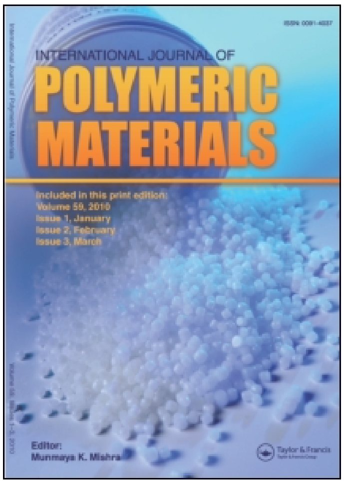

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P. Chowdhury[a]; M. C. Chakravorti[a]; C. K. Das[b]
[a] Department of Chemistry, I. I. T., Kharagpur, India [b] Materials Science Centre, I. I. T., Kharagpur, India

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The Role of Metal Oxides in Ammonium Benzoate Curing of Polyacrylic Rubber Both in Presence and Absence of Fillers

P. CHOWDHURY and M. C. CHAKRAVORTI
Department of Chemistry, I. I. T., Kharagpur 721302, India

and

C. K. DAS
Materials Science Centre, I. I. T., Kharagpur 721302, India

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Effects of metal oxides (viz. PbO, PbO_2 and CdO) on ammonium benzoate cure of polyacrylic rubber (ACM) have been evaluated with a view to elucidate the curing mechanism with special reference to the role of metal oxides. Carbon black (SRF), calcium carbonate ($CaCO_3$) and silica (SiO_2) have been used as fillers. Best results are obtained with PbO in the presence of ammonium benzoate. SRF acts as better reinforcing filler than both $CaCO_3$ and SiO_2. The formation of metal chloride during curing has been confirmed by XRD and XPS. Examination of FTIR spectra reveals that crosslinking occurs at the C—Cl cure site of the polymer. Based on spectral analysis a reaction mechanism has been put forward.

KEY WORDS Polyacrylic rubber, curing, metal oxides, ammonium benzoate, fillers

1. INTRODUCTION

Polyacrylic rubber (ACM) has saturated backbone, but cure is possible via inherent copolymerized reactive cure sites.[1,2] All commercially important polyacrylics have a small percentage (1–5%) of reactive cure sites, usually chlorine. Red lead (Pb_3O_4) is the commonly used metal oxide for curing of polyacrylic rubber in conjunction with ethylene thiourea.[3,4] Hexamethylene diamine carbamate[5] and ammonium benzoate[6] are effective curatives for acrylic rubber. Detailed crosslinking mechanism of each of these systems is yet to be established.

Recently we have studied the effects of metal oxides on curing polyacrylic rubber in the presence of sulphur bearing rubber accelerators.[7] The present paper reports the results of curing acrylic rubber (NIPOL-AR-51) in the presence of metal oxides (viz. PbO, PbO_2 and CdO) and ammonium benzoate covering (a) assessment of cure characteristics, (b) swelling studies, (c) evaluation of physical properties of the vulcanizates and (d) spectral probes to elucidate the curing mechanism. Studies on the reinforcing effect of carbon black (SRF), calcium carbonate ($CaCO_3$) and silica (SiO_2) have also been considered.

2. EXPERIMENTAL

Compounding formulations are given in Tables I, III and V. Polyacrylic rubber used was NIPOL-AR-51, obtained from Nippon Zeon Co. Ltd., Japan. Metal oxides used were PbO, PbO_2 and CdO. Ammonium benzoate (A.B) was used as a curative. The fillers used were carbon black (SRF), calcium carbonate ($CaCO_3$) and silica (SiO_2). Continuous cure characteristics were studied in Monsanto Rheometer at 170, 180 and 190°C. The state of cure ($T_{max} - T_{min}$) of the compounds has been determined[7] from the difference between maximum torque (T_{max}) and minimum torque (T_{min}) as obtained from Monsanto Rheographs at 170°C. Physical properties were studied on cured sheet both before and after aging. Aging in hot air oven was carried out for 72 hours at 150°C. Solvent swelling was studied at 25°C for 72 hours in toluene. X-ray diffraction patterns (XRD) were obtained employing Philip's PW 1840 diffractometer using nickel filtered Cu-K_α radiations. X-ray photoelectron spectra (XPS) were recorded with an ESCA spectrophotometer (V.G. Scientific, M.K.II, U.K.) using Mg-K_α radiations. FTIR spectra were taken on cured thin films using a Perkin Elmer spectrophotometer (No. 750).

3. RESULTS AND DISCUSSION

3.1 Cure Characteristics

Ammonium benzoate was tested, both in the presence and absence of metal oxides, to cure NIPOL-AR-51. The state of cure ($T_{max} - T_{min}$) of the ammonium benzoate containing system is improved in the presence of metal oxides (Figure 1). PbO and CdO give comparable results in conjunction with ammonium benzoate. PbO_2 is less effective than both PbO and CdO, probably due to its less basic character.

To find out optimum ratio of PbO to ammonium benzoate several compounds have been made (Table I) and their cure characteristics are shown in Figure 2 which reveals that both rate and state of cure increase with the increase of ammonium benzoate at fixed level of PbO (2 phr). The rate of cure attains maxima at around 2 phr of ammonium benzoate and then decreases with a further increase of benzoate. The state of cure increases sharply up to 2 phr of ammonium benzoate and then increases slowly with the increase of benzoate. Thus 2 phr of ammonium benzoate with 2 phr of PbO provides the highest rate of cure with optimum state of cure. The calculated mole ratio at this point is approximately ammonium benzoate to PbO is 1:0.5. The decrease of rate of cure with the increase of ammonium benzoate beyond maxima may be due to the presence of excess benzoic acid produced during reaction (vide mechanism shown later). Figure 3 shows the change of both state and rate of cure with the variation of PbO at fixed level of ammonium benzoate (2 phr). The state and

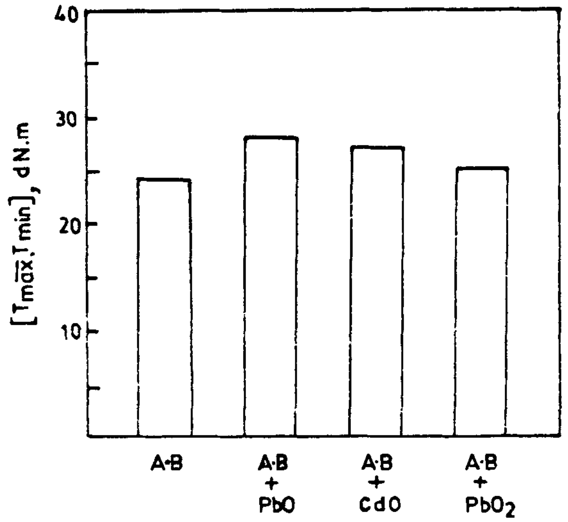


FIGURE 1 Histogram showing state of cure ($T_{max} - T_{min}$) of different compounds where A.B. stands for ammonium benzoate.

TABLE I

Compound formations for the gum state (in g)

Compound Nos.	A	B	C	D	E	F	G	H	I	J
NIPOL-AR-51	100	100	100	100	100	100	100	100	100	100
Ammonium benozate	-	1	2	3	4	2	2	2	2	2
PbO	2	2	2	2	2	-	2	4	6	8

rate of cure increase continuously exhibiting different slopes with the increase of PbO. The change in slope occurs at around 2 phr of PbO and then the systems maintain a marginal increase of state and rate of cure with the further increase of PbO. Thus with respect to state and rate of cure, the effective mole ratio of ammonium benzoate to PbO is 1:0.5.

In order to study the reinforcing effect of carbon black (SRF), calcium carbonate ($CaCO_3$) and silica, different compounds have been made (Tables III and V) and their cure characteristics are shown in Figures 4 and 5. Figure 4 shows that the state of cure increases with the increase of SRF at fixed level of PbO (4 phr) and ammonium benzoate (1 phr). It increases slowly up to 20 phr of SRF and then raises sharply up to 40 phr. Beyond 40 phr of SRF it increases marginally. Figure 4 also shows the variation of degree of reinforcement[8] with different amount of SRF. The nature of this curve is more or less similar to that of state cure vs composition curve suggesting that the presence of various levels of SRF does not change the reinforcing mechanism. Figure 5 shows the variation of state of cure with the compounds containing different ratios of SRF to $CaCO_3$ and SRF to silica at fixed level of PbO (4 phr) and ammonium

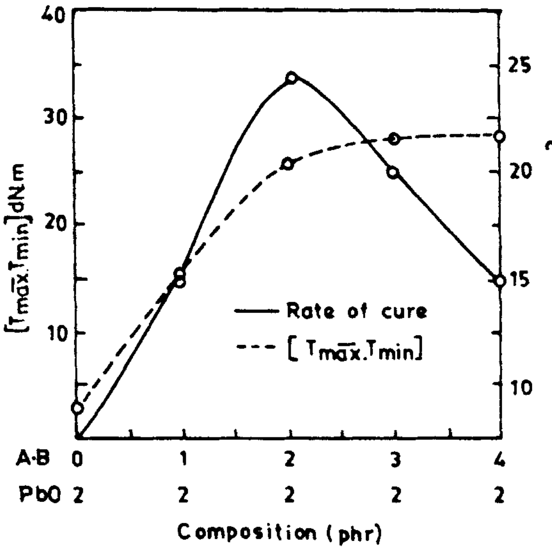


FIGURE 2 Variation of rate constant (K) and state of cure ($T_{max} - T_{min}$) with ammonium benzoate at fixed level of PbO (2 phr).

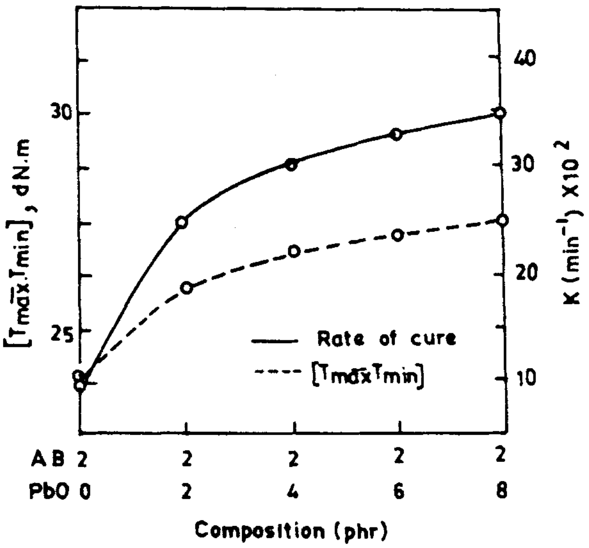


FIGURE 3 Variation of rate constant (K) and state of cure ($T_{max} - T_{min}$) with PbO at fixed level of ammonium benzoate (2 phr).

benzoate (1 phr). It is observed that the state of cure decreases with the replacement of SRF either by $CaCO_3$ or silica.

3.2 Solvent Swelling

Solvent swelling coefficients of the systems containing different ratios of ammonium benzoate to PbO are given in Table II which shows that swelling coefficient con-

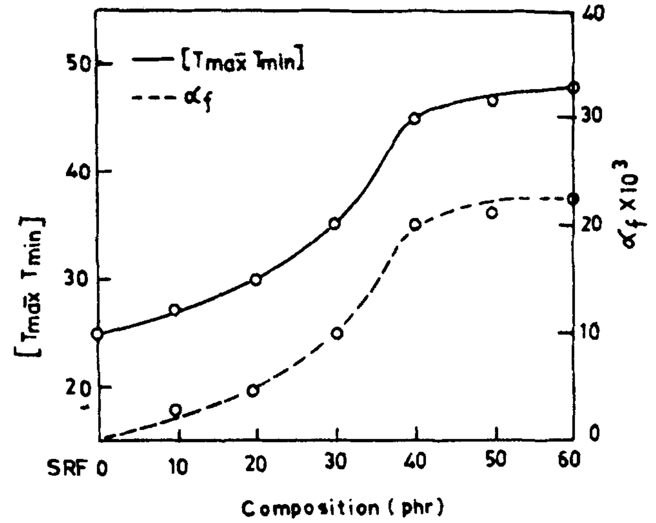


FIGURE 4 Variation of state of cure ($T_{max} - T_{min}$) and degree of reinforcement (α_f) with the increase of carbon black (SRF) loading.

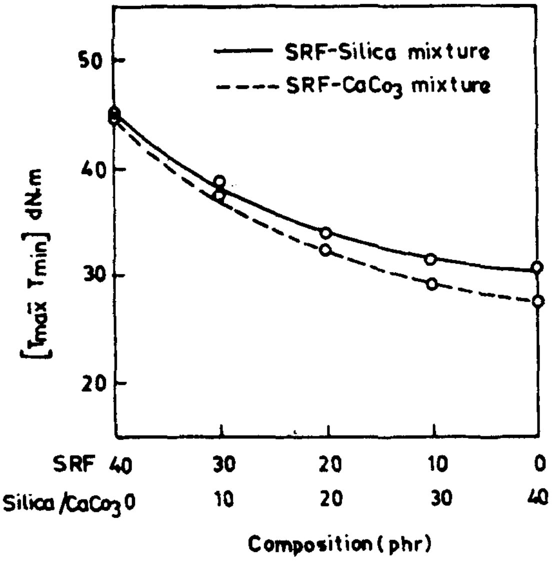


FIGURE 5 Variation of state of cure ($T_{max} - T_{min}$) with the compounds containing different ratios of SRF to $CaCO_3$ and SRF to Silica at fixed level of PbO (4 phr) and ammonium benzoate (1 phr).

tinues to decrease with the increase of ammonium benzoate at fixed level of PbO (2 phr). This means that the degree of crosslinking is gradually increasing with the increase of curatives concentration. The optimum curatives concentration is 2 phr PbO with 2 phr ammonium benzoate. Percentage of swelling of the systems containing different extent of SRF is given in Table IV which shows that swelling decreases with the increase of SRF content.

TABLE II

Physical properties of the gum vulcanizates, both before and after aging

Compound Nos.	A	B	C	D	E	F	G	H	I	J
Swelling (%)	600	520	380	375	370	490	380	370	360	350
Hardness (Share A)	15	18	25	26	27	20	25	35	38	40
Modulus (300%) ($N\text{-}mm^{-2}$)	0.05	0.20	0.25	0.26	0.27	0.22	0.25	0.26	0.27	0.28
Tensile strength ($N\text{-}mm^{-2}$)	0.5	1.5	3.0	2.5	2.0	1.0	3.0	3.5	3.5	4.0
Elongation at break (%)	1000	970	950	930	910	750	950	850	860	870
	Percentage of charge in properties after aging									
Hardness	+10	+67	+80	+70	+20	-50	+80	+40	+30	+25
Modulus	+20	+10	+20	+15	+10	-	+20	+20	+30	+43
Tensile strength	+12	-30	-33	-20	-15	-80	-33	-40	-35	-38
Elongation at break	-15	-20	-40	-22	-30	-25	-40	-30	-25	-20

TABLE III

Compound formulations for the filled state (in g)

Compound Nos.	K	L	M	N	O	P	Q
NIPOL-AR-51	100	100	100	100	100	100	100
Ammonium benzoate	1	1	1	1	1	1	1
PbO	4	4	4	4	4	4	4
SRF	-	10	20	30	40	50	60

3.3 Physical Properties

Physical properties of the gum vulcanizates, both before and after aging, are given in Table II which shows that hardness and modulus increase with the increase of PbO at fixed level of ammonium benzoate and vice-versa. Tensile strength increases with the increase of PbO at fixed level of benzoate and elongation at break decreases with the increase of benzoate at fixed level of PbO. The results of physical properties of the gum vulcanizates after aging reveal that hardness and modulus increase on

TABLE IV

Physical properties of the filled vulcanizates, both before and after aging

Compound Nos.	K	L	M	N	O	P	Q
Swelling (%)	487	300	270	230	200	190	180
Hardness (shore A)	35	40	50	60	80	85	90
Modulus (300%) (N-mm^{-2})	0.2	1.5	2.5	5.0	7.5	8.0	-
Tensile strength (N-mm^{-2})	2.0	3.0	5.0	8.0	11.0	11.5	12.0
Elongation at break (%)	510	460	450	420	400	350	260
Percentage change in properties after aging							
Hardness	+14	+12	+10	+8	+6	+7	+6
Modulus	+50	+20	+12	+10	-	-	-
Tensile strength	-25	-16	-10	-25	-27	-25	-24
Elongation at break	-22	-15	-22	-26	-81	-70	-90

aging, although elongation at break and tensile strength decrease except two ends composition (i.e. compounds A and F). For the system containing ammonium benzoate only as a curative (compound F) hardness, tensile strength and elongation at break decrease on aging while for the systems containing PbO only as a curative (compound A) hardness, modulus and tensile strength increase.

Physical properties of the filled vulcanizates, both before and after aging are given in Table IV. It is observed that hardness, modulus and tensile strength continue to increase with the increase of SRF. However, elongation at break decreases with the increase of carbon black. Hardness and modulus increase and tensile strength and elongation at break decrease sharply on aging (Table IV).

3.4 FTIR Spectral Analysis

Figure 6 shows the FTIR spectra of the original polymer (ACM) and polymer cured with ammonium benzoate and PbO (compound C). Comparison of the spectra reveals that a sharp peak at 700 cm^{-1} of the original is absent in the spectrum of compound C. Similarly a broad absorption peak at 3056 cm^{-1} of ammonium benzoate (spectrum is not given) is absent in the spectrum of compound C. Peaks at 7056 cm^{-1} are due to the C—Cl bond[9] of original polymer and the N—H bond of NH_4^+ ion[10] respectively. Thus it may be assumed that the C—Cl bond of original polymer and NH_4^+ ion of ammonium benzoate are involved in crosslinking reaction.

TABLE V

Compound formulations (in g)

Sample	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
NIPOL-AR-51	100	100	100	100	100	100	100	100	100	100
Ammonium benzoate	2	2	1	1	1	1	1	1	1	1
PbO	-	-	4	4	4	4	4	4	4	4
PbO_2	2	-	-	-	-	-	-	-	-	-
CdO	-	2	-	-	-	-	-	-	-	-
SRF	-	-	-	10	20	30	-	10	20	30
$CaCO_3$	-	-	40	30	20	10	-	-	-	-
Silica	-	-	-	-	-	-	40	30	20	10

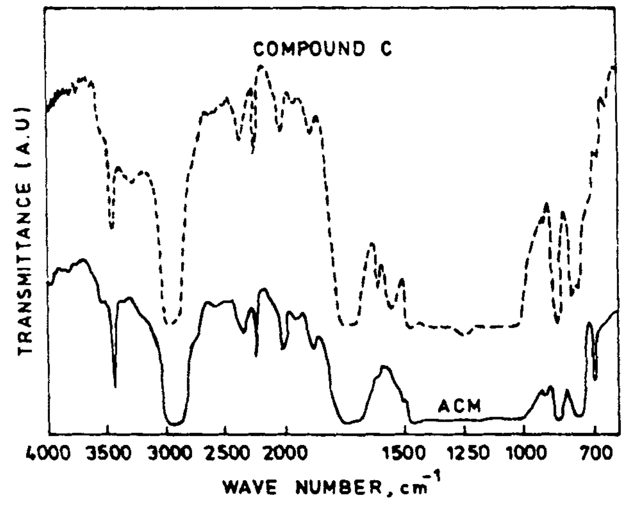


FIGURE 6 FTIR spectra of the polyacrylic rubber (ACM) and the compound C.

A new peak at 1250 and 1545 cm^{-1} appeared in the spectrum of compound C. Peak at 1250 cm^{-1} is due to skeletal vibration of carbon atom[11] which is joined to other four carbon atoms. Peak at 1545 cm^{-1} is due to the carboxylate anion.[11] Similar type of FTIR spectral observation is noticed in the compounds containing PbO_2 and CdO in the presence of ammonium benzoate.

3.5 X-Ray Diffraction Studies

Figure 7 shows the X-ray diffraction patterns of the original polymer with PbO (reference compound) and polymer cured with ammonium benzoate and PbO (com-

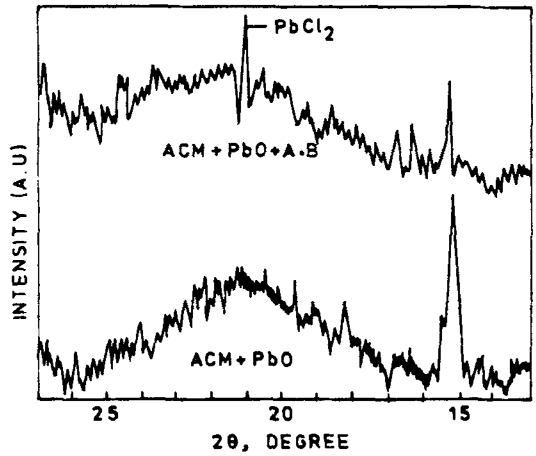


FIGURE 7 X-ray diffractogram of the polyacrylate (ACM) with PbO and the compound C.

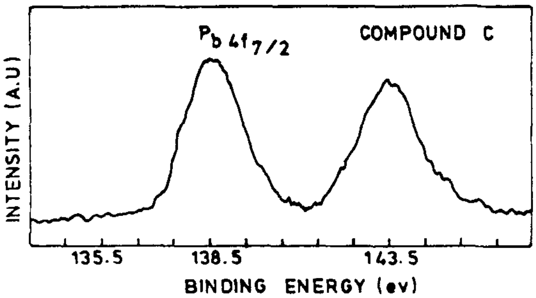


FIGURE 8 $Pb_{4f_{7/2}}$ X-ray photoelectron spectrum of the compound C.

pound C). A comparison of the patterns shows that the peak at 20 value of 21.0° which is present in the pattern of compound C is absent in the spectrum of reference compound. This peak at 21.0° is due to $PbCl_2$.[12] Similarly an examination of the XRD of the compound containing CdO and ammonium benzoate confirms the formation of $CdCl_2$ in the vulcanizate. Thus it may be assumed that metal chlorides are formed during crosslinking reaction.

3.6 X-Ray Photoelectron Spectral Analysis

Representative examples of X-ray photoelectron spectra (XPS) of polymer cured with ammonium benzoate (compound F) and polymer cured with ammonium benzoate and PbO (compound C) are shown in Figures 8, 9 and 10. Figure 8 shows the $Pb_{4f_{7/2}}$ spectra of the compound C which reveals that lead remains in bivalent oxidation state in the system. Considering the splitting of the $Pb_{4f_{7/2}}$ peak, the existence of higher binding energy component of this peak indicates the presence of $PbCl_2$ in the vulcanizate. Figure 9 shows the high resolution C_{1s} spectra of the compounds F and C. Comparison of the C_{1s} spectra of the compounds F and C shows the C—O and C=O content of the two systems are more or less equivalent.

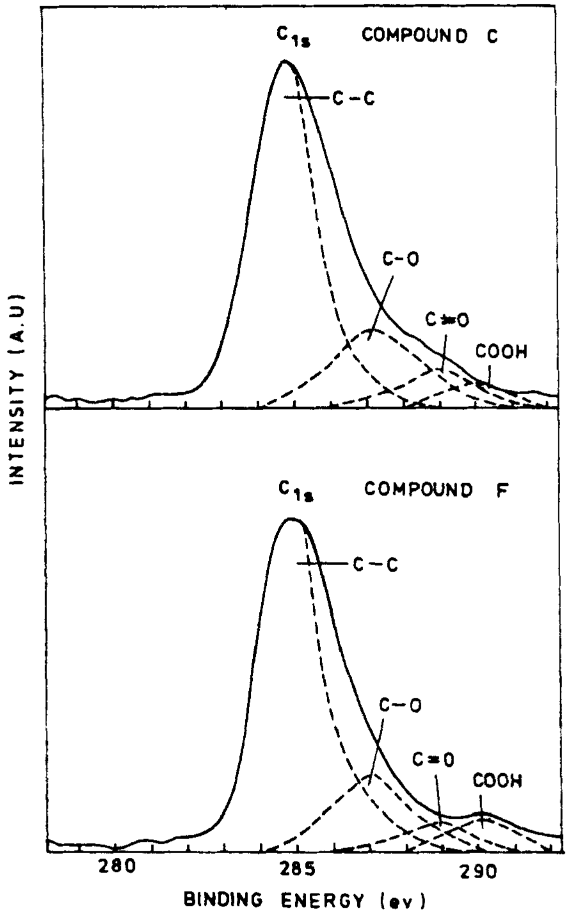
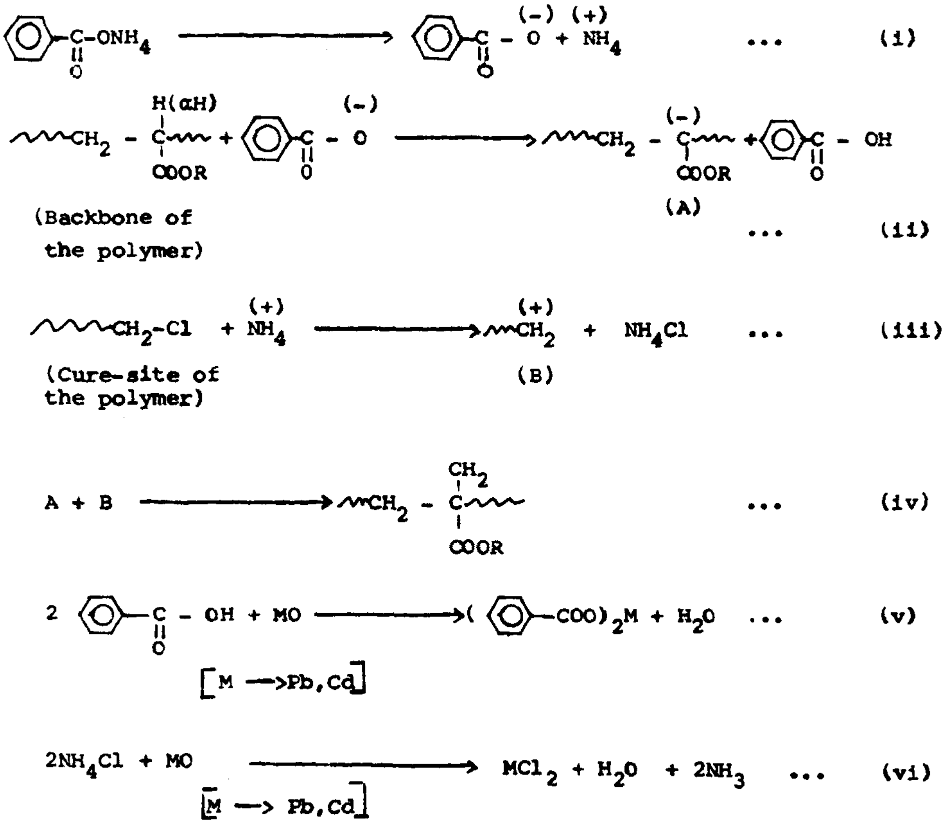


FIGURE 9 High resolution C_{1s} X-ray photoelectron spectra of the compounds C and F.

However C—C content is more in the system containing PbO (compound C) and COOH content is more in the system without PbO (compound F). Figure 10 is the O_{1s} spectra of the compounds F and C. Full width at half maxima of the O_{1s} spectra of the compound C indicates that the compound C contains more oxygen than compound F. However the height of the O_{1s} spectra of the compound F shows that compound F contains more COOH group than compound C.

Based on the spectral studies (IR, XRD and XPS), a reaction scheme is proposed as follows



At the curing conditions ammonium benzoate splits into ammonium ion and benzoate ion (Reaction i). In the presence of benzoate ion alpha hydrogen of the polymer is abstracted and benzoic acid is produced with a carbanion (A) through reaction (ii). Similarly in the presence of ammonium ion, active chlorine of the polymer is abstracted and ammonium chloride is produced with a carbonium ion (B) through reaction (iii). C—C type crosslink is occurred through the union of carbonium ion and carbanion (reaction iv). Metal oxide withdraws the benzoic acid and ammonium chloride from the system through the formation of metal benzoate and metal chloride respectively (reactions v and vi). Reactions (v) and (vi) are more favourable in the cases of PbO and CdO than PbO_2 due to their more basic nature. Thus PbO and CdO help crosslinking to a larger extent than PbO_2 in the presence of ammonium benzoate.

4. CONCLUSION

Ammonium benzoate is an effective curing agent for acrylic elastomer (NIPOL-AR-51). Its effectiveness is enhanced in the presence of metal oxides (viz. PbO and CdO). PbO and CdO are more active than PbO_2 in conjunction with ammonium benzoate. Metal oxides facilitates the crosslinking by absorbing benzoic acid and

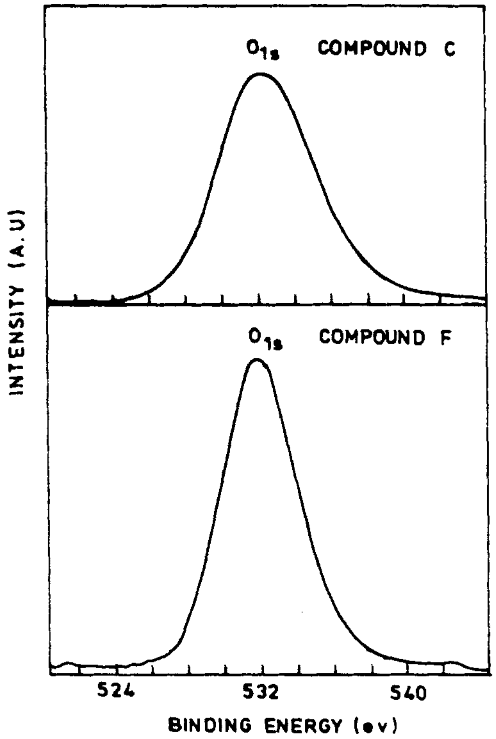


FIGURE 10 O_{1s} X-ray photoelectron spectra of the compounds C and F.

ammonium chloride from the system. Carbon black (SRF) acts as better reinforcing filler than both $CaCO_3$ and SiO_2 and they do not interfere the crosslinking mechanism.

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