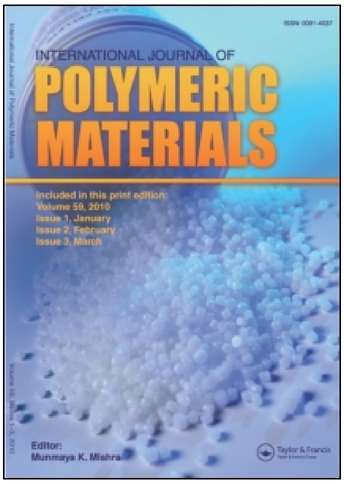

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Use of Group IVB Metal Oxides for Curing Polyacrylic Rubber

P. Chowdhury[a]; M. C. Chakravorti[a]; C. K. Das[b]
[a] Department of Chemistry, Indian Institute of Technology, Kharagpur, India [b] Materials Science Centre, Indian Institute of Technology, Kharagpur, India

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Use of Group IVB Metal Oxides for Curing Polyacrylic Rubber

P. CHOWDHURY and M. C. CHAKRAVORTI
Department of Chemistry, Indian Institute of Technology, Kharagpur - 721 302, India

and

C. K. DAS
Materials Science Centre, Indian Institute of Technology, Kharagpur - 721 302, India

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Group IVB metal oxides, both with and without ethylene thiourea (ETU) have been used to cure polyacrylic rubber (ACM). Curing characteristics and properties of the vulcanizates have been studied with a view to elucidate curing mechanism with special reference to the role of metal oxides (e.g. SnO, SnO_2, PbO, PbO_2 and Pb_3O_4). Best results are obtained with Pb_3O_4 in the presence of ETU and with SnO in the absence of ETU. PbO-SnO or PbO_2-SnO blends provide no synergistic effect. In the presence of ETU, the formation of metal sulphide and metal chloride in the vulcanizate is confirmed by XRD and XPS. Studies on IR spectra show that crosslink occurs at the C—Cl cure site of the polymer. Based on the experimental results a mechanistic reaction scheme has been put forward.

KEY WORDS Polyacrylic rubber, curing, metal oxide, ETU

INTRODUCTION

Polyacrylics (ACM) are speciality elastomers mostly used in automobiles. Their use in hot oil and high temperature applications dictates the criteria for designing their chemical structure as well as curing systems. Polyacrylics have saturated backbone but cure is possible via inherent and copolymerized reactive cure site.[1,2] All commercially important polyacrylics have a small percentage (1–5%) of reactive cure sites, usually a chlorine. The reactivity of the chlorine atom present in the reactive site largely influences the curing systems to be adopted. When the reactivity is not very high, powerful cure systems such as secondary polyamines/sulphur, triethylene tetramine/MBTS or Diak no. 1/Dyphos[3] have to be used. The development of more effective red lead/ethylene thiourea cure system[4,5] has been reported. The exact curing mechanisms of these systems are yet to be studied.

NIPOL-AR-51 is a new type of commercial polyacrylic rubber. Recently Das *et al.*[6,7] have studied the efficient blend and sulphenamide based cure systems of NIPOL-AR-51. In the present work, both bivalent and tetravalent metal oxides of

TABLE I

Formulation of compounds using different metal oxides (in g)

Compounds Nos.	A	B	C	D	E
Polyacrylic rubber (NIPOL-AR-51)	100	100	100	100	100
ETU	1	1	1	1	1
SnO	4	-	-	-	-
SnO_2	-	4	-	-	-
PbO	-	-	4	-	-
PbO_2	-	-	-	4	-
Pb_3O_4	-	-	-	-	4

TABLE II

Cure characteristics and physical properties

Compounds Nos.	A	B	C	D	E
Scorch time (minutes)	15	-	10	12	11
$[T_{max}-T_{min}]$ (dN.m)	5	-	8	7	12
Rate constant (min.$^{-1}$)	0.40	-	0.44	0.48	0.50
Tensile strength (KPa)	98	-	1275	687	1079
Elongation at break (%)	1400	-	1010	1000	1200
Modulus at 300% elongation (KPa)	10	-	88	78	98
Hardness (Shore A)	30	-	36	35	40
Swelling coefficient	15	-	9.5	10	8

group IVB have been used to achieve good curing in the presence and absence of ethylene thiourea (ETU). Crosslinking mechanism has been studied with the help of spectral analysis and special efforts have been made to find out an efficient blend of oxides to cure acrylic rubber.

TABLE III

Compound formulation using different ratios of ETU to metal oxides

Compound Nos.	F	G	H	I	J	K	L	M	N	O
Polyacrylic rubber (NIPOL-AR-51)	100	100	100	100	100	100	100	100	100	100
ETU	1.5	2	3	4	5	2	2	2	2	2
PbO	4	4	4	4	4	1	2	6	8	10

TABLE IV

Physical properties of the vulcanizates

Compound Nos.	F	G	H	I	J	K	L	M	N	O
Tensile strength (KPa)	1177	1080	1060	1020	785	880	1030	1687	3140	3140
Elongation at break (%)	950	890	880	860	850	870	890	1070	1110	1120
Modulus at 300% elongation (KPa)	108	118	98	78	58	59	68	147	196	215
Hardness (Shore A)	37	40	38	35	30	32	34	45	50	55
Swelling coefficient	6.0	5.0	5.5	5.6	5.7	5.7	5.6	4.8	4.5	4.4

EXPERIMENTAL

Compounding formulations are given in Tables I, III and V. The rubber was masticated and mixed with metal oxides and ethylene thiourea (ETU) in a two roll laboratory size (15.2 cm × 15.2 cm) open mixing mill with a nip gap 0.09 cm, friction ratio 1:1.25 and temperature 40 ± 2°C.

Polyacrylic rubber used was NIPOL-AR-51 of Nippon Zeon Co. Ltd., Japan. Metal oxides used were SnO_2, SnO, PbO, PbO_2 and Pb_3O_4. ETU was from Dupont, USA.

Continuous cure characteristics were studied in Monsanto Rheometer (R-100) at 170, 180 and 190°C. Physical properties were measured on cured sheets (15.2 cm × 15.2 cm × 0.15 cm). The curing was done in a hydraulic press using a mould at 170°C and 3000 psi up to optimum cure time (obtained from Rheometric t_{90} value). Tensile properties like tensile strength, modulus and elogation at break were measured with the help of a universal testing machine as per ASTM D412-

TABLE V

Compound formulations using mixture of metal oxides (in g)

Compound Nos.	M_1	M_2	M_3	M_4	M_5	M_6	M_7	M_8	M_9
Polyacrylic rubber (NIPOL-AR-51)	100	100	100	100	100	100	100	100	100
ETU	2	2	2	2	2	2	2	2	2
SnO	4	3	2	1	-	3	2	1	-
PbO	-	1	2	3	4	-	-	-	-
PbO_2	-	-	-	-	-	1	2	3	4

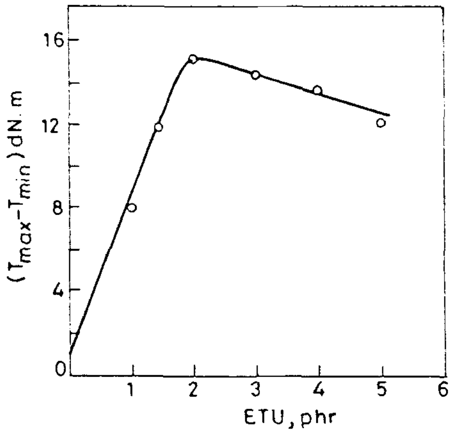

FIGURE 1 Variation of state of cure ($T_{max} - T_{min}$) with ethylene thiourea (ETU) at fixed level of PbO (4 phr).

80 test method. Hardness (shore A) was determined using a Durometer according to ASTM D1415-56T test method. Swelling coefficient was determined by swelling the vulcanizate in toluene at 25°C for 72 hours, using the relation[8]

$$q = \frac{m - m_0}{m_0} \times \frac{1}{p_1}$$

where q, m, m_0 and p_1 are the swelling coefficient, weight of the swollen sample, original weight of the sample and density of the solvent, respectively. Infrared spectra were recorded on press cured thin film using a Perkin Elmer (No. 883) spectrophotometer. X-ray diffraction patterns were obtained employing Philip's PW 1840 diffractometer using nickel filtered Cu-K_α radiation. Electron spectra for chemical analysis (ESCA) was done with ESCA spectrophotometer (V.G. Scientific, MK II, U.K.) using Mg-K_α radiations.

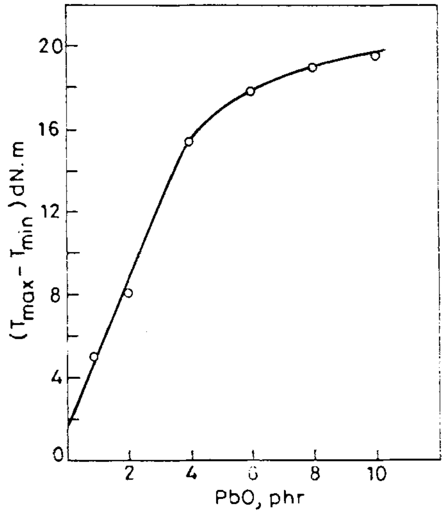

FIGURE 2 Variation of state of cure ($T_{max} - T_{min}$) with PbO at fixed level of ethylene thiourea (2 phr).

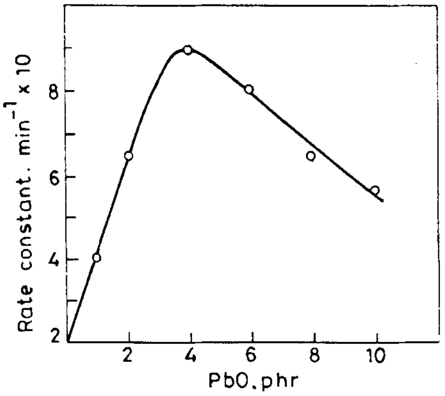

FIGURE 3 Variation of rate constant with PbO at fixed level of ethylene thiourea (2 phr).

RESULTS AND DISCUSSION

Cure Characteristics

Oxides of group IVB metals (SnO, SnO_2, PbO, PbO_2 and Pb_3O_4) were tested both in the presence (Table I) and absence of ETU to cure polyacrylic rubber (NIPOL-AR-51). In the absence of ETU, these oxides remain ineffective except SnO which gives rise to a low state of cure ($T_{max} - T_{min}$)† at 12 phr‡ of loading. However, in the presence of ETU, all the said oxides except SnO_2 are able to cure polacrylic, although to a different extent. Inability of SnO_2 may be due to its chemical inertness.

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†The difference between maximum and minimum rheometric torque which is termed as state of cure.

‡Abbreviation for parts per hundred grams of rubber.

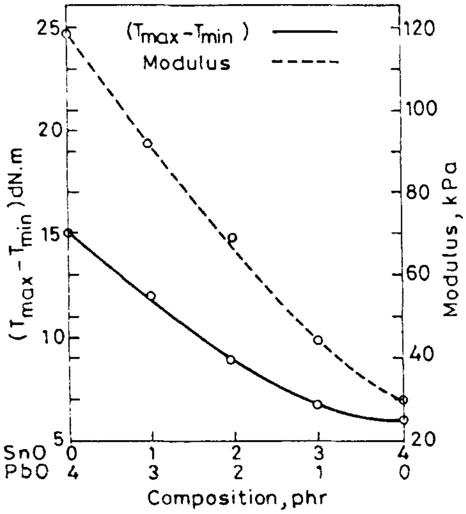


FIGURE 4 Variation of state of cure (T_{max} − T_{min}) and modulus at 300% elongation with the composition of SnO-PbO blends.

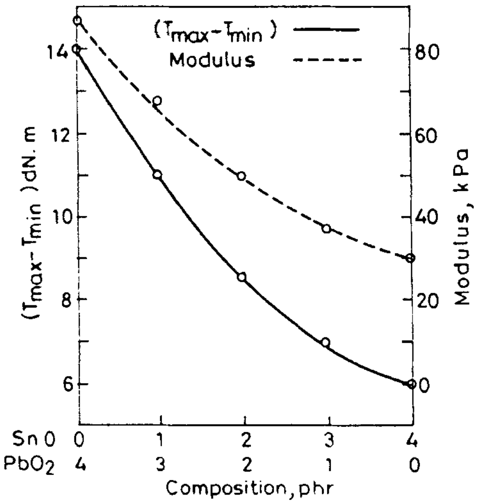


FIGURE 5 Variation of state of cure (T_{max} − T_{min}) and modulus at 300% elongation with the composition of SnO-PbO_2 blends.

Comparative cure characteristics of different compounds (A to E) containing group IV B metal oxides in the presence of ETU are shown in Table II. It is observed that the system containing Pb_3O_4 (compound E) gives rise to the highest state and rate of cure. PbO-ETU system (compound C) shows more state of cure than that of PbO_2-ETU system (compound D). SnO-ETU (compound A) exhibits much lower state and rate of cure. The highest scorch time of the system containing PbO_2 may be ascribed to its delayed action in the vulcanization.

To find out the optimum ratio of PbO to ETU, several compounds have been made (Table III) and their curing characteristics have been studied (Figures 1–3).

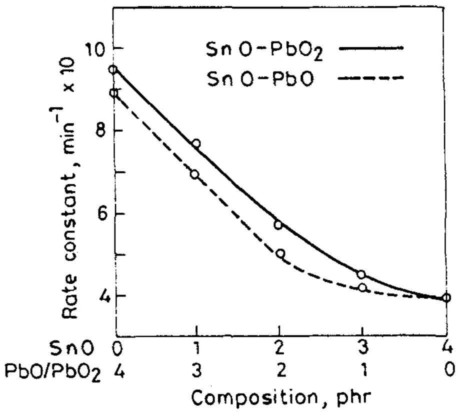


FIGURE 6 Variation of rate constant with the composition of both SnO-PbO and SnO-PbO$_2$ blend systems.

TABLE VI

Physical properties of the vulcanizates

Compound Nos.	M_1	M_2	M_3	M_4	M_5	M_6	M_7	M_8	M_9
Tensile strength (KPa)	108	390	590	880	1080	295	590	785	1080
Elongation at break (%)	1900	1200	1130	1040	890	900	900	830	910
Hardness (Shore A)	20	25	30	35	40	22	25	35	38
Swelling coefficient	12.2	12.1	8.0	6.0	5.0	12	10.5	10.3	5.6

Figure 1 shows that the state of cure increases with the increase of ETU content of the compounds at a fixed level of PbO (4 phr). The curve shows a maximum at 2 phr of ETU and then decreases with a further increase of ETU. Thus, 4 phr PbO with 2 phr ETU provides the highest extent of cure. The calculated mole ratio at the maximum is approximately PbO:ETU = 1:1. The decrease of state of cure with the increase of ETU content beyond the maximum may be due to the masking of PbO by ETU. Figure 2 shows the change of state of cure of the compounds with the variation of PbO content at a fixed level of ETU (2 phr). The state of cure increases continuously exhibiting different slopes with the increase of PbO content. The change in slope occurs at 4 phr of PbO, i.e. at the mole ratio PbO:ETU $\approx$ 1:1 and then the system maintains a marginal increment in the state of cure with the gradual increase of PbO content. This marginal increment of state of cure may be due to the effect of excess PbO. The variation of rate constant with PbO at fixed amount of ETU (2 phr) is shown in Figure 3. It is found that the rate of cure increases with the increase of PbO

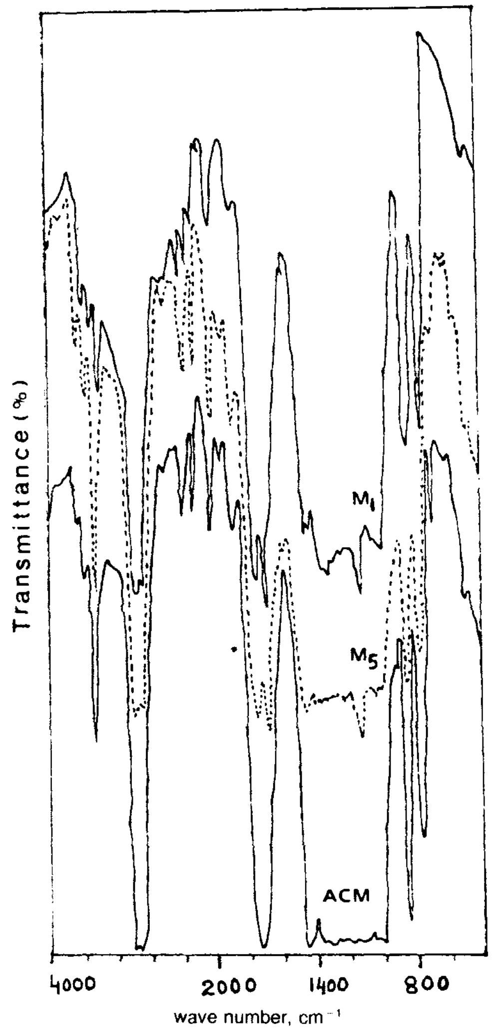


FIGURE 7 IR spectra of the polyacrylate (ACM), compound M_5 and compound M_1.

content and reaches a maximum at 4 phr of PbO and then drops. The most effective rate of cure is obtained at the mole ratio of PbO:ETU $\approx$ 1:1.

In order to examine the effect of binary mixture of oxides towards curing behavior, different compounds have been made (Table V) and their curing characteristics are studied (Figures 4–6). Gradual replacement of more basic PbO by less basic SnO leads to gradual decrease in the state (Figure 4) and rate of cure (Figure 6). Similarly, gradual replacement of strongly oxidizing PbO_2 by the strongly reducing SnO leads to gradual decrease of both state and rate (Figure 6) of cure.

Swelling Studies

Swelling coefficient values of the compounds containing different metal oxides with ETU are shown in Table II which shows that the swelling coefficient of the system

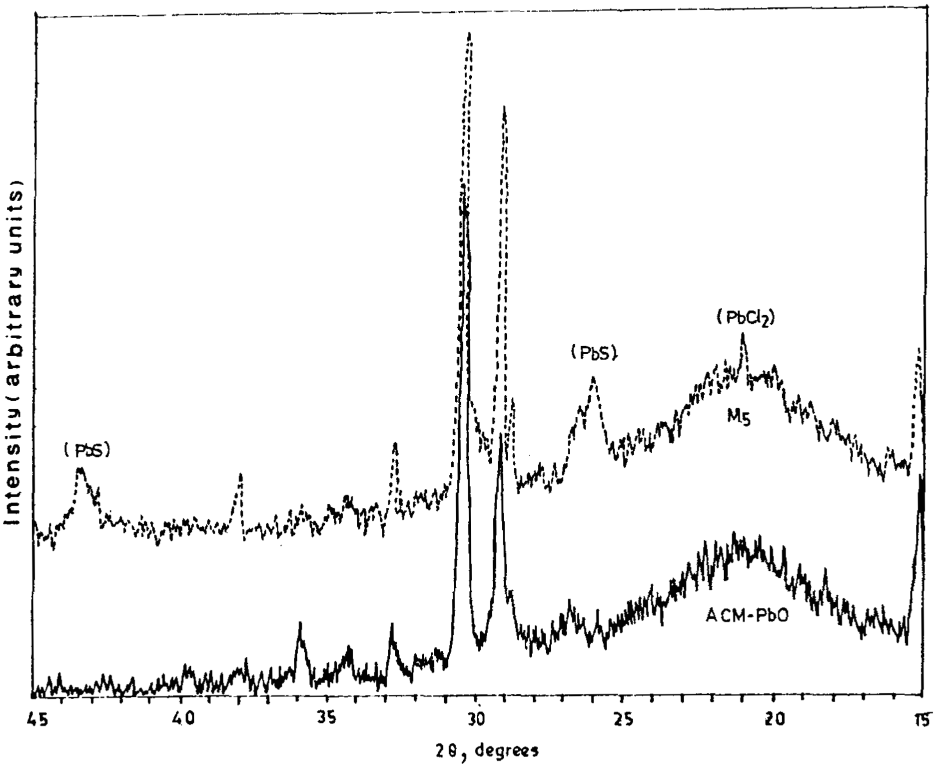


FIGURE 8 X-ray diffractogram of the polyacrylate (ACM) with PbO and compound M_5.

containing Pb_3O_4 (compound E) is least. This means that crosslink density is the highest in the vulcanizate having Pb_3O_4 as accelerator. The system containing SnO_2 (compound B) is highly swelled in the test solvent. Swelling coefficients of the compounds (F to O) containing different PbO:ETU ratio are given in Table IV which shows that when PbO loading is fixed at 4 phr, the curing system containng 2 phr of ETU (compound G) gives rise to the lowest swelling coefficient value. However at 2 phr of ETU, swelling coefficient continues to decrease marginally with gradual increase of PbO content (from compounds K to O). This result exhibits good consistency with the state of cure values. Swelling coefficients of the compounds (M_1 to M_9) having mixed metal oxides are shown in Table VI. Gradual replacement of either SnO by PbO or SnO by PbO_2 decreases the swelling coefficient value (compounds M_1 to M_5 and M_6 to M_9, respectively).

Physical Properties

Physical properties of the compounds containing different metal oxides with ETU are shown in Table II. The system containing Pb_3O_4 (compound E) provides the highest modulus and hardness, followed by PbO (compound C). However, the system containing PbO gives rise to the highest tensile strength. It is observed that the system containing SnO (compound A) is associated with poor physical properties.

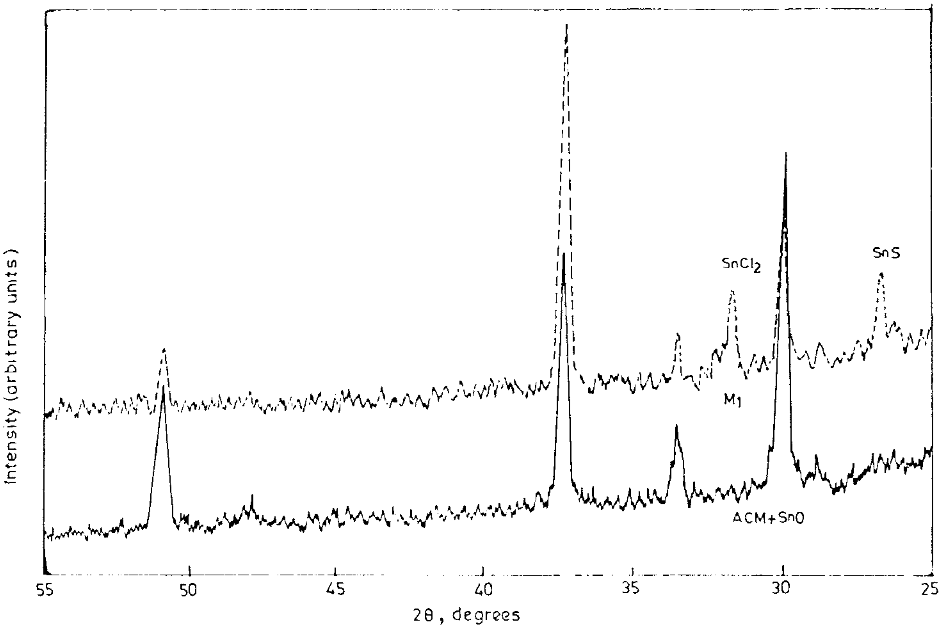


FIGURE 9 X-ray diffraction of the polyacrylate (ACM) with SnO and compound M_1.

Physical properties of the systems containing different ratios of PbO to ETU are given in Table IV which shows that tensile strength increases with the increase of PbO content up to 8 phr loading and then remains constant. However, tensile strength decreases continuously with the gradual increase of ETU loading at fixed level of PbO. Curing systems containing 2 phr of ETU with 8 phr of PbO (compound N) provides the best tensile strength. Elongation at break decreases with the increase of ETU content while elongation at break increases with the increase of PbO content.

Physical properties of the combined metal oxide systems are shown in Table VI. Tensile strength increases as SnO is being replaced by PbO or PbO_2. However, elongation at break decreases drastically with the replacement of stannous oxide by lead oxides (PbO and PbO_2). The change of modulus, according to the composition (Figures 4 and 5), shows that modulus increases with the incrase of lead oxides (PbO or PbO_2) content which is in line with the variation of state of cure with composition. Hardness value attains its highest in the system which contains exclusively either PbO or PbO_2.

Infrared Spectral Analysis

Figure 7 shows the IR spectra of the original polymer (ACM), polymer cured with PbO and ETU (compound M_5) and polymer cured with SnO and ETU (compound M_1). A sharp peak at 700 cm^{-1} which is present in the original polymer is absent in the spectra of M_5 and M_1. A comparison of the spectra also shows that the broad absorption band at 1746 cm^{-1} of the original polymer is split in the spectrum of the vulcanizates and a new peak at 1720 cm^{-1} appears in the spectra of M_5 and

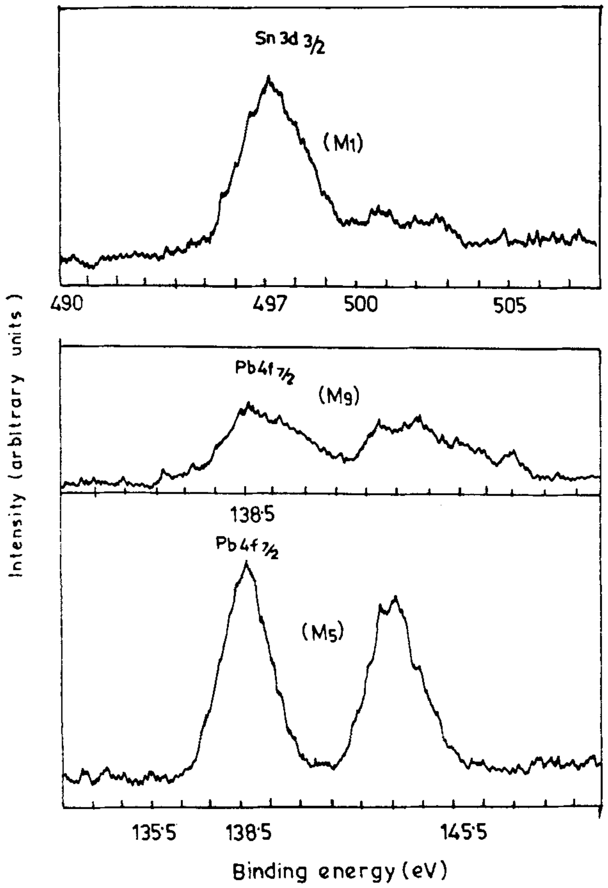


FIGURE 10 $Pb_{4f_{7/2}}$ X-ray photoelectron spectra of the compounds M_5 and M_9 and $Sn_{3d_{3/2}}$ spectra of the compound M_1.

M_1. Peaks at 700 and 1720 cm^{-1} are due to C—Cl[9] and C═O (carbonyl group of five membered cyclic structure)[10,11] bond stretching frequencies respectively. Thus, it may be assumed that the C—Cl of the original polymer is reacting and a compound having a five membered cyclic structure is formed during crosslinking reaction. The presence of a peak at 1170 cm^{-1} in the spectra of M_5 and M_1 may be due to the presence of C—N bond of a tertiary amine.[10,12]

X-ray Diffraction Studies

Representative examples of the X-ray diffraction patterns of the reference compound containing polymer (ACM) and PbO and compound M_5 containing polymer in presence of PbO and ETU are given in Figure 8. A comparison of the patterns of compound M_5 with that of the reference compound reveals that peaks at 2θ values of 21.0, 26.6, 28.8 and 43.5° which are present in the spectra of M_5 are absent in the spectrum of the reference compound. According to literature[7] a peak at 2θ value of 21.0° is due to $PbCl_2$ while PbS gives peaks at 26.6 and 43.5 degrees.

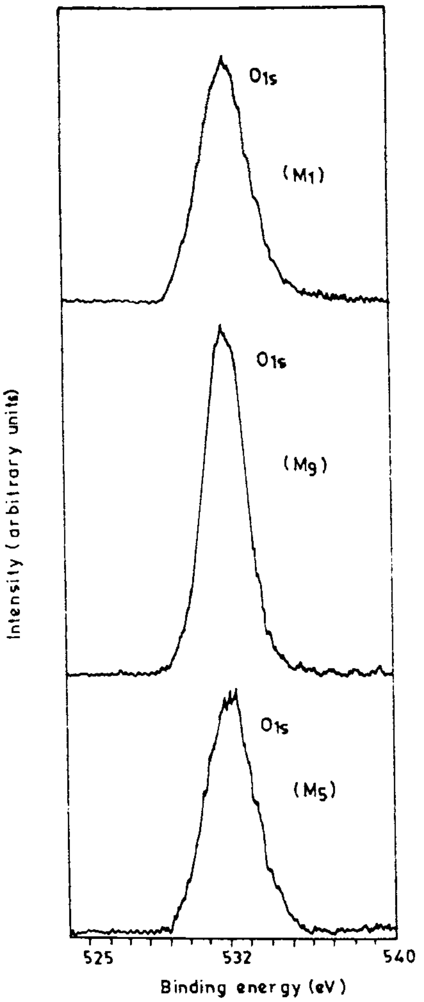


FIGURE 11 O_{1s} X-ray photoelectron spectra of the compounds M_5, M_9 and M_1.

Thus it may be assumed that $PbCl_2$ and PbS are formed during crosslinking reaction. X-ray diffraction patterns for the reference compound containing polymer and SnO and compound M_1 containing polymer with SnO and ETU are shown in Figure 9. Inspection of the spectra of compound M_1 and the reference compound shows that peak at 2θ values of 26.4 and 31.8 degrees which are present in the spectra of M_1 are absent in the spectra of the reference compound. Peaks at 2θ values of 26.4 and 31.8 degrees are due to SnS and $SnCl_2$, respectively.[13]

Electron Spectroscopy for Chemical Analysis

Representative examples of the X-ray photoelectron spectra (XPS) of the polymer cured with PbO and ETU (compound M_5), polymer cured with PbO_2 and ETU (compound M_9) and polymer cured with SnO and ETU (compound M_1) are shown

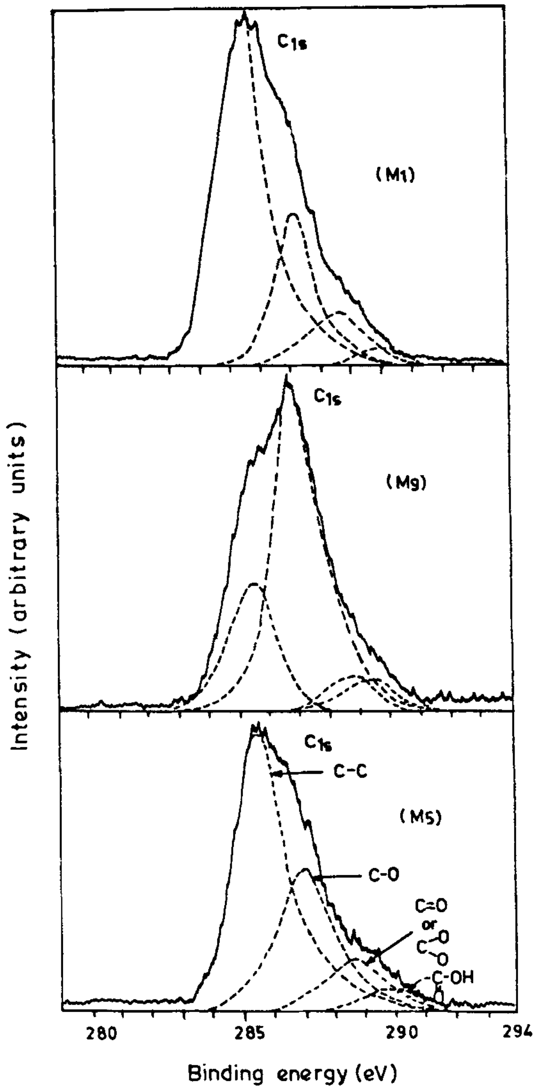
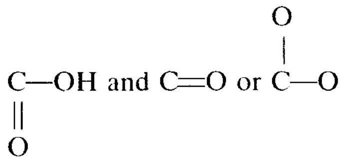


FIGURE 12 High resolution C_{1s} X-ray photoelectron spectra of the compounds M_5, M_9 and M_1.

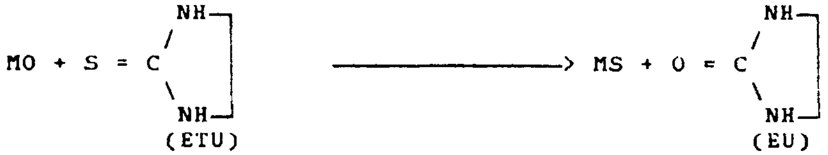
in Figures 10–12, respectively. Figure 10 shows the $Pb_{4f_{7/2}}$ spectra of compounds M_5 and M_9 and $Sn_{3d_{3/2}}$ spectrum of compound M_1. Figures 11 and 12 show the O_{1s} and high resolution C_{1s} spectra, respectively. Comparison and characterization of the $Pb_{4f_{7/2}}$ spectra of M_5 and M_9 reveal that lead remains in single distinct oxidation state in the system containing PbO (compound M_5) and two distinct oxidation state in the system containing PbO_2 (compound M_9). $Sn_{3d_{3/2}}$ spectrum (Figure 10) also shows the presence of single oxidation state of Sn in the system containing SnO. Considering the splitting of the peaks, the existence of higher binding energy component of $Pb_{4f_{7/2}}$ peak (Figure 10) indicates the presence of $PbCl_2$ in the system containing oxides of lead. Similarly slightly lower binding energy component of $Sn_{3d_{3/2}}$ peak (Figure 10) also suggest the formation of $SnCl_2$ during crosslinking reaction. As observed from Figure 11, the oxygen content in the environment is the highest in M_9 followed by M_1 and M_5 systems. C_{1s} spectra (Figure 12) of the systems reveal that



$$\underset{\underset{O}{\|}}{C}\text{—OH and C=O or }\overset{\overset{O}{|}}{C}\text{—O}$$

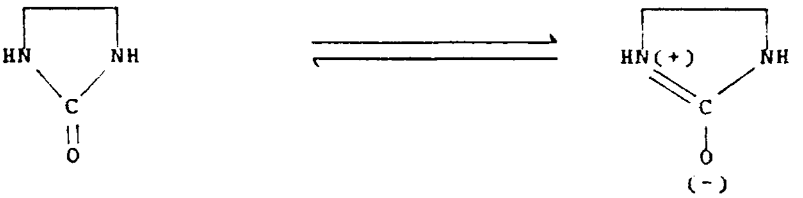
content of three systems are more or less equivalent. However C—O content is more and C—C content is less in the system containing PbO_2 as compared to PbO and SnO containing systems. This observation suggests the probable formation of metal ion bridge type crosslinking through O—C in the case of the system containing PbO_2.

Based on the spectral studies (IR, XRD and ESCA) the following reaction scheme for the curing system containing group IVB metal oxide and ethylene thiourea may be proposed.

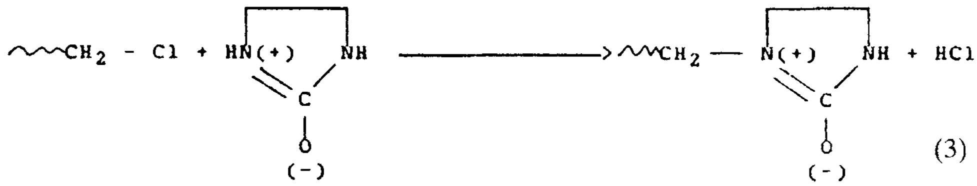


(1)

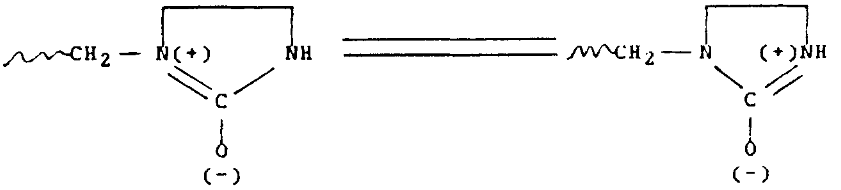
M = Pb or Sn



(2)



(3)



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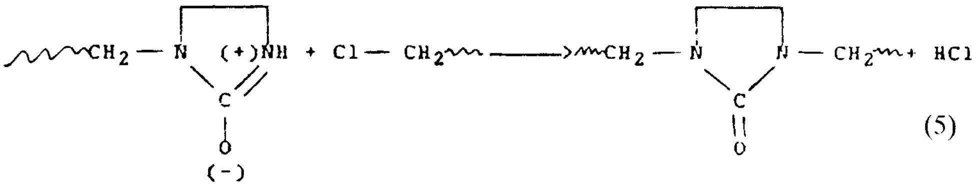

(5)

$$2HCl + MO \longrightarrow MCl_2 + H_2O\ (g) \qquad (6)$$

Reaction (1) is probably responsible for the onset of curing, which is delayed in the case of PbO_2 and to a large extent in the case of SnO_2. However, production of higher amount of ethylene urea (EU) through reaction (1) per mole of PbO_2, probably responsible for higher rate of cure in the case of PbO_2. The reaction (6) is facilitated largest extent in the case of PbO, probably due to its more basic nature than the others. The combined effect of PbO and PbO_2 in Pb_3O_4 is reflected in the higher rate and state of cure. Easy aerial oxidation of SnO and its weaker basicity may be responsible for the lower reactivity of SnO. It appears that in the presence of PbO_2, apart from crosslinking as shown in Equation (5), there may be some additional crosslinkage involving metal ion bridge as evident from ESCA.

CONCLUSIONS

Amongst the group IVB metal oxides Pb_3O_4 gives the highest rate and state of cure. This is probably due to synergistic effect of PbO and PbO_2. PbO facilitates the crosslinking by absorbing hydrogen chloride and PbO_2 through increasing the oxidation level of the polymer. Metal oxides help the crosslinking through the formation of metal sulphide and metal chloride and to some extent by metal ion bridging. No boosting effect has been observed in the case of SnO/PbO or SnO/PbO_2 mixed oxides systems.

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