

Studies on Xanthate/Dithiocarbamate Accelerator Combination in NR/BR Blends

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ABSTRACT: Zinc butyl xanthate [Zn(bxt)₂] was prepared in the laboratory. The effect of this xanthate with zinc diethyl dithiocarbamate (ZDC) on the vulcanization of natural rubber (NR), polybutadiene rubber (BR), and NR/BR blend has been studied at different temperatures. The amounts of Zn (bxt)₂ and ZDC in the compounds were optimized by varying the amount of ZDC from 0.75 to 1.5 phr and Zn (bxt)₂ from 0.75 to 1.5 phr. The cure characteristics were also studied. HAF filled NR, BR, and NR/BR blend compounds were cured at different temperatures from 60 to 150°C. The sheets were molded and properties such as ten-

sile strength, tear strength, crosslink density and elongation at break, compression set, abrasion resistance, etc. were evaluated. The results show that the mechanical properties of 80NR/20BR blends are closer to that of NR vulcanizates, properties of 60NR/40BR blends are closer to BR vulcanizates, while the 70NR/30BR blends show an intermediate property. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3516–3520, 2007

Key words: natural rubber; polybutadiene rubber; NR/BR blend; low temperature curing; mechanical properties

INTRODUCTION

Synthetic rubbers are classified into general purpose rubbers and special purpose rubbers. Polybutadiene is classified as general purpose rubbers intended for the manufacture of tires and general mechanical products. However, one type of rubber may not possess all the physical properties desired in a finished product. Much attention is currently being devoted to the simplest route for combining the outstanding properties of different existing polymers, i.e., the formation of polymer blends.^{1–5} For example, in tread compounds, the high abrasion resistance under certain conditions conferred by the use of BR is desirable, but the poor road holding and rib tearing properties are not, hence blends of BR with NR and styrene-butadiene rubber are employed.⁶

Compatibility is the fundamental property, deciding the practical utility of a polymer blend.^{7–9} If the two elastomers in a blend are incompatible, it will exist in the form of two separate phases and the cured blend will show inferior properties.¹⁰ The properties of miscible blends will follow relationships that are functions of composition and to some extent, the degree of interaction between the blend components.^{11,12}

The mechanical properties of nonstress crystallizing rubbers can be greatly improved by the incorpo-

ration of carbon black. When a filler is added to a binary elastomer blend, it goes to the less viscous polymer. When the viscosity of the less viscous polymer becomes equal to that of the highly viscous polymer, the filler will be taken up by both the polymers.¹³ So the low viscosity polymer gets highly loaded.

In NR/BR blends, BR shows improved tread wear and groove cracking resistance without reduction in resilience.¹⁴ Sarbach et al. reported a 20% higher tread wear index for 50/50 NR/BR over straight NR.^{15,16} The most important advantage of adding BR to NR is the improved abrasion resistance.

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 industry, the rubber products are molded at very high temperatures. In addition to the high energy consumption, high temperature vulcanization also affects 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.^{17,18} It is found that the mechanical properties of the NR vulcanizate are improved with decrease in vulcanization temperature. The properties are reported to be maximum when the vulcanization temperature is 60°C.¹⁹ Low temperature vulcanization is also applicable during the repairing of a rubber product. For example, in a tire industry, a tire having surface defects, after repair, is revulcanized at high temperature. This will

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TABLE I
Formulation of Mixes

Mix	A1 (phr)	A2 (phr)	A3 (phr)	A4 (phr)
NR	70	70	70	70
BR	30	30	30	30
ZnO	5	5	5	5
Stearic acid	2	2	2	2
HAF	50	50	50	50
Aromatic oil	7.0	7.0	7.0	7.0
Vulcanox HS	0.5	0.5	0.5	0.5
40-20	0.5	0.5	0.5	0.5
ZDC	0.75	1.0	1.25	1.50
Zn(bxt) ₂	1.0	1.0	1.0	1.0
Sulfur	2.2	2.2	2.2	2.2

result in the over vulcanization of the rubber compound and shrinking of the nylon cord inside the tire. So, repairing at a lower temperature can prevent deterioration in the quality and lifetime of the repaired product. The low temperature curing property of xanthate/ZDC accelerator combination is investigated through this work.

This paper reports the vulcanization of NR, BR, and NR/BR blend using Zn(bxt)₂/ZDC accelerator combination at various temperatures, and the effect of temperature of curing on the mechanical properties of the vulcanizates.

EXPERIMENTAL

Materials used

NR (ISNR-5, Mooney Viscosity ML (1 + 4) 100°C value of 82), was supplied by the Rubber Research Institute of India, Kottayam. BR (97% 1,4(cis); Mooney viscosity ML (1 + 4) at 100°C, 48.0). Compounding ingredients, such as zinc oxide, stearic acid, ZDC, carbon black (HAF N 330), aromatic oil, vulcanox 40-20, HS, and sulfur, were of commercial grade. *n*-Butyl alcohol, potassium hydroxide, carbon disulphide and toluene used for swelling studies were of reagent grade. Zinc sulfate used for precipitation was of commercial grade.

TABLE II
Formulation of Mixes

Mix	B1 (phr)	B2 (phr)	B3 (phr)	B4 (phr)
NR	70	70	70	70
BR	30	30	30	30
ZnO	5	5	5	5
Stearic acid	2	2	2	2
HAF	50	50	50	50
Aromatic oil	7.0	7.0	7.0	7.0
Vulcanox HS	0.5	0.5	0.5	0.5
40-20	0.5	0.5	0.5	0.5
ZDC	1.0	1.0	1.0	1.0
Zn(bxt) ₂	0.75	1.0	1.25	1.5
Sulfur	2.2	2.2	2.2	2.2

TABLE III
Cure Characteristics of the Mixes Given in Tables 1 and 2

Mix no.	Min. torque (N/m)	Max. torque (N/m)	Scorch time (min)	Optimum cure time (min)	Cure rate
A1	0.04102	0.4213	0.752	2.08	0.5102
A2	0.04541	0.4883	0.662	1.86	0.5678
A3	0.04248	0.4150	0.620	1.99	0.4952
A4	0.04395	0.4512	0.560	2.10	0.4930
B1	0.03965	0.3896	0.671	2.14	0.3896
B2	0.04539	0.4882	0.662	1.86	0.5679
B3	0.04651	0.4816	0.516	1.87	0.5658
B4	0.04662	0.4796	0.462	1.93	0.5236

Zn(bxt)₂ was prepared in the laboratory as per the procedure reported earlier.²⁰ Black filled NR, BR, and NR/BR blend compounds were prepared on a mixing mill.

To optimize the amount of accelerator for vulcanization, the concentration of ZDC was changed from 0.75 to 1.5 phr as shown in Table I, and the concentration of Zn(bxt)₂ was changed from 0.75 to 1.5 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.

NR, BR, and NR/BR blend were compounded on a (6 × 12") laboratory mixing mill according to the formulations given in Table IV. As compared with NR, BR requires less sulfur and more accelerators.²¹ So, when the amount of BR in the blend is changed, the concentration of accelerators and the concentration of sulfur are slightly changed as shown in Table IV. The cure curves of the mixes A, B, and D (given in Table IV) at 150°C are shown in Figure 1. The optimum cure times of the compounds A to E (given in Table IV) were determined at various temperatures from 60 to 150°C and are reported in Table V. These compounds were molded in an electrically heated laboratory hydraulic press at various temper-

TABLE IV
Formulation of Mixes

Mix	A (phr)	B (phr)	C (phr)	D (phr)	E (phr)
NR	100	–	80	70	60
BR	–	100	20	30	40
ZnO	5	5	5	5	5
Stearic acid	2	2	2	2	2
HAF	50	50	50	50	50
Aromatic oil	7.0	7.0	7.0	7.0	7.0
Vulcanox HS	0.5	0.5	0.5	0.5	0.5
40-20	0.5	0.5	0.5	0.5	0.5
ZDC	0.75	1.0	0.9	1.0	1.1
Zn(bxt) ₂	1.0	1.5	0.9	1.0	1.1
Sulfur	2.5	2.0	2.3	2.2	2.1

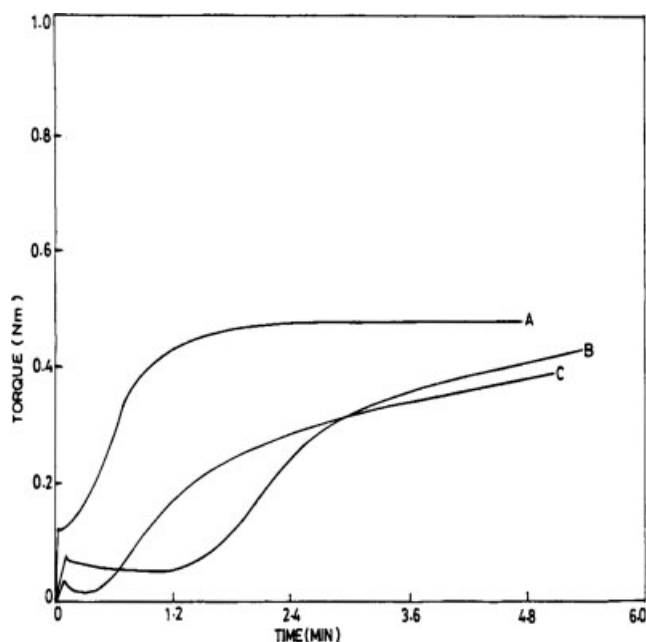


Figure 1 Cure curves of the mixes A, B, and D given in Table IV.

atures up to their optimum cure times at a pressure of 200 kg/cm². Dumb bell shaped tensile test pieces were punched out of these compression molded sheets along the mill grain direction. Crosslink density of the samples was determined by equilibrium swelling method using toluene as the solvent. The degree of crosslinking was calculated using the Florey Rehner equation²² and is shown in Figure 2. The tensile properties of the vulcanizates were evaluated on a Zwick universal testing machine using a cross-head speed 500 mm/min according to ASTM.D.2240 and are graphically represented in Figures 3–5. Compression set was determined by compressing to a constant deflection (25%) as per ASTM. D. 395-61, method B (Fig. 6). Abrasion resistance was tested using DIN abrader according to DIN 53,516 (Fig. 7).

RESULTS AND DISCUSSION

Table III gives the cure characteristics of the mixes given in Tables I and II. It shows that compound B₂ and B₃ have the same optimum cure times. But the

TABLE V
Optimum Cure Times in Minutes

Temp. (°C)	A	B	C	D	E
150	1.26	4.0	1.41	1.86	3.86
125	6.11	13.0	6.36	7.1	11.96
100	21.24	41.0	22.02	23.16	38.64
80	53.62	–	55.42	56.98	–
60	78.31	–	80.16	–	–

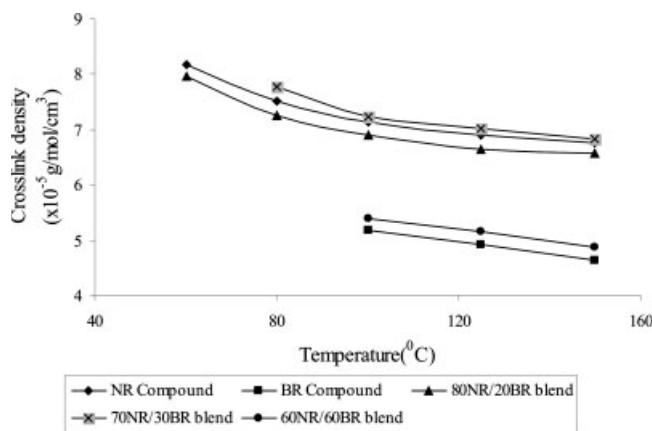


Figure 2 Effect of temperature on the crosslink density of the compounds given in Table IV.

maximum torque and cure rate are high for the compound B₂. This compound is having enough scorch safety also. So 1.0 phr ZDC and 1.0 phr Zn(bxt)₂ are taken as the optimum dosage for the 70/30 NR/BR blend.

Figure 1 shows the cure curves of the mixes A, B, and D at 150°C. It is seen that the 100% NR based compound (compound A), cures faster than all the other compounds and the scorch time is found to be very low. But in 100% BR based compound (compound B), the curing is very slow as expected. Since the double bond in NR is more active because of the presence of –CH₃ group, the curatives will be slightly more soluble in NR, which leads to a high cure rate for NR (compared to BR). The blend compound (compound D) gives enough scorch safety and at the same time, the cure time is very close to that of NR. This shows that blending of BR with NR improves scorch safety without much change in the cure time.

Table V shows the optimum cure times of the compounds given in Table IV at different tempera-

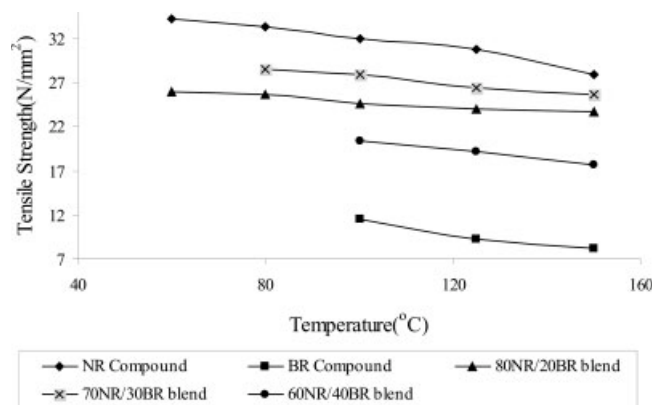


Figure 3 Effect of temperature on the tensile strength of the compounds given in Table IV.

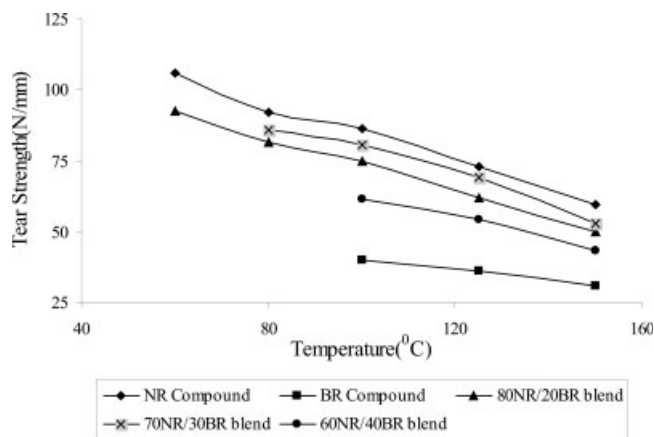


Figure 4 Effect of temperature on the tear strength of the compounds given in Table IV.

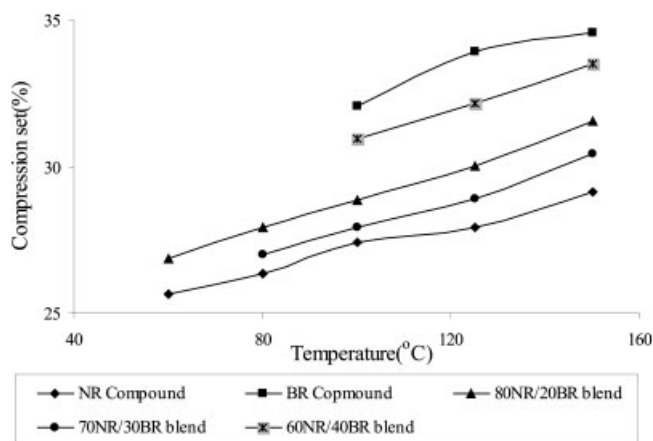


Figure 6 Effect of temperature on the compression set of the compounds given in Table IV.

tures. Compound A undergoes curing at all temperatures from 150 to 60°C with gradual increase in cure time. Compound B doesn't cure below 100°C. Compound C undergoes curing up to 60°C and the cure times are closer to that of pure NR compounds. With compound D, curing takes place only up to 80°C. At 60°C, curing is incomplete even after 2 h. Compound E doesn't cure below 100°C. So it is clear that low temperature curing becomes difficult as the amount of BR in the blend increases and it is impossible with 100% BR compounds.

Figure 2 shows the total crosslink density of the compounds A to E. Compared to NR vulcanizates, crosslink density of BR vulcanizates is very low. Among the blends, 80/20 NR/BR blend shows a crosslink density comparable to pure NR vulcanizates. Crosslink density of 70/30 blend is slightly higher than that of NR vulcanizates. 60/40 blend shows low crosslink density, closer to that of pure BR vulcanizates.

Figures 3–5 show the tensile properties of the mixes given in Table IV. The results show that the tensile strength and tear strength increases and elongation at

break decreases when the temperature of curing is changed from 150 to 60°C. This may be due to lesser degradation of the rubber at lower temperatures and also due to the higher stability of the accelerator at lower temperatures. At a particular temperature, the tensile properties are maximum for NR compounds, minimum for BR compounds and in between for the blends. But the tensile properties of the blends are closer to the NR compounds than that of BR compounds. The elongation at break is also close to the arithmetic average. Among the three blends, the tensile properties are maximum for the 70/30 blend.

Figure 6 shows the compression set of the mixes A to E at different temperatures. Compression set values of the BR compounds is high compared to that of NR compounds. The values for the blends are intermediate between that of NR and BR.

Figure 7 shows the abrasion resistance of the vulcanizates given in Table IV. The abrasion resistance is high for the BR compounds at high temperatures than that of NR compounds. The abrasion resistance values of the 70/30 and 60/40 blends are closer to

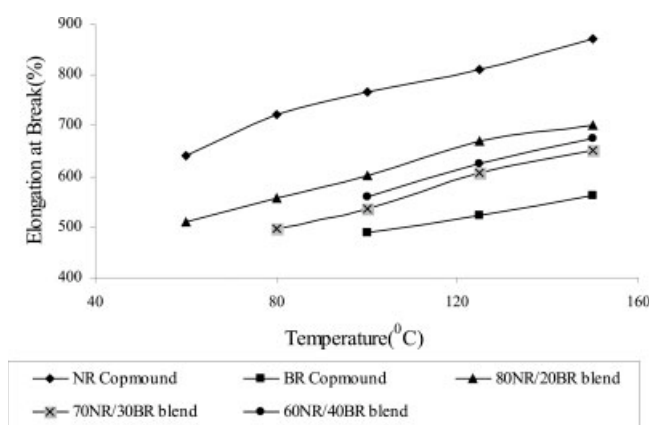


Figure 5 Effect of temperature on the elongation at break of the compounds given in Table IV.

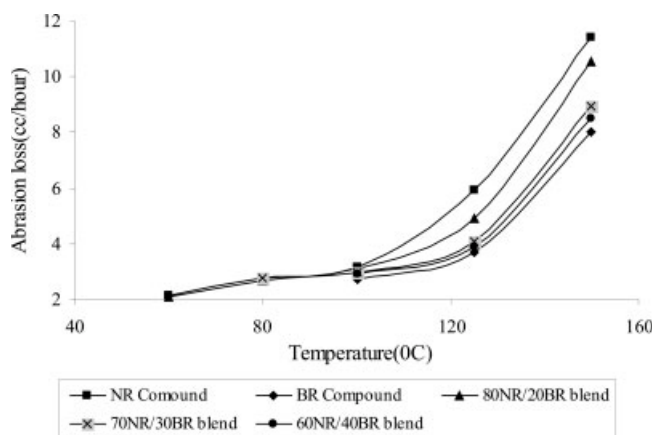


Figure 7 Effect of temperature on the abrasion resistance of the compounds given in Table IV.

that of the 100% BR based compounds at or below 100°C. The 80/20 blend shows abrasion resistance value closer to that of the NR compounds. Below 100°C, the abrasion resistance values of all the blends are closer to that of NR vulcanizates and a high value is shown by the 70/30 blend. So, addition of BR to NR improves the abrasion resistance, at high temperatures.

The 80NR/20BR blend shows more or less the properties of NR alone because of the low concentration of BR. When the amount of BR in the blend increases to 30 phr, the properties settle at an intermediate value between those of BR and NR. This may be due to the good compatibility of the two rubbers resulting in an almost single phase behavior.^{23,24} When the amount of BR in the blend is 40 phr, the properties are closer to BR

CONCLUSIONS

1. Zn(bxt)₂/ZDC accelerator combination can vulcanize NR at all temperatures from 150 to 60°C; but it can vulcanize BR only upto 100°C. Among the NR/BR blends, 80/20 blend undergoes curing at all temperatures from 150 to 60°C, 70/30 blend cures only upto 80°C, and 60/40 blend cures only upto 100°C.
2. Addition of BR to NR increases the scorch time of the compound.
3. The tensile properties of the pure BR compounds are poor compared to the NR compounds.
4. The mechanical properties of the 80NR/20BR blends are more closer to that of NR vulcanizates, that of 60/40 blends are more closer to the BR vulcanizates, while the 70/30 blends shows an intermediate property.
5. The 70/30 NR/BR blend and 60/40 NR/BR blend show better abrasion resistance than the NR vulcanizates when cured at higher temperatures.

References

1. Walters, M. H.; Keyte, O. N. *Rubber Chem Technol* 1965, 38, 62.
2. Railsback, H. E.; Cooper, W. T.; Stumpe, N. A. *Rubber Chem Technol* 1959, 32, 308.
3. Paul, D.R.; Newman, S. *Polymer Blends*, Vols. 1 & 2; Academic Press: New York, 1978.
4. Bruins, P.F., Ed. *Polyblend and Composites*; Appl Polym Symp 15, 1970.
5. Bhowmick, T. K.; Bhattacharya, A. K.; Gupta, B. R.; Anil, K. B. *Plast Rubber Compos Process Appl* 1988, 10, 105.
6. Corish, P. J. *Rubber Chem Technol* 1967, 40, 324.
7. Utracki, L. A. *Polym Plast Technol Eng* 1984, 22, 27.
8. Sarah, Y. K. *Plast Eng* 1987, 41.
9. Xanthos, M.; Dagli, S. S. *Polym Eng Sci* 1991, 31, 929.
10. Manson, J. A.; Sperling, L. M. *Polymer Blends and Composites*; Plenum: New York, 1976.
11. Kovar, J.; Fortelny, J.; Bodhanecky, M. *Int Polym Sci Technol* 1982, 9, T/50.
12. Martuscelli, E.; Palumbo, R.; Kryszewski, M. *Polymer Blends*, New York, 1980.
13. Walters, M. H.; Keyte, D. N. *Rubber Chem Technol* 1965, 38, 63.
14. Hess, M. W.; Vegvari, P. C.; Swor, R. A. *Rubber Chem Technol* 1985, 58, 350.
15. Sarbach, D. V. *Rubber Age* 1961, 89, 283.
16. Sarbach, D. V.; Hallman, R.W.; Cavicchia, M. A. *Rubber Age* 1966, 98, 67.
17. Palaty, S.; Joseph, R. *Plast Rubber Compos* 2001, 30, 6.
18. Sasidharan, K. K.; Gopalakrishnan, K. S.; George, K. E. *J Appl Polym Sci* 2005, 94, 1164.
19. Shiny, P.; Rani, J. *Iranian Polym J* 2004, 13, 85.
20. Shiny, P.; Rani, J. *J Appl Polym Sci* 2000, 78, 1769.
21. Balckley, D. C. *Synthetic Rubbers*; Applied Sciences Publishers: London, 1983.
22. Flory, P. J.; Rehner, J. *J Chem Phys* 1943, 11, 512.
23. Inoue, T. *Int Polym Sci Technol* 1981, 8, T65.
24. Baranwal, K. C.; Son, P. N. *Rubber Chem Technol* 1974, 47, 88.