Low Temperature Curing by Using Zinc-2-mercaptobenzothiazole (ZMBT) in Combination with Dithiocarbamates (DC) and Amine Curing Systems

Cross-linking · Accelarator combinations · ZMBT · ZBEC · ZDC · Amine · Curing kinetics · Ultimate properties

Studies have been done to explore possibilities of low temperature curing in typical natural rubber based compounds. Combination of fast accelerators together with amine activation has been used in this approach. It has been found that it is possible to lower the vulcanization temperature as low as 60 °C and still obtain sufficient cure. The combination of ZMBT/ZDC/Amine provides a best compromise with regard to cure kinetics and ultimate properties. In consideration with N-Nitrosamine safe system, the combination of ZBEC/ZMBT/DPG provides an optimum solution. A three variable experimental design was executed to optimize the recipe comprising of ZBEC/ZMBT/DPG systems.

Vulkanisation bei niedrigen Temperaturen

Vernetzung · Beschleunigerkombinationen · ZMBT · ZBEC · ZDC · Amin · Vernetzungskinetik · Festigkeitseigenschaften

Die Möglichkeiten zur Vulkanisation bei niedrigen Temperaturen wurde in NR-Rezepturen untersucht. Dabei wurden Kombinationen von schnellen Beschleunigern mit Aminen eingesetzt. Es wurde gefunden, dass auch noch bei 60 °C eine ausreichende Vernetzung stattfindet. Die Kombination ZMBT/ZDC/Amin liefert den besten Kompromiss bezüglich der Vernetzungskinetik wie auch der Festigkeitseigenschaften. Mit Bezug auf die Nitrosaminproblematik stellt die Kombination ZBEC/ZMBT/DPG eine optimale Lösung dar. Die Eigenschaftsoptimierung wurde am Beispiel dieser Beschleunigerkombination anhand eines statistischen Versuchsplans mit drei Parametern durchgeführt.

Low temperature cure (LTC) or room temperature vulcanization (RTV) is becoming popular especially in the retread/repair industry. There is strong demand to design a formulation, probably N-Nitrosamine safe or free, which can cure at low temperature. Although some information on this subject is available, the solutions are mostly protected by patents [1–3]. A general study addressing low temperature vulcanization has not been published and public information is scanty.

In practice, LTC or RTV can be done by using single- or dual- package systems [4]. The results are reported in this paper using a single cure package concept.

Experimental

Four dithiocarbamates, namely zinc dimethyldithiocarbamate (ZDMC), zinc ethylpropyldithiocarbamate (ZEPC), tellurium diethyldithiocarbamate (TDEC) and zinc dibenzyldithiocarbamate (ZBEC) were selected in this study. Zinc-2-mercaptobenzothiazole (ZMBT), 2-mercaptobenzothiazole (MBT) and Diphenyl Guanidine (DPG) are commercial samples used without any purification. Cyclohexylammonium dibenzyldithiocarbamate (CHA-BEC) was prepared accordingly to the procedure as stated underneath:

Synthesis of Cyclohexylammonium dibenzyldithiocarbamate (CHA-BEC)

To 500 ml water, 162.1 g of a 28.2 % solution (0.1 mol) of sodium dibenzyldithiocarbamate was added at room temperature with continuous stirring. To this solution 9.9 g (0.1 mol) cyclohexyl amine was added slowly in 0.5 h. During the addition the solid precipitates. To the heavy slurry 250 mL water was added and stirring continued for another 0.5 h. The product was then isolated and washed four times with distilled water. The product was dried at 45 °C in an air oven and characterized by NMR and IR measurements. Yield: 32 g (81 %), m.p: 125 °C. The structure of CHA-BEC is shown in *Fig. 1*.

Formulations of the compound are shown in *Tab. 1–3*.

Compound mixing was carried out in two stages. In the first phase rubber was mixed with carbon black, zinc oxide and all other ingredients except accelerators and sulfur for five minutes in an internal mixer of capacity 5 L at a dump temperature of 130–135 °C. The masterbatch was kept for 24 h

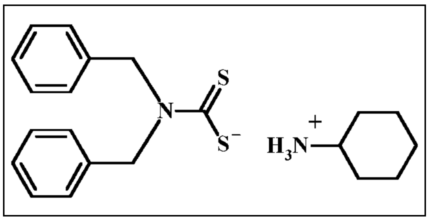

Fig. 1. Structure of CHA-BEC

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Tab. 1. Model formulations – Comparison of DTC's

Ingredients/ Mixes	A ZDMC/ ZMBT/ DPG	B ZEPC/ ZMBT/ DPG	C TDEC/ ZMBT/ DPG	D ZBEC/ ZMBT/ DPG	E ZBEC/ MBT/ DPG	F ZBEC/ ZMBT/ DPG/ APDS	G CHA-BEC ZMBT/ DPG
NR SMR CV	80	80	80	80	80	80	80
BR CB 10	20	20	20	20	20	20	20
N-375	55	55	55	55	55	55	55
Zinc oxide	4	4	4	4	4	4	4
Stearic acid	2	2	2	2	2	2	2
Aromatic oil	8	8	8	8	8	8	8
Santoflex 6PPD	2	2	2	2	2	2	2
ZDMC	1.5	0	0	0	0	0	0
ZEPC	0	1.5	0	0	0	0	0
TDEC	0	0	1.5	0	0	0	0
ZBEC	0	0	0	1.5	1.5	1.5	0
CHA-BEC	0	0	0	0	0	0	1.5
ZMBT	0.5	0.5	0.5	0.5	0.5	0	1.5
MBT	0	0	0	0	0.5	0	0
DPG	0.5	0.5	0.5	0.5	0.5	0.5	0.5
APDS	0	0	0	0	0	0.5	0
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5

Tab. 2. Formulations (Design experiment) – Optimization

Ingred., phr/ Mixes	01	02	03	04	05	06	07	08	09	10
MB	171	171	171	171	171	171	171	171	171	171
MBT	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
ZMBT	3.0	2.0	1.0	2.0	2.0	2.0	2.0	1.0	2.0	3.0
ZBEC	3.0	2.0	1.0	3.7	2.0	2.0	0.3	3.0	2.0	1.0
DPG	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sulfur	1.0	2.0	1.0	2.0	2.0	2.0	2.0	1.0	0.3	1.0

MB signifies masterbatch comprising of NR, 80; BR, 20; N-375, 55; Zinc oxide, 4; Stearic acid,2; Aromatic oil, 8; 6PPD, 2.

Tab. 3. Formulations (Design experiment) – Optimization

Ingred., Phr/ Mixes	11	12	13	14	15	16	17	18	19	20
MB	171	171	171	171	171	171	171	171	171	171
MBT	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
ZMBT	2.0	0.3	2.0	3.0	1.0	3.0	1.0	3.7	2.0	2.0
ZBEC	2.0	2.0	2.0	1.0	1.0	3.0	3.0	2.0	2.0	2.0
DPG	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sulfur	3.7	2.0	2.0	3.0	3.0	3.0	3.0	2.0	2.0	2.0

MB signifies masterbatch comprising of NR, 80; BR, 20; N-375, 55; Zinc oxide, 4; Stearic acid,2; Aromatic oil, 8; 6PPD, 2.

before finalizing on a two roll mill. The mixes were characterized by using MDR 2000 EA. Non-isothermal cure curves were taken for some selected recipes using Rubber Processing Analyzer (RPA 2000). For the experimental design, we selected a central composition with a quadratic model having MBT and DPG fixed and ZMBT, ZBEC and Sulfur variables (ranging from 1.0–3.0 phr). Studies were done with scorch (ts 2), optimum cure time (t 90) and delta torque (delta S) as responses.

Physical testing was carried out following the ISO norms as reported earlier [5].

Results and discussion:

Effect of different dithiocarbamates (DTC):

ZDMC, ZEPC, TDEC and ZBEC are compared and evaluated in a cure system comprising ZMBT, DPG and Sulfur. The choice of these combinations is based on the following facts: ZMBT, ZDC are fast cure accelerators and DPG is a cure activator. The comparative data are tabulated in *Tab. 4*. It is evident from the data that ZEPC starts curing much earlier than the other accelerators. ZDMC, TDEC and ZBEC behave similar with respect to ts 2 but t 90 differs significantly. ZBEC will be a system of choice when N-Nitrosamine safe compounds are under consideration. With this in mind, our objective was to further activate the ZBEC/ZMBT/DPG system by using certain commercially available activators such as dialkyldiphenoldisulfide (APDS). The recipe is shown in Tab. 1 (mix F). The cure data are tabulated in Tab. 4 (mix F). Incorporation of APDS decreases the scorch but t90 virtually remains unchanged. It is interesting to mention that the CHA-BEC shows the best cure kinetics (Mix G). RPA isotherms of mixes D, F and G are shown in *Fig. 2*. It is clear that ZBEC together with ZMBT plus DPG provides a possibility to lower the vulcanization temperature.

Optimization of the ZBEC/ZMBT/ DPG system

In this study the levels of ZMBT/ZBEC and sulfur have been varied from 1.0 to 3.0 phr with MBT and DPG being fixed at 0.5 phr. The model selected is quadratic and the design is "Central composition" with number of experiment 20. The compound formulations are shown in Tab. 2 and 3.
The cure data of the mixes are depicted in *Tab. 5* and *6*.
The response surfaces on delta S and ts2 are shown in *Fig. 3–5*. It is very clear that certain combinations of accelerators will provide a cure profile suitable for low temperature curing as required.
In the design, a target was set up at 120 °C; Delta S = 1; Ts 2, 4' and t 90 = 8'. With the design expert analysis a recipe was formulated comprising of ZMBT, 3.7; ZBEC, 0.7 and Sulfur, 2.0 with DPG, 0.5 & MBT, 0.5 phr which is expected to provide the desired goal. The compound was

Tab. 4. Cure data at 100 °C							
Ingredients/ Mixes	A ZDMC/ ZMBT/ DPG	B ZEPC/ ZMBT/ DPG	C TDEC/ ZMBT/ DPG	D ZBEC/ ZMBT/ DPG	E ZBEC/ MBT/ DPG	F ZBEC/ ZMBT/ DPG/ APDS	G CHA-BEC/ ZMBT DPG
Delta S, Nm	0.87	0.94	1.05	0.84	0.82	0.92	0.92
ML, Nm	0.11	0.11	0.10	0.10	0.11	0.11	0.10
Ts 2, min	35.0	15.6	37.4	40.8	45.1	33.0	10.0
T 90, min	81	23	48	53	66	50	32
Cure rate, T 90-ts2,min	46	7.4	10.6	12.2	20.9	17	22

Tab. 5. Cure data of the mixes at 100 °C										
Mixes	01	02	03	04	05	06	07	08	09	10
Delta S, Nm	0.82	1.14	0.75	1.15	1.12	1.11	1.00	0.74	0.14	0.72
Ts 2, min	40.5	26.9	48.1	28.6	29.8	27.7	36.9	53.2	120	43.6
T 90, min	53.0	38.0	65.0	38.0	39.0	38.0	55.0	68.0	–	50.0

Tab. 6. Cure data of the mixes at 100 °C										
Mixes	11	12	13	14	15	16	17	18	19	20
Delta S, Nm	1.62	1.06	1.14	1.40	1.36	1.46	1.25	1.12	1.06	1.08
Ts 2, min	16.1	35.6	26.5	19.3	18.7	19.3	27.2	23.9	31.7	30.2
T 90, min	30.0	45.0	38.0	30.0	30.0	30.0	42.0	40.0	50.0	48.0

mixed and the results are tabulated in *Tab. 7*.

The cure curve of the final compound is shown in *Fig. 6*. It is clear that even at 120 °C, the cure system comprising of 3.7 phr ZMBT, 0.7 phr ZBEC and 2.0 phr sulfur together with 0.5 phr DPG and 0.5 phr MBT provides fast cure kinetics.

The final compound together with a couple of other compounds was selected from the design for determination of stress-strain properties. The data are tabulated in *Tab. 8*.

All the compounds show a high level of strength properties.

Tab. 7. The goal and the results (at 120 °C)		
Response	Goal	Results
Delta S, Nm	1	1.15
Ts 2, min	4	4.4
T 90,min	8	8.3

Conclusions

It can be concluded from this study that it is possible to select a cure package from the available accelerators suitable for low temperature vulcanization. The cure package consists of ZMBT, ZBEC and sulfur together with DPG and MBT.

From the design of experiment it was possible to arrive at particular levels of combination of accelerators to achieve the target properties. It has been demonstrated that with the formulation comprising ZMBT, 3.7; ZBEC, 0.7; DPG, 0.5; MBT, 0.5 and Sulfur 2.0 attains target properties. The stress strain properties of the vulcanizates cured at 150 °C/4′ are in line with the target properties.

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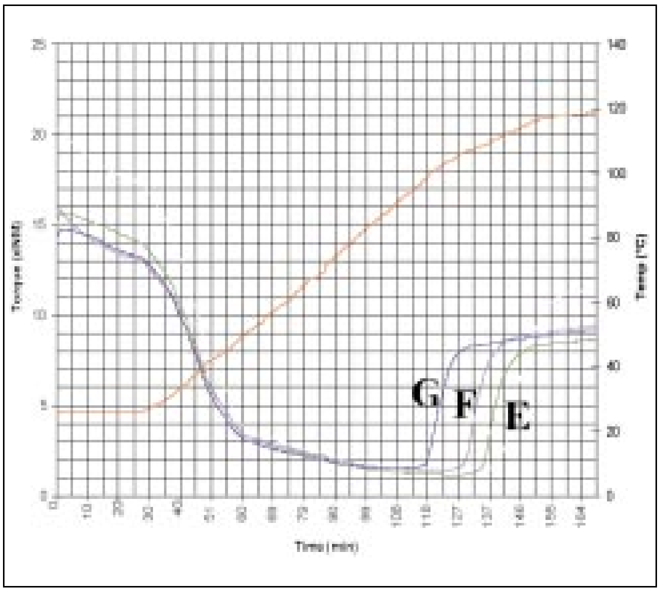

Fig. 2. RPA non-isotherm curves

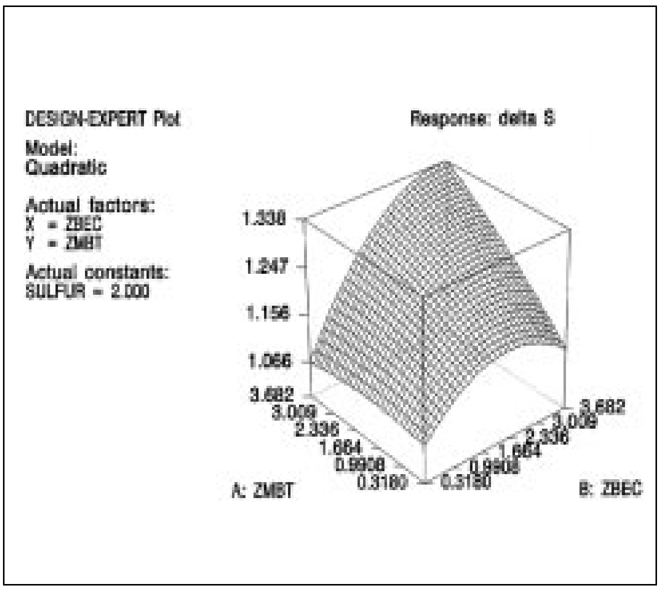

Fig. 3. Response: Delta S

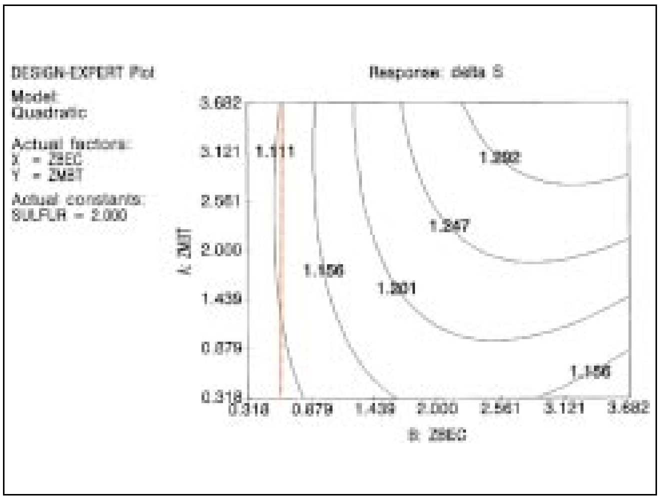

Fig. 4. Response: Delta S

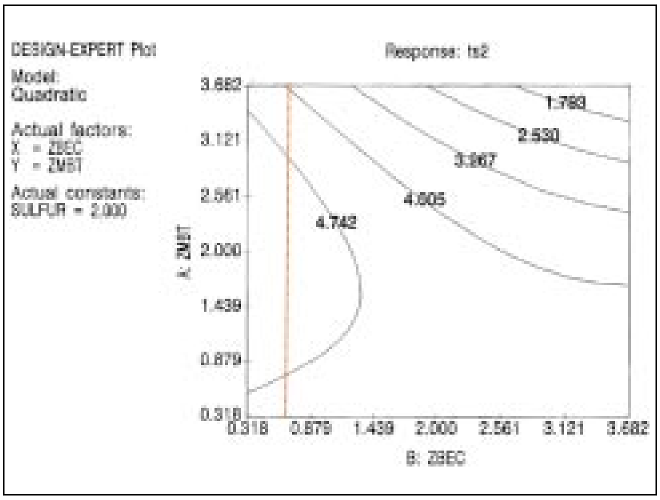

Fig. 5. Response: Ts 2

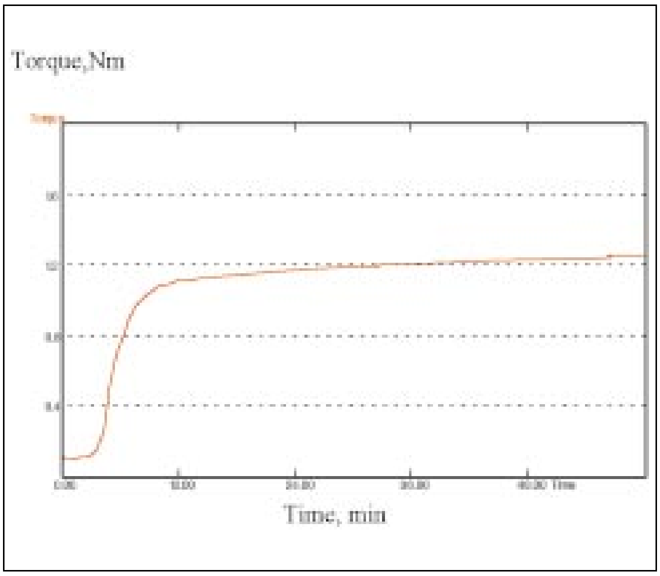

Fig. 6. Cure characteristics at 120 °C

Tab. 8. Stress-strain data (150 °C/4′)

Properties	02	12	FINAL
	2.0 ZBEC 2.0ZMBT 2.0 S	2.0 ZBEC 0.3 ZMBT 2.0 S	0.7 ZBEC 3.7 ZMBT 2.0 S
Mod 100 [MPa]	2.38	2.04	2.10
Mod 300 [MPa]	8.63	7.67	8.01
Tensile [MPa]	18.30	22.76	21.10
Elongation [%]	440	530	510

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