%), MPa	0.61	0.59
Modulus (200%), MPa	0.90	0.89
Modulus (300%), MPa	1.16	1.13
Elongation at break (%)	1347.93	1356.07

were conducted at ambient temperature and an average value of five repeated tests was taken for each sample. The results are reported in Table II. Effect of thermal ageing at 70°C for 24 h on cross-link density and tensile properties of prevulcanized latex films were studied as per ASTM D 865-88 and are reported in Table III. The cross-link density change was calculated by dividing the difference in the cross-link den-

$$H_3C-CH_2-CH_2-CH_2-OH + KOH + CS_2$$

n-Butanol

$$H_3C-CH_2-CH_2-CH_2-OH + NaOH + CS_2$$

n-Butanol

Figure 1 shows the FTIR spectrum of sodium butyl xanthate. The peaks at 2959.84 cm⁻¹ and 2874.52 cm⁻¹ correspond to asymmetric and symmetric stretching of C—H bond in terminal CH₃ group, the peaks at 1462.00 cm⁻¹ and 1380.04 cm⁻¹ correspond to asymmetric and symmetric deformation of C—H bond in CH₃ group. The peak at 897.20 cm⁻¹ corresponds to C—C stretching in *n*-alkanes. The peaks at 1230.00 cm⁻¹ and 1048.16 cm⁻¹ correspond to asymmetric and symmetric C—O—C stretching vibrations. The peaks at 1109.60 cm⁻¹ and 650.00 cm⁻¹ correspond to —C=S and —C—S stretching vibrations.

Figure 2 shows the ¹H NMR spectrum of Nabxt. There is a three proton triplet at $\delta = 0.8$, a two proton sextet at $\delta = 1.3$, a two proton pentet at $\delta = 1.6$ and a two proton triplet at $\delta = 4.3$ showing the presence of CH₃—CH₂—CH₂—CH₂ group in Nabxt.

Figure 3 shows the TGA curve of sodium butyl xanthate. The decomposition of Nabxt occurs $>30^{\circ}$ C and it involves different steps. The intermediate compounds of decomposition have only transient existence. One of the intermediate compounds, corresponding to the weight loss of 47% was H₂SO₃. The net weight loss is about 80%, indicating the formation of H₂S as final decomposition product. The DTA curve recorded for 8.126 mg of Nabxt given in Figure 4 shows parallel peaks corresponding to

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sities of the vulcanisates after and before the thermal ageing by the initial cross-link density.

$$\Delta X_c(\%) = (X_c^{\text{aged}} - X_c^{\text{ini}}) / X_c^{\text{ini}} \times 100$$

where X_c^{aged} and X_c^{ini} indicate the cross-link densities of the vulcanisates after and before the thermal ageing, respectively, and the values are reported in Table III. The FTIR spectra of films prepared from room temperature prevulcanized NRL using Nabxt and Kbxt were given in Figures 12 and 13.

RESULTS AND DISCUSSION

The preparation of potassium and sodium butyl xanthate takes place according to the following equations.

-S-K



+
$$CS_2 \longrightarrow H_3C-CH_2-CH_2-CH_2-O-C-S-Na$$

Sodium butyl xanthate

 $H_3C - CH_2 - CH_2 - CH_2 - O - CH_2$

weight losses in TGA curves. The curve shows an endothermic peak at 238° C corresponding to the decomposition of Nabxt to H₂S. The concomitant oxidation reaction which occurs along with decomposition reaction results in exothermic peak in DTA curves.

Figure 5 shows the FTIR spectrum of potassium butyl xanthate. The peaks at 2960.09 cm⁻¹ and 2873.46 cm⁻¹ corresponds to asymmetric and symmetric stretching of C—H bond in terminal CH₃ group, the peaks at 1462.43 cm⁻¹ and 1380.52 cm⁻¹ correspond to asymmetric and symmetric deformation of C—H bond in CH₃ group. The peak at 896.38 cm⁻¹ corresponds to C—C stretching in *n*-alkanes. The peaks at 1233.60 cm⁻¹ and 1047.90 cm⁻¹

 TABLE III

 Effect of Thermal Ageing at 70°C for 24 h on Properties

Properties	А	В
Swell index	3.9	4.2
Apparent crosslink density	0.256	0.238
Chemical crosslink	$5.03 imes 10^{-5}$	4.69×10^{-5}
density (g/mol/cm ³)		
Tensile strength (MPa)	26.76	24.44
Modulus (100%), MPa	0.68	0.67
Modulus (200%), MPa	1.01	0.99
Modulus(300%), MPa	1.32	1.30
Elongation at break (%)	1496	1595
Cross-link density change (%)	24.19	22.13



Figure 5 FTIR spectrum of potassium butyl xanthate.

correspond to asymmetric and symmetric C–O–C stretching vibrations. The peaks at 1109.06 cm⁻¹ and 650.00 cm⁻¹ correspond to –C=S and –C–S stretching vibrations.

Figure 6 shows the ¹H NMR spectrum of Kbxt. There is a three proton triplet at $\delta = 0.8$, a two proton sextet at $\delta = 1.3$, a two proton pentet at $\delta = 1.6$ and a two proton triplet at $\delta = 4.3$ showing the presence of CH₃—CH₂—CH₂—CH₂ group in Kbxt.

Figure 7 shows the thermogram of potassium butyl xanthate. The first stage of decomposition occurs >30°C and terminates at about 50°C. The net weight loss of about 44% corresponds to decomposition of potassium butyl xanthate to H₂SO₃. The second stage of decomposition sets in the sample at about 225°C and is completed at 255°C. The net weight loss is about 80%, resulting in the formation of H₂S. Figure 8 illustrates the DTA curve recorded for 6.672 mg of Kbxt. The curve shows an endothermic peak at about 80°C corresponding to the decomposition of Kbxt to H₂SO₃. The thermal decomposition reactions are usually endothermic.



Figure 7 TGA curve of potassium butyl xanthate.

Another endothermic peak at 225° C corresponds to the decomposition of Kbxt to H₂S.

Figure 9 shows the variation of swell index with prevulcanization time for NRL films prepared from latex compounds A and B. Swell index is a measure of the degree of cross-linking. As cross-linking increases value of swell index decreases. Thus, the extends to which sample swells is an inverse measure of cross-link formation. As prevulcanization time increases swell index decreases which indicate a corresponding increase in cross-linking of rubber molecules with prevulcanization time. Films prepared from compound A and B shows a swell index value of 6.5 and 7 respectively, even after first day of prevulcanization which corresponds to moderately vulcanized state. For compound A and B, after 7 days swell index value decreases to below 5 which correspond to fully vulcanized state. Thus Kbxt/ ZDC and Nabxt/ZDC accelerator combination can bring about prevulcanization of NRL at room temperature and it takes 7 days for optimum prevulcanization. On each day swell index value of films prepared from compound A is slightly lower than that prepared from compound B which shows



Figure 6 ¹H NMR spectrum of potassium butyl xanthate.



Figure 8 DTA curve of potassium butyl xanthate.

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Figure 9 Variation of swell index with prevulcanization time.

that the cross-linking occurs slightly faster in the case of Kbxt/ZDC system compared with Nabxt/ZDC system.

Both apparent cross-link density and chemical cross-link density values of NRL films prepared from compound A and compound B, reported in Figures 10 and 11, respectively, show a steady increase with prevulcanization time. This is also due to the increase in cross-linking between rubber molecules with increase in prevulcanization time. Here also increase in both apparent and chemical cross-link density values with prevulcanization time of



Figure 10 Variation of apparent cross-link density with prevulcanization time.

Figure 11 Variation of chemical cross-link density with prevulcanization time.

NRL films prepared from compound A is slightly higher than compound B. From swell index, apparent cross-link density and chemical cross-link density values, it is found that optimum time for room temperature prevulcanization of NRL using Kbxt/ZDC and Nabxt/ZDC accelerator combination is 7 days.

Table II reports the tensile properties of films prepared from compound A and B measured after optimum prevulcanization time (7 days). From the Table II, also it is clear that films prepared from compound A has better tensile properties compared with films prepared from compound B. Tensile property measurement also suggest that Kbxt/ZDC accelerator combination gives better properties to NRL films compared with Nabxt/ZDC accelerator combination.



Figure 12 FTIR spectrum of prevulcanized NR latex film containing sodium butyl xanthate.

Table III shows the effect of thermal ageing at 70°C for 24 h on physical properties of vulcanisate A and B. In the case of vulcanisate A and B, tensile strength, modulus and cross-link density increases after thermal ageing. The increased cross-linking after the thermal ageing can be explained with the formations of new cross-links by free curative residues such as elemental sulfur, cure accelerator residues, and zinc complexes remained in the vulcanisate.^{11,12} The free sulfur remained in the vulcanisate reacts well with rubber chains and makes new cross-links. A pendent sulfide group terminated by an accelerator residue reacts with another pendent group of the neighboring rubber chains leading to the formation of new cross-links. Thus combination of pendent groups bonded to the rubber chains increases the cross-link density of vulcanisate after thermal ageing. After thermal ageing films prepared from compound A showed better properties than that of compound B.

Figure 12 shows the FTIR spectrum of NRL films prepared from room temperature prevulcanized NRL using Nabxt. The peak at 2950.00 cm⁻¹ corresponds to asymmetric stretching of C-H bond in $-CH_3$ group. The peak at 1443.64 cm⁻¹ and 1372.96 cm⁻¹ correspond to asymmetric and symmetric deformation of C-H bond in CH₃ group. The peak at 2918.95 cm⁻¹ and 2853.64 cm⁻¹ correspond to asymmetric and symmetric stretching of C-H bond in CH_2 group. The peaks at 1245.86 cm⁻¹ and 1019.44 correspond to asymmetric and symmetric cm^{-1} C-O-C stretching vibrations. The peaks at 1083.77 cm^{-1} and 665.89 cm^{-1} correspond to -C=S and -C-S stretching vibrations. The peak at 832.62 cm⁻¹ correspond to C-H out of plane bending of cis-1,4addition, peak at 1654.79 cm^{-1} corresponds to C=C stretching vibration. The peaks at 1578.24 cm⁻¹, 3445.00 cm⁻¹, 737.84 cm⁻¹, and 3310.00 cm⁻¹ correspond to N-H deformation, N-H stretching, N-H wagging and NH₃⁺ stretching (charged amine derivative) vibrations and all these vibrations characterize the protein present in the latex. All these peaks represent the vulcanized state of NR chains.

Figure 13 shows the FTIR spectrum of NRL films prepared from room temperature prevulcanized NRL using Kbxt. The peak at 2955.55 cm⁻¹ corresponds to asymmetric stretching of C-H bond in $-CH_3$ group. The peak at 1444.74 cm⁻¹ and 1373.16 cm⁻¹ correspond to asymmetric and symmetric stretching of C–H bond in CH₃ group. The peak at 2919.30 cm⁻¹ and 2854.04 cm⁻¹ correspond to asymmetric and symmetric and symmetric stretching of C–H bond in CH₂ group. The peaks at 1237.76 cm⁻¹ and 1020.95 cm⁻¹ correspond to asymmetric and symmetric and symmetric C–O–C stretching vibrations. The peaks at 1090.15 cm⁻¹ and 665.07 cm⁻¹ correspond to -C=S and -C–S stretching vibrations. The peak



Figure 13 FTIR spectrum of prevulcanized NR latex film containing potassium butyl xanthate.

at 832.79 cm⁻¹ correspond to C—H out of plane bending of *cis*-1,4-addition, peak at 1655.88 cm⁻¹ corresponds to C=C stretching vibration. The peaks at 1586.33 cm⁻¹, 3446.28 cm⁻¹, 743.00 cm⁻¹, and 3311.72 cm⁻¹ correspond to *N*—H deformation, *N*—H stretching, *N*—H wagging and NH₃⁺ stretching (charged amine derivative) vibrations and all these vibrations characterize the protein present in the latex. All these peaks again represent the vulcanized state of NR chains.

CONCLUSIONS

Sodium and potassium butyl xanthates can be prepared in the laboratory. They are used as effective accelerators for room temperature prevulcanization of NRL. Sodium and potassium butyl xanthates being water soluble, their mixing to latex is easy. From equilibrium swelling experiments and tensile property measurements, optimum time needed for prevulcanization is found to be 7 days. Tensile properties were found to be superior for films prepared from room temperature prevulcanized NRL using Kbxt/ZDC accelerator system compared with that of films prepared using Nabxt/ZDC accelerator prevulcanized NRL. Thermal ageing at 70°C for 24 h improved the tensile properties of room temperature prevulcanized NRL films. The main advantage of using Nabxt/ZDC and Kbxt/ZDC accelerator systems is that NR latex can be prevulcanized without temperature, which leads to high energy saving and making the process more economic. Again, colloidal stability of the latex can be improved due to the nonapplication of temperature.

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