

# Role of PbO in Covulcanization of Carboxylated Nitrile-Polyacrylic Rubber Blend in the Presence of Ethylene Thiourea or Mercaptobenzothiazole

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## SYNOPSIS

The effects of metal oxide (PbO) on covulcanization of the blend [carboxylated nitrile rubber (XNBR)-Polyacrylic rubber (ACM) = 50 : 50] in the presence of 2-mercaptobenzothiazole (MBT) or ethylene thiourea (ETU) have been evaluated to elucidate the curing mechanism. The optimum mole ratio of ETU-PbO and MBT-PbO with respect to cure characteristics and physical properties have been found to be 1 : 1.5 and 1 : 0.5, respectively. The examination of infrared (IR) spectra reveals that crosslinking occurs at the C—Cl cure site of the ACM and COOH cure site of the XNBR. Based on the optimum mole ratios and spectral analysis a scheme of reactions has been proposed. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

The modification of polymer properties through blending has been increasing in order to obtain an inexpensive material with improved properties. Carboxylated nitrile rubber (XNBR) has excellent performance at moderate temperatures and excellent oil resistance, but its high-temperature application and ozone resistance are not satisfactory.<sup>1</sup> Blending of XNBR with infrared (IR), epichlorohydrin-ethylene oxide copolymer (ECO), chlorosulfonated polyethylene (CSM), poly chloroprene (CR), poly vinyl chloride (PVC), and epoxidized natural rubber for better properties have been examined by several authors.<sup>2-7</sup> Polyacrylic rubbers (ACM) have excellent swell, heat, and ozone resistance properties. However, its low-temperature flexibility and processibility are not satisfactory.<sup>8</sup> Recently, Das et al. have studied the ACM-NBR blends<sup>9</sup> to improve its properties. We have already determined the optimum mole ratio of ethylene thiourea-metal oxide (ETU-PbO) (1 : 1) and 2-mercaptobenzothiazole-PbO (MBT-PbO) (1 : 2) in curing acrylic rubber.<sup>10-11</sup>

In the present work we have proposed to study the 50 : 50 blend of XNBR and polyacrylic rubber, and reported the optimum mole ratio of ETU-PbO and MBT-PbO covulcanization of the blend. Based on this mole ratio and IR spectral studies, a scheme of reaction has been put forward.

## EXPERIMENTAL

Compounding formulations are given in Tables I and II. Mixing was done in a two-roll laboratory size open mixing mill. Polyacrylic rubber and XNBR used were Nipol-AR-51 and Nipol-N-34 varieties, respectively, of Nippon Zeon Co Ltd., Japan. Metal oxide used was PbO. Ethylene thiourea was from DuPont, USA, and MBT was from ICI Ltd., India. Continuous cure characteristics were studied in Monsanto rheometer (R-100) at 170, 180, and 190°C. Physical properties were measured on cured sheets. The curing was done in a hydraulic press using a mold at 170°C and 3000 psi, up to the optimum cure time (obtained from rheometric  $t_{90}$  value). Tensile properties such as tensile strength and elongation at break were measured with the help of a universal testing machine. Hardness was determined using a durometer. Swelling coefficient was calculated by swelling the vulcanizate in the toluene

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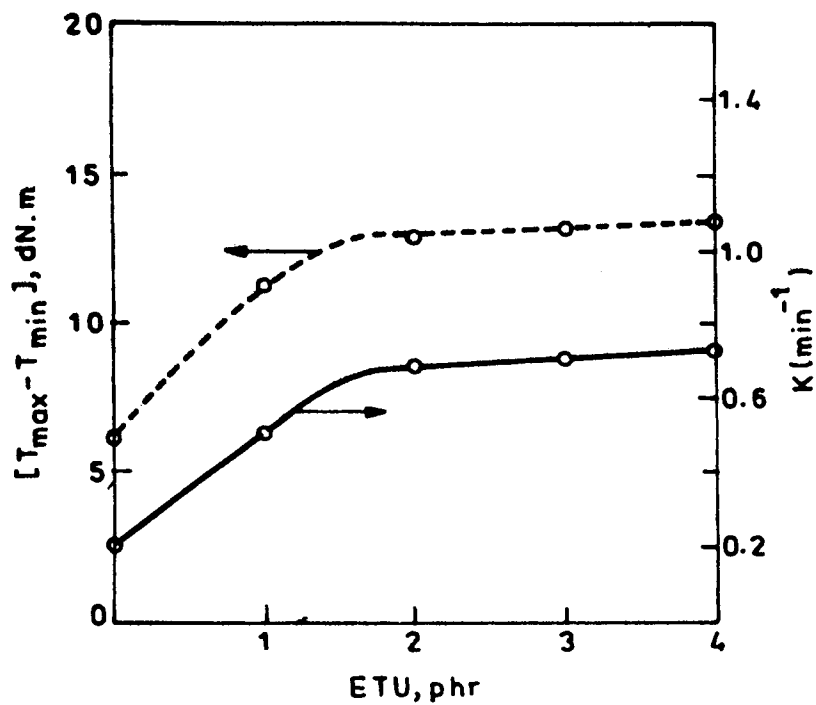


Figure 1 Variation of the state ( $T_{max} - T_{min}$ ) and rate constant ( $k$ ) of cure with the ETU at fixed level of PbO (4 phr).

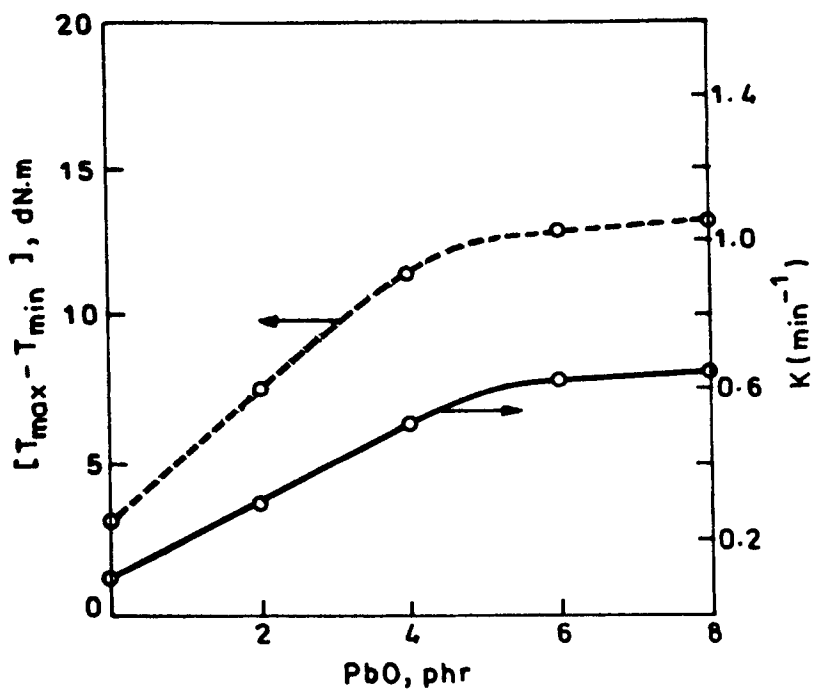


Figure 2 Variation of the state ( $T_{max} - T_{min}$ ) and rate constant ( $k$ ) of cure with the PbO at fixed level of ETU (1 phr).

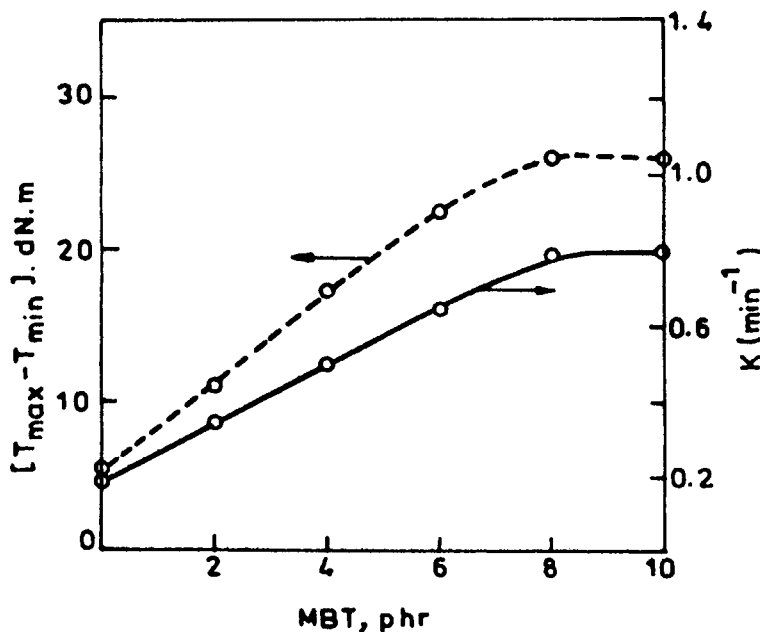


Figure 3 Variation of the state ( $T_{max} - T_{min}$ ) and rate constant ( $k$ ) of cure with the MBT at fixed level of PbO (4 phr).

of crosslink density with the increase of curative concentration.

### Physical Properties

Physical properties of the vulcanizates containing ETU and PbO are given in Table III, which reflects

that the hardness, modulus, and tensile strength increase, however, elongation at break decreases with the increase of either ETU (at a fixed level of PbO) or PbO (at a fixed level of ETU). Similar trends are noticed in the system containing MBT (Table IV) where hardness, modulus, and tensile strength increase and elongation at break decreases as concentration of curatives are increased.

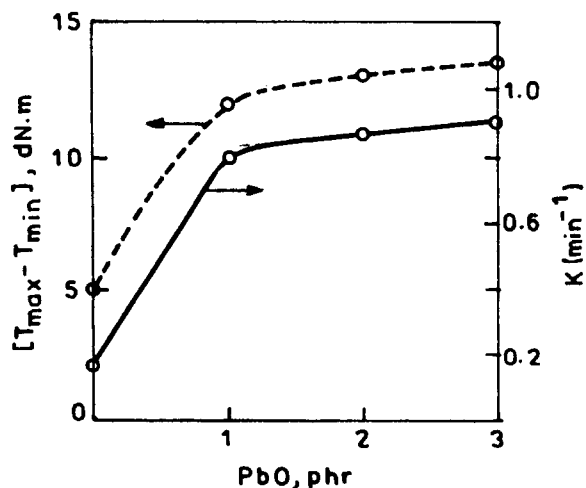


Figure 4 Variation of the state ( $T_{max} - T_{min}$ ) and rate constant ( $k$ ) of cure with the PbO at constant level of MBT (2 phr).

### Spectral Analysis

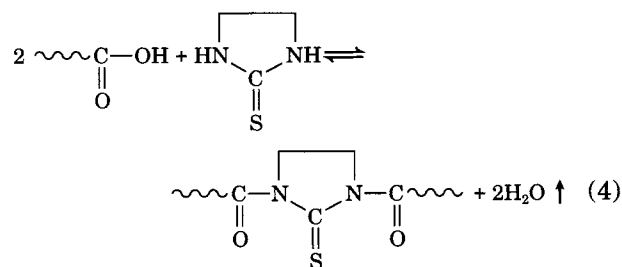
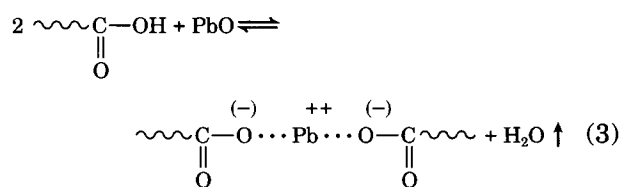
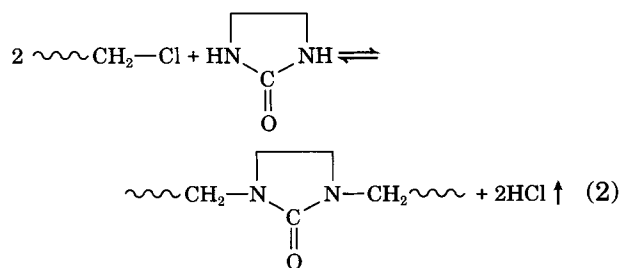
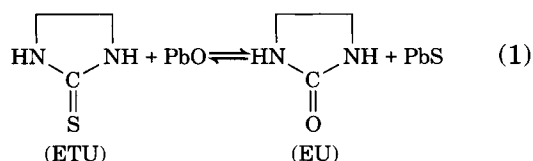
Figure 5 shows the IR spectra of the blend (ACM-XNBR) and the blend cured with ETU and PbO (compound B). A sharp peak at  $700\text{ cm}^{-1}$ , which is present in the spectrum of the blend, is absent in the spectrum of compound B. A comparison of the spectra also shows that the broad absorption band at  $1703\text{ cm}^{-1}$  of the blend is split, and new peaks appear at  $1720$  and  $1640\text{ cm}^{-1}$  in the spectrum of compound B. The peaks at  $700$ ,  $1703$ ,  $1720$ , and  $1640\text{ cm}^{-1}$  are due to the C—Cl,<sup>13</sup> carboxylic acid group,<sup>14</sup> carbonyl group of five-membered cyclic structure,<sup>15</sup> and C=O of an amide,<sup>16</sup> respectively. Thus it may be assumed that the C—Cl and COOH cure sites of the blend react, and a five-membered cyclic bridge with an amide type of linkage are formed (see mechanism given later). The presence of peaks at  $1170$

**Table III Physical Properties of the Vulcanizates (Cured at 170°C)**

Sample Nos.	A	B	C	D	E	F	G	H	I
Swelling (%)	557	450	445	440	435	580	500	445	440
Hardness (shore A)	40	60	62	64	65	35	50	63	64
Modulus, 300% (N/mm <sup>2</sup> )	0.02	0.05	0.06	0.07	0.08	0.01	0.02	0.06	0.07
Tensile strength (N/mm <sup>2</sup> )	0.13	0.40	0.45	0.50	0.55	0.10	0.20	0.50	0.52
Elongation at break (%)	1650	1200	1180	1160	1150	1700	1500	1150	1140

and 1600 cm<sup>-1</sup> in the spectrum of compound B may be due to the presence of C—N bond of a tertiary amine<sup>17</sup> and carboxylate anion.<sup>18</sup> Figure 6 shows the IR spectra of the blend (ACM-XNBR) and compound C<sub>5</sub>, which contains MBT and PbO as curatives. Like the ETU system, a sharp peak at 700 cm<sup>-1</sup> of the blend is absent in the spectrum of compound C<sub>5</sub>, and new peaks appear at 1150, 1600, and 686 cm<sup>-1</sup> in the spectrum of compound C<sub>5</sub>. The absorption peaks at 700, 1600, and 685 cm<sup>-1</sup> are assigned as the stretching frequencies of the C—Cl,<sup>13</sup> ether linkage (C—O—C),<sup>10</sup> carboxylate anion,<sup>18</sup> and C—S—C linkages,<sup>19</sup> respectively.

Based on the above cure characteristics and spectral analysis, a probable scheme of reactions for the system containing ETU and PbO is proposed as follows:


**Table IV Physical Properties of the Vulcanizates (Cured at 170°C)**

Sample Nos.	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>
Swelling (%)	560	530	470	380	350	345	560	525	520	515
Hardness (shore A)	40	45	55	65	70	72	42	44	46	48
Modulus, 300% (N/mm <sup>2</sup> )	0.02	0.05	0.10	0.15	0.20	0.25	0.04	0.06	0.08	1.0
Tensile strength (N/mm <sup>2</sup> )	0.13	0.40	0.80	1.0	1.2	1.3	0.15	0.50	0.60	0.70
Elongation at break (%)	1650	1370	1230	1100	1050	1040	1500	1350	1370	1390

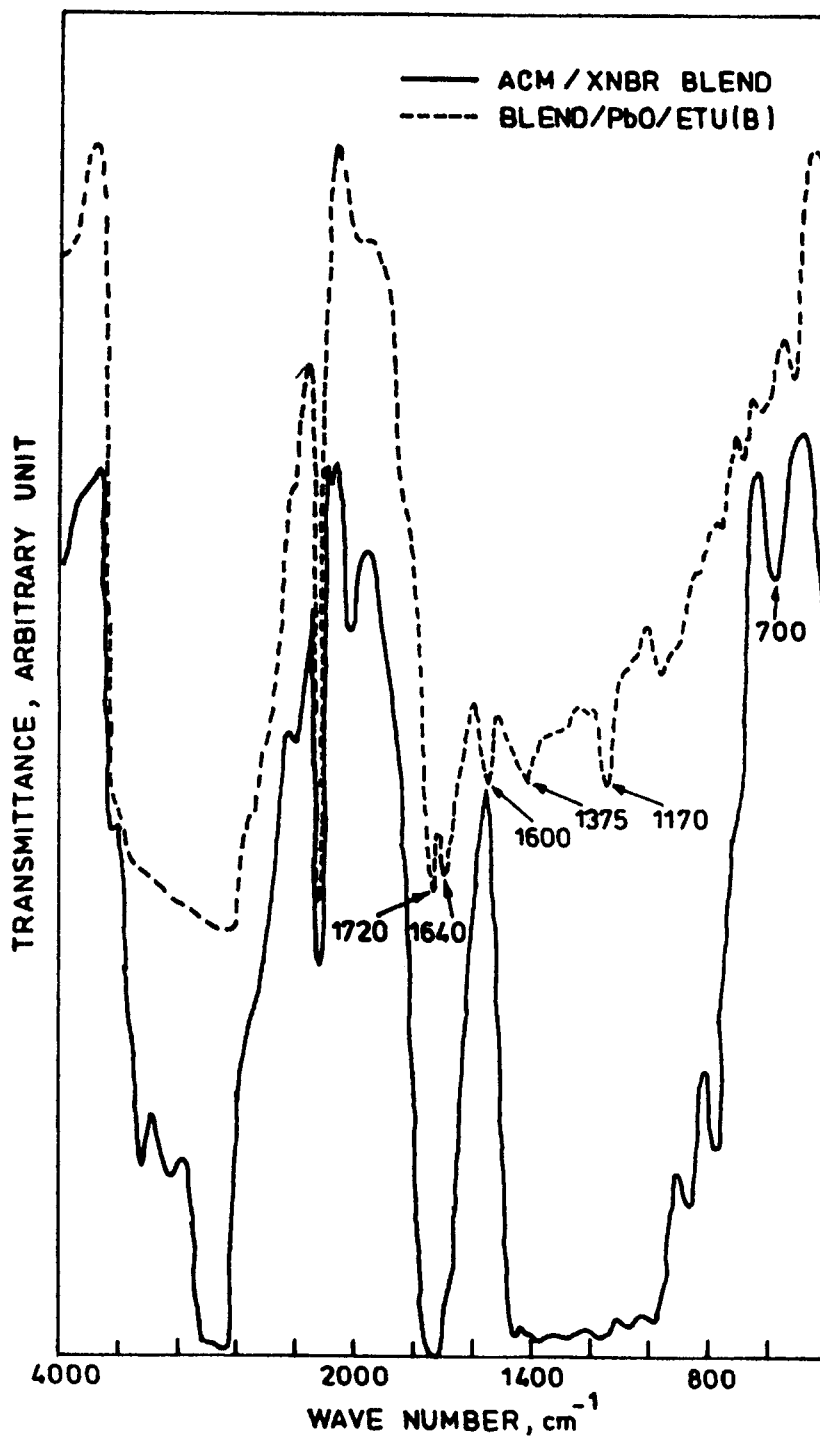


Figure 5 IR spectra of the blend (ACM-XNBR = 50 : 50) and compound B.

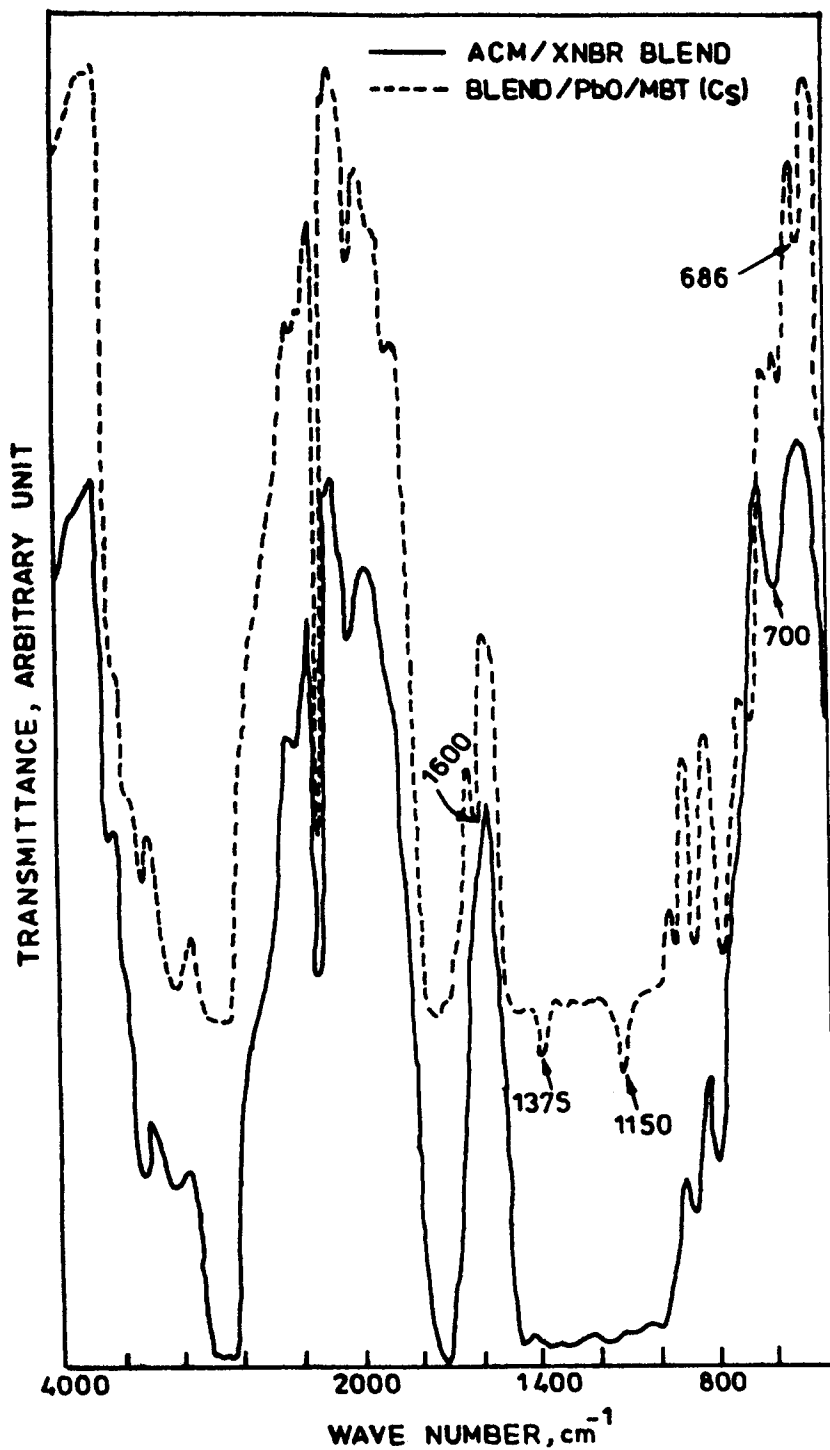
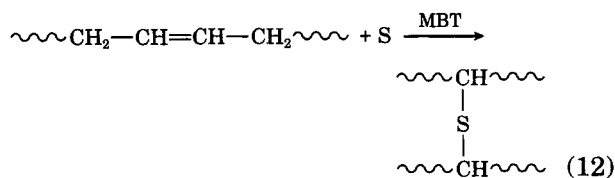
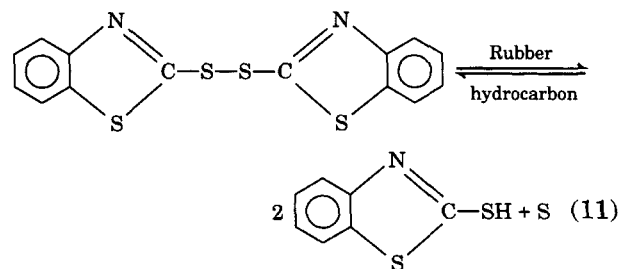
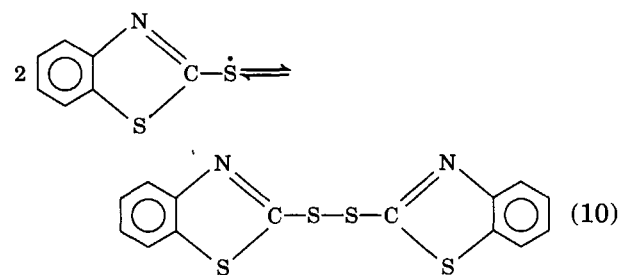
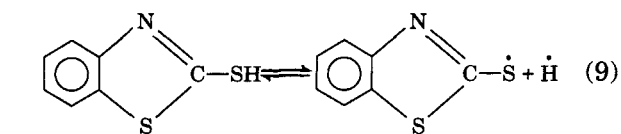
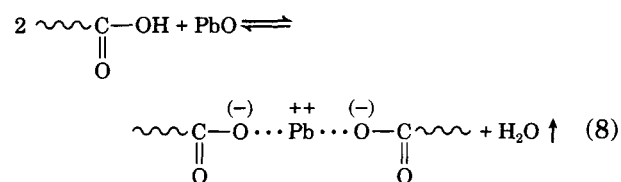
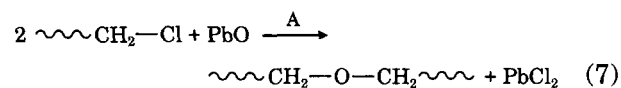
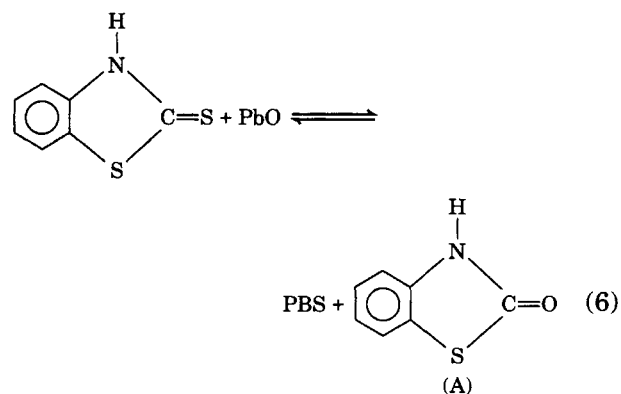
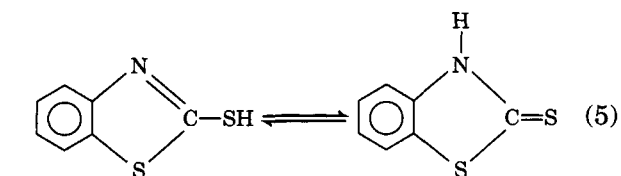


Figure 6 IR spectra of the blend (ACM-XNBR = 50 : 50) and the compound C<sub>5</sub>.

Similarly, a scheme of reactions for the system containing MBT and PbO is proposed as follows:



The formation of PbS through reactions (1) and (5) has been confirmed by chemical analysis as described earlier.<sup>10</sup> The slow release of ethylene urea (EU) through reaction (1) initiate the formation of five-membered cyclic bridge<sup>20</sup> (reaction 2). PbO reacts with carboxylic acid group of the polymer and forms a metal ion bridge<sup>21</sup> [reactions (3) and (8)]. Ethylene thiourea can react with the COOH group of polymer, forming the amidic type of linkage through reaction (4). But this type of crosslinking may not be predominant as at the optimum ratio, the PbO consumption in the blend is more than in the polyacrylic rubber alone,<sup>10,11</sup> suggesting the formation of a salt bridge. The formation of an ether type of linkage through reaction (7) has been confirmed earlier.<sup>10</sup> It has been reported<sup>22</sup> that the free sulfur is released through reactions (9)–(11) in the presence of rubber hydrocarbon. This free sulfur in conjunction with MBT leads to the formation of monosulfidic linkage (reaction 12). Reactions (3), (4), and (12) are probably responsible for the ability of PbO, ETU, and MBT alone in curing the blend. The higher state of cure in the case of MBT–PbO system than ETU–PbO system and the consumption of comparatively more amount of MBT suggest the formation of sulfidic linkage resulting in a high tensile strength.

## CONCLUSIONS

The effectiveness of ethylene thiourea and mercaptobenzothiazole in cocuring of the 50 : 50 blend of the acrylic rubber and carboxylated nitrile rubber is enhanced in the presence of PbO, which facilitates the crosslinking through the formation of lead sulfide and metal ion bridges. In conjunction with PbO, mercaptobenzothiazole lead to a higher extent of curing of the blend than ethylene thiourea, probably through the monosulfidic linkages.

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