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Tribasic Lead Sulphate as Efficient Curing Agent for Polychloroprene

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SUMMARY:

Tribasic lead sulphate is tried as a practical curing agent for polychloroprene. The cure characteristics of the compounds as well as the technical properties of the vulcanizates show that it can act as a potential curative.

ZUSAMMENFASSUNG:

Dreibasisches Bleisulfat wurde als für die Praxis geeignetes Vernetzungsmittel für Polychloropren geprüft. Sowohl die Vernetzungscharakteristika als auch die technischen Eigenschaften der Vulkanisate zeigen, daß es als Vulkanisierungsmittel eingesetzt werden kann.

Introduction

Polychloroprene (CR) is a speciality rubber noted for its flame resistance and resistance to oxidative ageing[1,2]. There are two common grades of CR: G type (sulphur modified) and W type (non-sulphur modified). Within each group a number of polymers are commercially available varying in Mooney viscosity. CR vulcanizes in a considerably different manner from that of natural rubber and such synthetic rubbers as styrene-butadiene rubber. Unlike normal vulcanization with sulphur, metallic oxides are necessary to vulcanize CR. The metallic oxides most often used are zinc oxide as crosslinking agent and magnesium oxide which is mainly used as an acid acceptor. The effects obtained differ greatly in the G and W tyes of CR. In G types, metallic oxides generally give satisfactory vulcanization by themselves. On the other hand W types have less tendency to crosslink and therefore require not only metallic oxides but also special accelerators like ethylene thiourea[3,4].

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Polychloroprene can be vulcanized with several other metallic oxides apart from magnesium oxide and zinc oxide. Lead oxide (PbO) and red lead (Pb_3O_4) are used particularly when low water absorption and high resistance to acids are required. However, with the exception of these lead oxides, none of the other metallic oxides whether used alone or in combination gives properties that even approximate to those obtained with MgO/ZnO vulcanization system[3].

Tribasic lead sulphate, a common heat stabilizer for PVC, has both the crosslinking and acid acceptor properties. Hence it is tried as a curing agent for polychloroprene. It is comparatively cheaper than the conventional curing agents for polychloroprene and is likely to produce good resistance to water, acids, and other solvents similar to the lead oxide cured vulcanizates.

Experimental

Materials

Polychloroprene (supplied by Dupont, U. S. A.); (a) W type, Mooney viscosity (ML1 + 4 at 100 °C) 47, (b) GN type, Mooney viscosity (ML1 + 4 at 100 °C) 46, MgO (light magnesia), ZnO (white seal), stearic acid, ethylene thiourea (NA-22), phenyl-β-naphthylamine (PBN), naphthenic oil (all rubber grade), carbon black (semi reinforcing furnace black, N 741), Pb_3O_4 (Glaxo, India) and tribasic lead sulphate (TBLS) (PVC grade).

Determination of Cure Characteristics

The formulations of the mixes employed for determining the cure characteristics are shown in Tab. 1. The compounds were prepared in a Brabender Plasticorder model PL3S, using a roller type mixer with a rotor speed of 30 rpm, at near ambient temperature (28 °C). The cure characteristics were determined in a Monsanto Rheometer model R100 at 150 °C. The cure curves are shown in Fig. 1, 2, and 3.

Determination of Technical Properties

The formulations employed for determining the technical properties and their cure characteristics are shown in Tab. 2. The compounds were prepared in a laboratory mixing mill and then the cure characteristics were determined in a Monsanto Rheometer model R100 at 150 °C. The compounds were then vulcanized up to the respective cure times in a steam heated laboratory press. The tensile properties were deter-

Tab. 1. Formulations employed for determining the cure characteristics.

Formulations	A	B	C	D	E	F	G	H	I	J
Polychloroprene (W)	100	100	100	100	—	—	—	—	—	—
Polychloroprene (GN)	—	—	—	—	100	100	100	100	100	100
MgO	4	—	4	—	4	—	4	—	—	—
ZnO	5	—	5	—	5	—	5	—	—	—
TBLS	—	5	—	5	—	5	—	5	10	15
NA-22	—	—	0.5	0.5	—	—	0.5	0.5	—	—

Tab. 2. Formulations employed for determining the technical properties.

Formulations	I	II	III	IV
Polychloroprene (GN)	100	100	100	100
MgO	4	—	—	—
ZnO	5	—	—	—
Pb_3O_4	—	15	—	—
TBLS	—	—	5	10
SRF black	50	50	50	50
Naphthenic oil	10	10	10	10
PBN	1.5	1.5	1.5	1.5
Stearic acid	2.0	2.0	2.0	2.0
Cure characteristics				
Scorch time (min)	2.0	1.5	1.5	1.25
Optimum cure time (min)	14.0	37.5	26.5	32.0
Maximum torque (dN · m)	92.0	102.0	71.0	90.0
Reversion (No. of units dropped in 10 min)	Nil	Nil	Nil	Nil

mined at 28 °C as per ASTM 412 (1980) using dumb-bell shaped test pieces at a cross-head speed of 500 mm/min. The ageing characteristics of the samples were determined by keeping them at 100 °C for 48 h in an air oven and then measuring the reten-

tion in the tensile properties. The hardness of the vulcanizates was determined according to ASTM 2240 (1968) and expressed in shore A units. The compression set was determined according to ASTM D 395-69 under constant deflection. The solvent resistance of the vulcanizates was determined by allowing circular specimens of 1 cm diameter (approximately 60 mg) to stand in an excess of the solvent at 28 °C for 20 days.

Results and Discussion

Fig. 1. shows the cure characteristics of W type CR. The MgO/ZnO system in the absence of an accelerator cures very inefficiently and at a very slow rate as expected. The behaviour of TBLS without an accelerator is

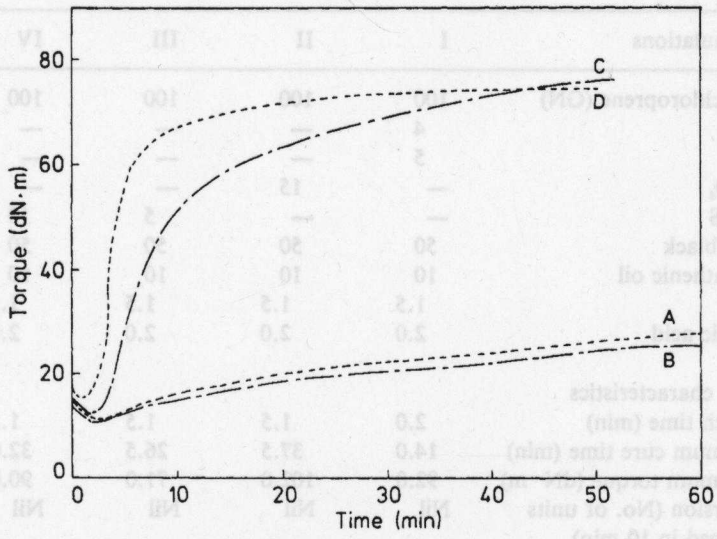

Fig. 1. Cure curves of W type CR. (A) MgO/ZnO, (B) TBLS, (C) MgO/ZnO + NA-22, (D) TBLS + NA-22.

found to be more or less the same. The curing rate is very slow and the maximum torque, a measure of the amount of crosslinks, is also very low. The curing of this type of CR with MgO/ZnO system in presence of 0.5 phr (per hundred rubber) NA-22 is faster and efficient as expected. The behaviour of TBLS in presence of 0.5 phr NA-22 is also found to be similar implying that

TBLS could act as a potential curative for W type CR in presence of an accelerator like NA-22. However, the scorch safety of the compound with TBLS and NA-22 is found to be a little less than that of the compound with MgO/ZnO and NA-22. This behaviour seems to be similar to that of other lead oxide curing systems[3]. The amount of the accelerator was varied keeping the amount of TBLS at 5 phr (not shown in figure). Higher amounts of accelerator produced marginal increase in the maximum torque but at the expense of the scorch safety.

Fig. 2 shows the cure characteristics of GN type CR. MgO/ZnO system acts as an efficient curative in this case even without an accelerator as expected. Addition of an accelerator produces only marginal increase in the maximum torque. The behaviour of the TBLS is also similar implying that TBLS could act as a potential curative for GN type CR even without an

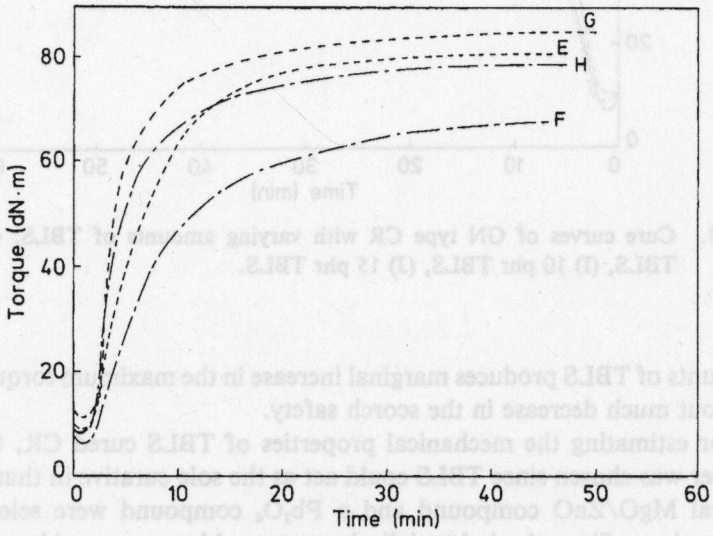

Fig. 2. Cure curves of GN type CR. (E) MgO/ZnO, (F) TBLS, (G) MgO/ZnO + NA-22, (H) TBLS + NA-22.

accelerator. The amount of crosslinks, as reflected in the maximum torque values, seems to be a little less at this level of TBLS than that obtained with the MgO/ZnO system. Fig. 3 shows the effect of varying the amount of TBLS in the curing behaviour of GN type CR. It is found that increasing the

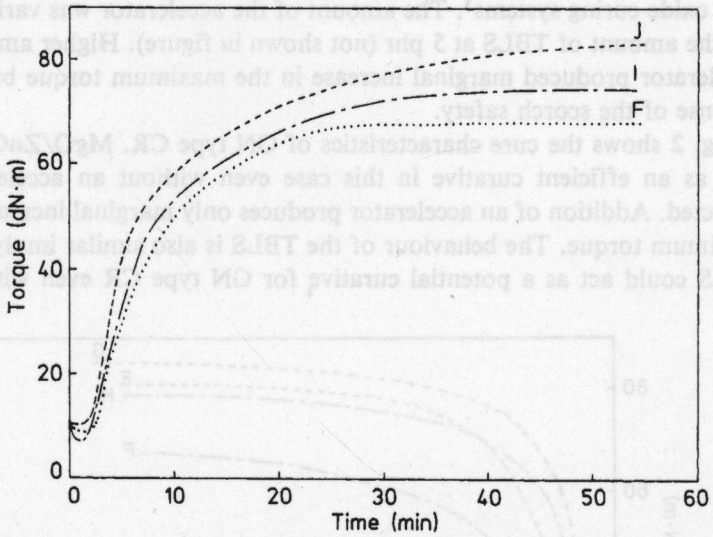

Fig. 3. Cure curves of GN type CR with varying amounts of TBLS: (F) 5 phr TBLS, (I) 10 phr TBLS, (J) 15 phr TBLS.

amounts of TBLS produces marginal increase in the maximum torque values without much decrease in the scorch safety.

For estimating the mechanical properties of TBLS cured CR, GN type rubber was chosen since TBLS could act as the sole curative in that case. A typical MgO/ZnO compound and a Pb_3O_4 compound were selected for comparison. Since the industrially important chloroprene rubbers contain fillers and antioxidants, 50 phr SRF black along with 10 phr naphthenic oil and 1.5 phr PBN were also added in each case (Tab. 2). An examination of the mechanical properties (Tab. 3) reveals that the TBLS cured vulcanizates show the maximum tensile strength and elongation even at 5 phr concentration. Increasing the amount of TBLS to 10 phr shows marginal increase in tensile strength but at the expense of elongation at break. This again might imply that additional crosslinks are introduced in the matrix with increase in the amount of TBLS. The hardness and compression set values confirm the observation. The vulcanizate cured by Pb_3O_4 seems to be the best in ageing resistance. However, the values shown by the TBLS cured vulcanizates are also within reasonable limits for practical applications.

The TBLS cured vulcanizates exhibit very good resistance to solvents (Tab. 4) even at 5 phr concentration particularly in water and acetic acid,

Tab. 3. Mechanical properties of the vulcanizates.

Properties	Vulcanizate			
	I	II	III	IV
Tensile strength (MPa)	15.8	15.9	16.5	16.7
Elongation at break (%)	580	475	670	490
300% Modulus (MPa)	8.7	9.7	6.5	9.8
Hardness (Shore A)	63.0	65.0	55.0	63.0
Compression set (%)	50	35	45	40.5
Tensile properties after ageing				
Tensile strength (MPa)	14.4	15.0	15.0	15.5
Elongation at break (%)	425	420	500	400
300% Modulus (MPa)	10.6	11.0	7.8	11.6

Tab. 4. Solvent resistance of the vulcanizates (% increase in weight in 20 days at 28 °C).

Solvent	Vulcanizate			
	I	II	III	IV
Water	12.8	1.42	3.97	1.75
Acetic acid	62.88	8.49	7.20	4.35
Acetone	13.45	14.96	13.70	11.20
Toluene	165.5	134.49	169.34	136.53
Carbon tetrachloride	274.93	227.82	289.10	238.68

compared to the MgO/ZnO and Pb_3O_4 cured vulcanizates. Increasing the amount of TBLS produces further improvements in solvent resistance as shown by the vulcanizate which contains 10 phr TBLS.

Conclusions

Tribasic lead sulphate has been identified as a potential curative for CR. Compared to the conventional curatives, it has the following advantages:

1. It is effective in low proportions.
2. It produces better mechanical properties.
3. It imparts better solvent resistance.

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[4] S. W. Schmitt, in Rubber Handbook, R. O. Babbit (Ed.), R. T. Vanderbilt Company, Norwalk, Connecticut 1978, p. 137