

The Cross-Linking of Acrylic Rubber in the Presence of Group IIB Metal Oxides

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SYNOPSIS

Effects of group IIB metal oxides (viz., ZnO, CdO, and HgO) on ethylene thiourea (ETU) accelerated the curing of acrylic rubber (ACM) have been evaluated with a view to elucidate the cross-linking mechanism with special reference to the role of metal oxides. Best results are obtained with CdO in the presence of ETU. ZnO—CdO or CdO—HgO blends provide no synergism in the state and rate of cure. Formation of metal sulfide and chloride during the cross-linking reaction has been confirmed by XRD and XPS. Examination of FTIR spectra reveals that cross-linking occurs at the C—Cl cure site of the acrylic polymer. Based on spectral and chemical analysis, a reaction mechanism has been put forward.

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INTRODUCTION

Acrylic rubber (ACM) has a saturated backbone, but cure is possible via the inherent and copolymerized reactive cure site.^{1,2} All commercially important polyacrylics have a small percentage (1–5%) of a reactive cure site, usually of the chlorine type. Red lead (Pb_3O_4) is the commonly used metal oxide for the curing of acrylic rubber in conjunction with ethylene thiourea (ETU).^{3,4} Other metal oxides such as MgO in the presence of trithiol triazine have been developed for halogen-containing acrylic rubber.⁵ Details of the cross-linking mechanism of each of these cure systems are yet to be established. Recently, Das et al.⁶ studied the effects of group IVB metal oxides on curing of polyacrylics. The present article reports the results of curing of acrylic rubber (NIPOL-AR-51) in the presence of group IIB metal oxides and the ETU accelerator covering (a) assessment of curing characteristics, (b) solvent swelling studies, (c) evaluation of physical properties of the vulcanizates, and (d) chemical and spectral probes to elucidate the curing mechanism.

EXPERIMENTAL

Compounding formulations are given in Tables I–III. The acrylic rubber used was NIPOL-AR-51, made by Nippon Zeon Co., Japan. The metal oxides used were ZnO, CdO, and HgO. ETU was supplied by DuPont, USA. Continuous cure characteristics were studied in a Monsanto Rheometer (R-100) at 170, 180, and 190°C. The physical properties were studied on cured sheets that were cured at 170°C up to optimum cure time (t_{90}), obtained from a rheograph. Scorch time (t_2) was determined from a rheograph at 170°C. The rate constant (K) was calculated from the rheograph as per the equation developed earlier.⁷ Tensile testing was carried out by a universal testing machine, and solvent swelling was studied at 25°C for 72 h in toluene. X-ray diffraction patterns were obtained employing a Philips (PW 1840) diffractometer using nickel-filtered $CuK\alpha$ radiation. X-ray photoelectron spectra were recorded with ESCA spectrophotometer (V.G. Scientific, MK II, UK) using $MgK\alpha$ radiation.

RESULTS AND DISCUSSION

Cure Characteristics

Oxides of group IIB metals (ZnO, CdO, and HgO) were tested both in the presence and absence of ETU

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Table I Compound Formulations, Cure Characteristics, and Physical Properties (Cured at 170°C)

Compound	NIPOL (g)	ETU (g)	ZnO (g)	CdO (g)	HgO (g)	Scorch Time t_2 (min)	$T_{\max} - T_{\min}$ (dN-m)	K (min^{-1})	Swelling Coefficient	Modulus 300% (kPa)	Tensile Strength (kPa)	Elongation at Break (%)
A	100	1	4	—	—	15	4	0.4	8.4	10	110	2400
B	100	1	—	4	—	5	16	0.9	6.1	110	1000	730
C	100	1	—	—	4	20	6	0.5	7.8	20	150	2450

to cure NIPOL-AR-51. In the absence of ETU, all oxides remained ineffective. However, in the presence of ETU, all the above oxides were able to cure the polyacrylic, although to different extents. Comparative cure characteristics of different metal oxides in the presence of ETU are shown in Table I. The CdO-containing system (compound B) gives rise to the highest state[†] and rate of cure, followed by HgO-ETU (compound C) and ZnO-ETU (compound A), respectively. The CdO-ETU system provides the least scorch time, perhaps due to the higher basicity of CdO compared to ZnO and HgO.⁸

To determine the optimum ratio of CdO to ETU, several compounds were made (Table II) and their cure characteristics studied. Figure 1 shows that the state of cure increases with the increase of ETU content at a fixed level of CdO (4 phr). It attains maxima at 2 phr of ETU and then decreases with a further increase of ETU. Thus, 4 phr of CdO with 2 phr of ETU provides the highest extent of cure. The calculated mol ratio at the maxima is approximately ETU : CdO = 1 : 1.5. The decrease of the state of cure with the increase of ETU content beyond maxima may be due to excess ETU masking the entire CdO and thus decreasing curing efficiency. Figure 2 shows the change of the state of cure with the variation of CdO content at a fixed level of ETU (2 phr). The state of cure increases continuously, exhibiting different slopes with the increase of CdO content. The change in slope occurs at 4 phr of CdO, i.e., at the mol ratio ETU : CdO = 1 : 1.5, and then the system maintains a marginal increase of the state of cure with the gradual increase of CdO content. The variation of rate constant with ETU at a fixed level of CdO and vice versa (Figs. 1 and 2) shows a maximum at the mol ratio ETU : CdO = 1 : 1.5. Thus, with respect to rate and state of cure, the most effective mol ratio of ETU : CdO is 1 : 1.5.

To study the effect of a binary mixture of oxides toward curing behavior, different compounds were made (Table III) and their cure characteristics studied. Figures 3 and 4 represent the state and rate of cure vs. composition of CdO—ZnO and CdO—HgO blends, respectively. Gradual replacement of amphoteric ZnO and extremely less basic HgO by comparatively more basic CdO leads to an increase of both the state and rate of cure, exhibiting different slopes.

[†] According to Monsanto nomenclature, the "state of cure" is defined as the difference between maximum rheometric torque and minimum rheometric torque ($T_{\max} - T_{\min}$).

Table II Compound Formations and Physical Properties

Compound No.	NIPOL (g)	ETU (g)	CdO (g)	Swelling Coefficient	Hardness (Shore A)	Modulus - 300 (kPa)	Tensile Strength (kPa)	Elongation at Break (%)
D	100	0.5	4	7.0	30	60	1020	800
E	100	2.0	4	3.8	50	180	600	38
F	100	3.0	4	4.2	44	100	580	350
G	100	4.0	4	4.5	35	80	550	330
H	100	2	1	7.0	30	60	540	350
I	100	2	2	4.5	35	80	550	360
J	100	2	3	4.3	40	90	570	370
K	100	2	6	3.6	52	200	610	600
L	100	2	8	3.4	53	210	650	700
M	100	2	10	3.3	55	220	650	700

Swelling Studies

Swelling coefficient values of the systems containing different metal oxides with 1 phr of ETU are shown in Table I. It shows that the swelling coefficient of the CdO-containing system (compound B) is the least, which means that compound B has the highest cross-link density compared to both ZnO- and HgO-containing systems. Swelling coefficients of the systems containing different ratios of ETU to CdO are given in Table II, which shows that when CdO loading is fixed at 4 phr, the system containing 2 phr of ETU gives rise to the lowest swelling coefficient value. However, at 2 phr of ETU, the swelling coefficient continues to decrease marginally with a gradual increase of CdO content. This variation of the swelling coefficient with different cure systems is in accordance with the state of cure values. Swelling coefficients of the combined metal oxides are shown in Table III. Gradual replacement of either ZnO or HgO by CdO decreases the swelling coefficient values continuously.

Physical Properties

Physical properties of the compounds containing different metal oxides with 1 phr of ETU are given in Table I. The system containing CdO provides the highest modulus and tensile strength, followed by HgO and then ZnO. However, elongation at break value is the least in the case of the CdO-containing system (compound B) in comparison to the other two oxides.

Physical properties of the systems containing different ratios of ETU to CdO are given in Table II, which shows that the tensile strength increases with the increase of CdO content up to 8 phr and then remains constant. However, the tensile strength decreases continuously with a gradual increase of ETU loading at fixed level of CdO. Elongation at break decreases with the increase of ETU content, whereas it increases with the increase of CdO content up to 8 phr of loading.

The physical properties of the combined metal oxide systems are shown in Table III. Gradual re-

Table III Compound Formulations and Physical Properties

Compound	NIPOL (g)	ETU (g)	ZnO (g)	CdO (g)	HgO (g)	Swelling Coefficient	Hardness (Shore A)	Modulus - 300 (kPa)	Tensile Strength (kPa)	Elongation at Break (%)
N	100	2	4	—	—	8.1	34	30	110	2000
O	100	2	3	1	—	7.5	38	70	250	1200
P	100	2	2	2	—	4.8	42	110	350	800
Q	100	2	1	3	—	4.0	46	150	450	500
R	100	2	—	—	4	7.5	38	40	170	2050
S	100	2	—	1	3	6.4	41	90	260	1100
T	100	2	—	2	2	5.2	44	130	380	600
U	100	2	—	3	1	4.3	47	160	460	510

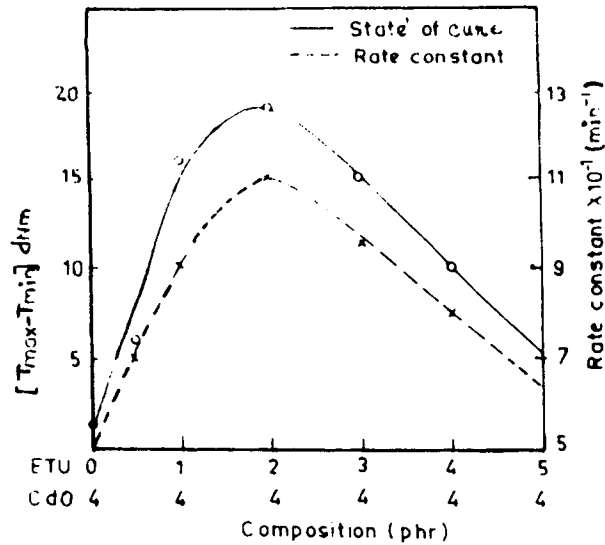


Figure 1 Variation of state of cure ($T_{max} - T_{min}$) and rate of cure with ETU at fixed level of CdO (4 phr).

placement of either ZnO or HgO by CdO increases the tensile strength, hardness, and modulus and decreases the elongation at break drastically. Systems containing pure CdO (compound E) provides the highest tensile strength, hardness, and modulus value and the lowest elongation at break value.

FTIR Spectral Analysis

Figure 5 shows the FTIR spectra of the original polymer (ACM), polymer cured with 1 phr of ETU

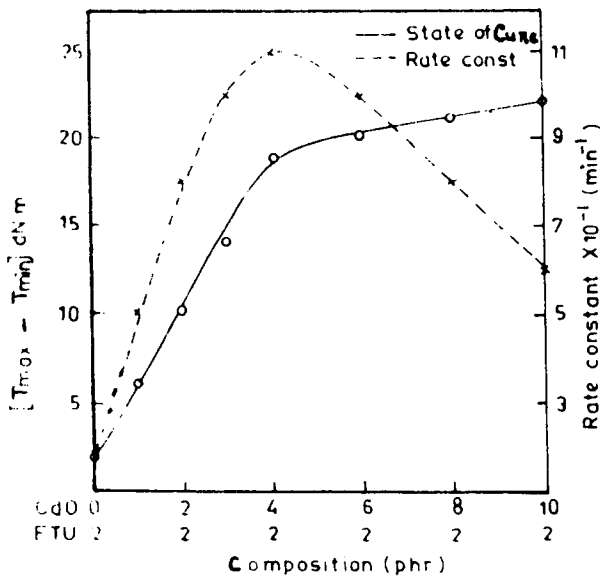


Figure 2 Variation of state of cure ($T_{max} - T_{min}$) and rate of cure with CdO at fixed level of ETU (2 phr).

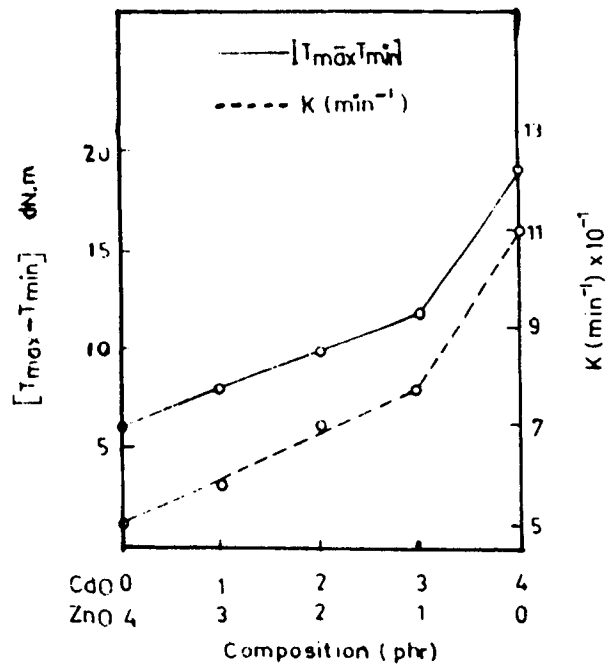


Figure 3 Variation of state ($T_{max} - T_{min}$) and rate of cure with the composition of CdO—ZnO blends.

and 4 phr of CdO (compound B), and polymer cured in the presence of 2 phr ETU and 8 phr of CdO (compound L). The intensity of the sharp peak at 700 cm^{-1} , due to the C—Cl bond⁶ of the original polymer, is reduced in the spectrum of compound B and almost completely removed in the spectrum of compound L. Thus, it may be assumed that the

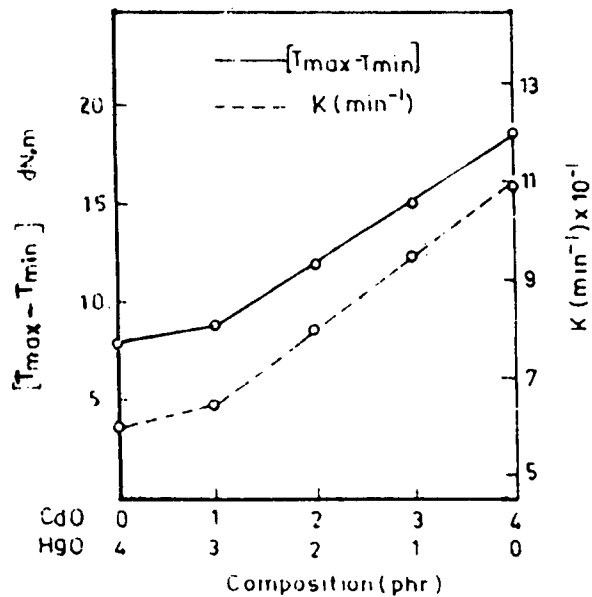


Figure 4 Variation of state ($T_{max} - T_{min}$) and rate of cure with the composition of CdO—HgO blends.

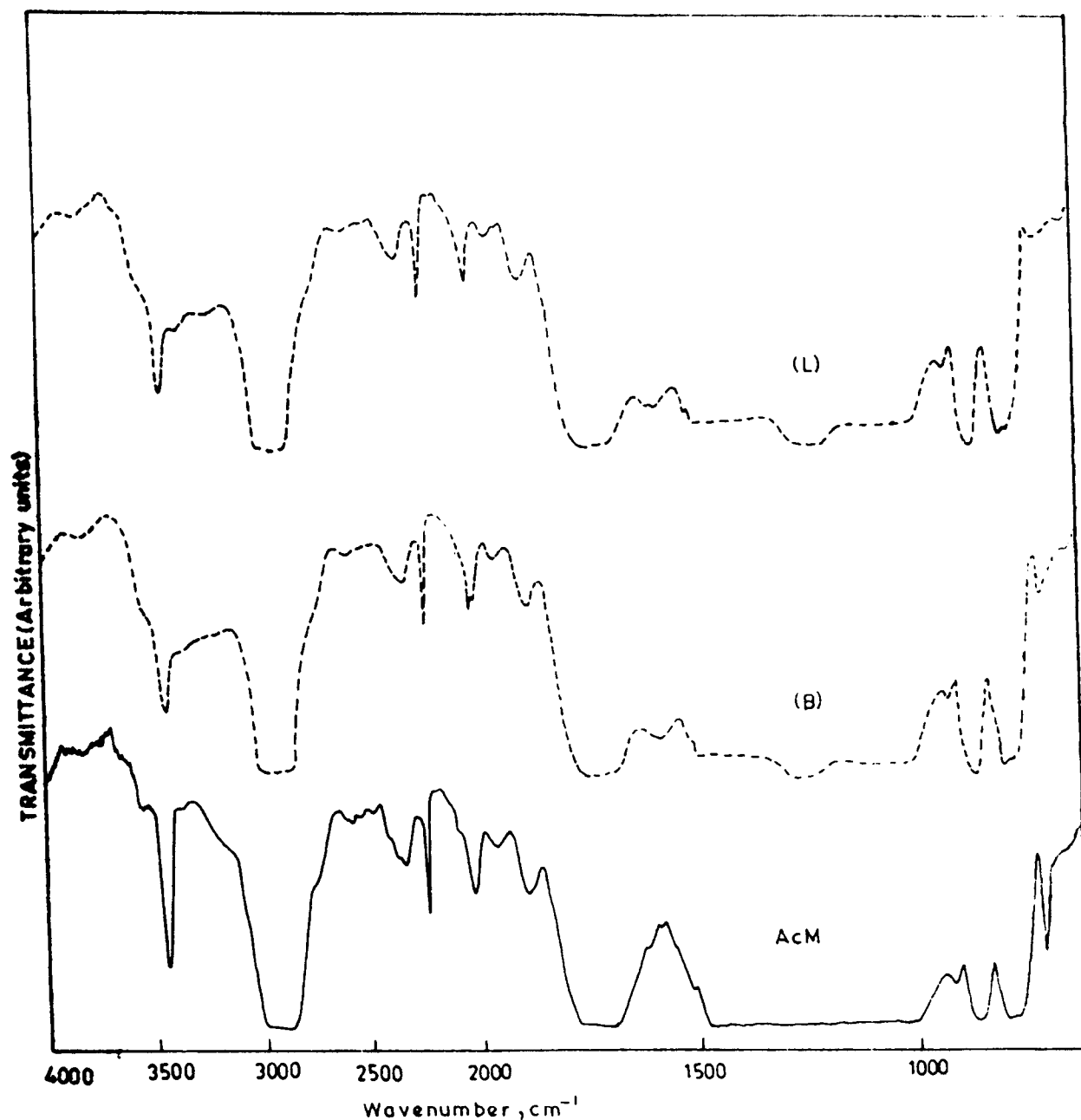


Figure 5 FTIR spectra of the polyacrylate (ACM) and compounds B, and L.

C—Cl bond of the original polymer is taking part in the reaction and its concentration is decreasing with the increase of the curatives (CdO + ETU) concentration and ultimately is removed at a higher level of curative concentration. The appearance of a new peak at 1246 cm^{-1} in the spectra of both compounds B and L may be assigned to skeletal vibration of the carbon atom that is linked to the other four carbon atoms.⁹ A similar type of FTIR spectral ob-

servations are noticed in the system containing ZnO + ETU and HgO + ETU.

X-ray Diffraction Studies

Figure 6 shows the X-ray diffraction patterns of the original polymer (ACM) with CdO (reference compound), ACM with CdO and ETU (compound E), ACM with ZnO and ETU (compound N), and ACM

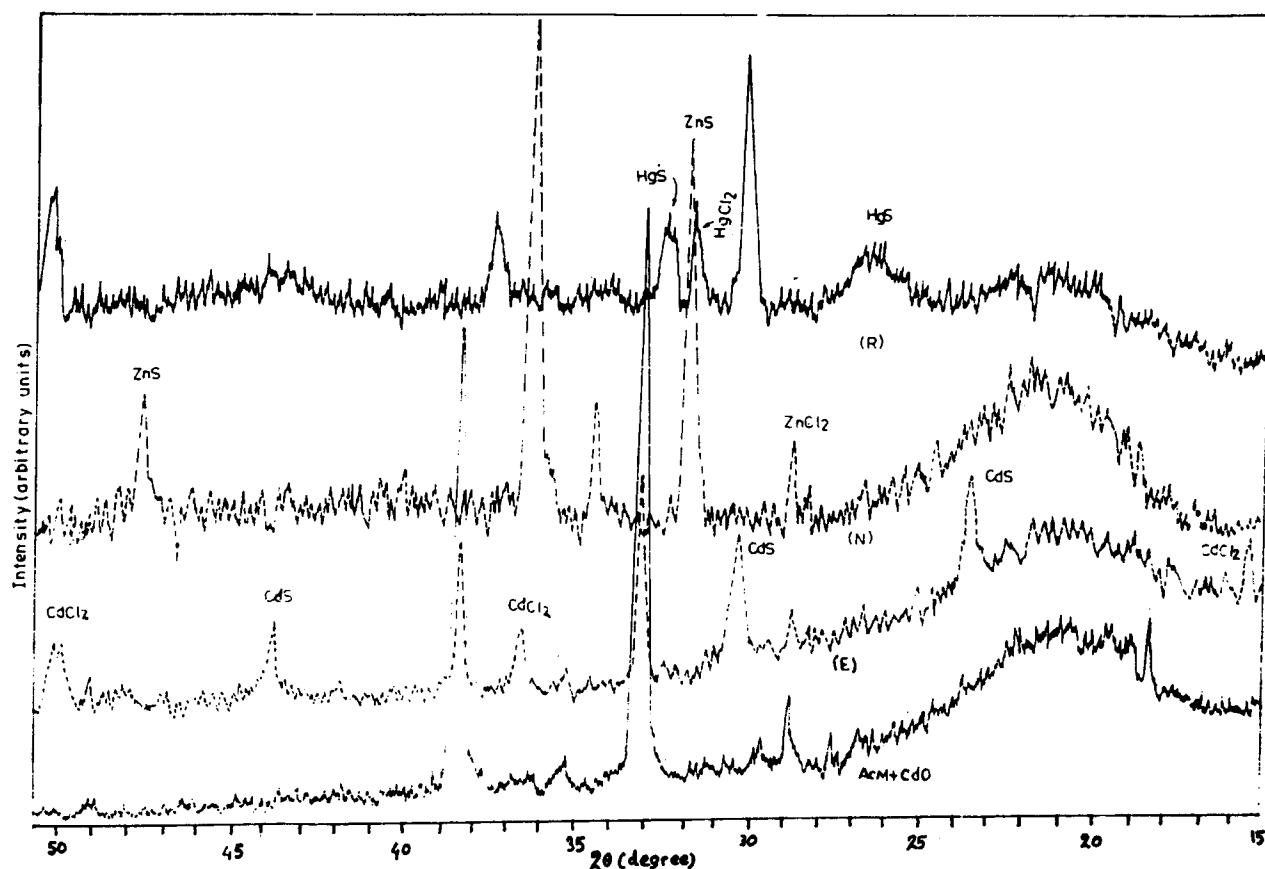


Figure 6 X-ray diffractogram of polyacrylate (ACM) with CdO and compounds E, N, and R.

with HgO and ETU (compound R). A comparison between the patterns of the reference compound and compound E shows that peaks at 2θ values of 15.2° , 24.0° , 30.8° , 37.3° , 43.8° , and 50.0° that are present in compound E are absent in the reference compound. Peaks at 15.2° , 37.3° , and 50.0° correspond to CdCl_2 and 24.0° , 30.8° , and 43.8° are due to CdS .¹⁰ An X-ray diffractogram of compound N reveals that peaks at 2θ values of 30.5° and 47.6° are due to ZnS , whereas a peak at 28.8° is due to ZnCl_2 .¹⁰ Broad peaks at 26.0° and 31.2° in the spectra of compound R signify the presence of HgS , and a peak at 30.4° represents the existence of HgCl_2 .¹⁰ Thus, X-ray studies confirm the formation of metal sulfides and chlorides during the cross-linking reaction in the presence of metal oxides and ETU.

X-ray Photoelectron Spectral Analysis

Representative examples of $\text{Cd}_{3d_{5/2}}$, O_{1s} , and C_{1s} X-ray photoelectron spectra of the polymer cured with CdO and ETU (compound E) are shown in Figure

7. Characterization of the $\text{Cd}_{3d_{5/2}}$ spectrum reveals that cadmium remains in a single distinct bivalent oxidation state in the systems. The existence of a higher binding energy component of the $\text{Cd}_{3d_{5/2}}$ peak indicates the presence of CdCl_2 in the vulcanizate. C_{1s} spectra of the compound reveal that the vulcanizate contains C—O, C=O, and COOH along with the C—C bond. It is observed that the C—O bond content is less than the C—C link. Peak height and full-width at half-maxima of the O_{1s} spectra of the compound indicates that the oxygen content of the system is considerable, although it is less than the system containing PbO_2 and ETU, as observed earlier.⁷ Thus, it may be assumed that C—C linkage is predominantly formed along with the formation of CdCl_2 during cross-linking reactions.

Chemical Analysis

Individual oxides of group IIB metals (ZnO , CdO , and HgO) with ETU have been heated 170°C for a few minutes and the mixture is subjected to chemical

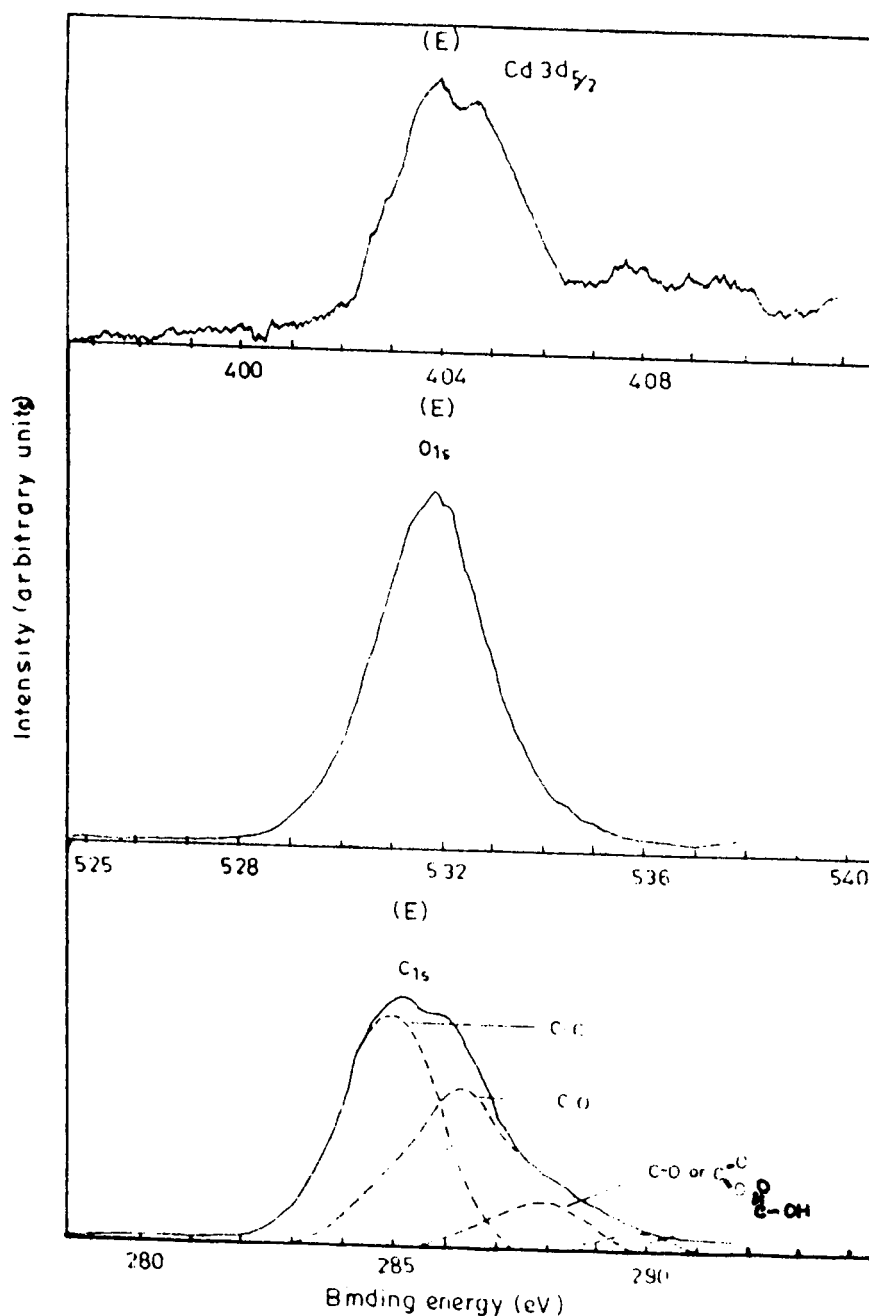
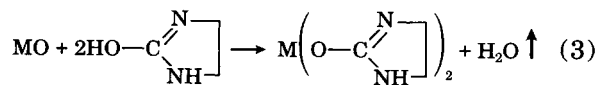
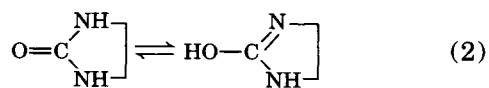
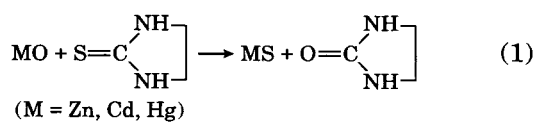
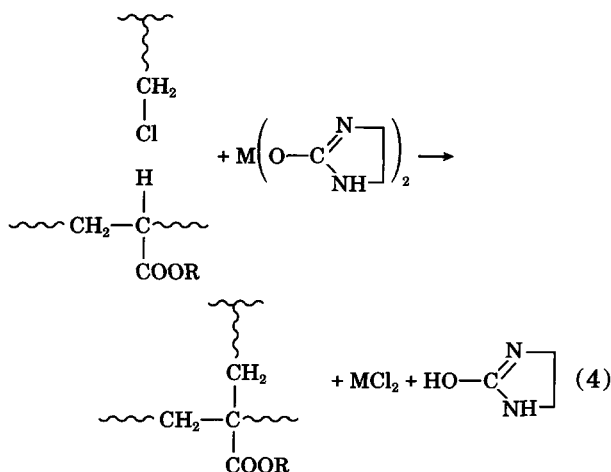


Figure 7 Cd_{3d_{5/2}}, O_{1s}, and C_{1s} X-ray photoelectron spectra of compound E.

analysis for the metal sulfides¹¹ and the test was positive.

Based on spectral and chemical analyses, a reaction scheme of group IIB metal oxide-ETU cure systems has been proposed as follows:





Salt formation with metal oxides [reaction (3)] is easier with CdO than with both ZnO and HgO, probably due to the more basic nature of CdO. Thus, the efficiency of curing through reaction (4) is the highest in the case of CdO among the group IIB metal oxides. Reaction (1) is more favorable in the case of HgO than in that of ZnO, perhaps due to higher sulfur binding ability of mercury.¹² Thus, HgO is more efficient than is ZnO.

CONCLUSION

Among the used metal oxides, CdO gives the highest rate and state of cure compared to that of other group IIB metal oxides studied, probably due to more basic nature of CdO. Metal oxides help the cross-linking through the formation of metal sulfide and metal chloride, as evident from XRD and XPS. No

boosting effect was observed in the ZnO/CdO and HgO/CdO blend systems.

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