

New oligomer-bound antioxidants for improved flex crack resistance and ozone resistance

P.B. Sulekha^a, Rani Joseph^{a,*}, K.N. Madhusoodanan^b, K.T. Thomas^b

^aDepartment of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin-682 022, India

^bRubber Research Institute of India, Kottayam, India

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Abstract

New oligomer-bound antioxidants have been prepared by condensation reaction. The efficiency and permanence of these oligomer-bound paraphenylene diamines as antioxidants has been compared with conventional amine type antioxidants in NR, SBR, IIR and NBR and in elastomer blends like NR/BR and NR/SBR. The oligomer-bound antioxidants are found to impart improved ozone, flex resistance and mechanical properties to the vulcanizates of NR, SBR, IIR and NBR and to blends of NR/BR and NR/SBR in comparison with those containing conventional antioxidants. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Paraphenylene diamine; Bound-antioxidant; Ozone ageing resistance; Flex resistance

1. Introduction

Although ozone is present in the atmosphere at concentrations normally in the range 0–7 pphm [1], it can severely attack non-resistant rubbers. The interaction of rubber with ozone is best noted when the rubber is stressed or stretched in use. A series of cracks develop, over time, which are perpendicular to the applied stress. Further exposure of these cracked surfaces to ozone cause the crack to become wider and deeper until the rubber fails.

The use of antiozonants is an effective means of protecting rubber against surface cracking. The general subject of protection of rubber against ozone attack has been reviewed by a number of authors [2–4].

Several theories have appeared in the literature regarding the mechanism of antiozonant protection. The “scavenger” model states that the antiozonant blooms to the surface and preferentially reacts with ozone so that the rubber is not attacked until the antiozonant is exhausted [4,5]. The “protective film” theory is similar,

except that the ozone–antiozonant reaction products form a film on the rubber surface that prevents ozone attack on the rubber [6]. A third “relinking” theory states that the antiozonant prevents scission of the ozonised rubber or recombines severed double bonds [7].

The antiozonant effect was found to increase with the initial surface concentration of antiozonant and the reaction rate was reported to be related to antiozonant efficiency [8–10].

During recent years there has been a gradually increasing demand from tyre manufacturers for additives which will protect rubber compounds from attack by ozone and search for new and improved types of antiozonants is going on. In any classification of chemical protective agents for rubber, no clear distinction can be made between antioxidants and antiozonants. Some chemicals already known as antioxidants have been shown to possess antiozonant properties also. One of the main drawbacks of conventional antioxidant is its high volatility. This led to search of a new class of antioxidants having higher molecular weights i.e. polymer bound antioxidants.

Polymer bound antioxidants have many advantages but one of the main disadvantages is that the mobility of the antioxidant is restricted. Hence it does not bloom to the surface and ozone attack cannot be effectively controlled. Most of the polymer bound antioxidants have

* Corresponding author. Tel.: +91-484-555723; fax: +91-484-532495.

E-mail address: hodpsrt@md2.vsnl.net.in (R. Joseph).

unsaturated backbone, so during the process of vulcanisation their backbone gets attached to the main chain through sulphur crosslinking and it loses its mobility still further [11]. The synthesis of polymer-bound antioxidant adduct concentrates by a high-shear mixing procedure is outlined by Scott [12].

The preparation and characterisation of new oligomer-bound antioxidants with saturated backbones was reported in our earlier papers [13,14]. In the present study we have evaluated the efficiency of these antioxidants in NR, SBR, IIR, NBR and in elastomer blends such as NR/SBR and NR/BR by comparing their flex resistance, mechanical properties and ozone resistance with their counterpart containing conventional antioxidants.

2. Experimental

2.1. Materials

Natural rubber (NR) (ISNR-5, Mooney viscosity ML(1+4) 100°C-82) was supplied by the Rubber Research Institute of India, Kottayam. Styrene-butadiene rubber (SBR, 1502) of Japanese Synthetic Rubber (JSR) Co. Ltd. was supplied by Sreevidhya Enterprises Ltd., Mumbai and had a Mooney viscosity [ML(1+4), at 100 °C] of 45. Acrylonitrile-butadiene rubber (NBR; N 553) was obtained from Apar Polymers Ltd. Gujarat, India. Polysar Butyl 301 supplied by polysar, Canada. Neoprene supplied by Distugil, Paris. Polyisobutylene (PIB) with molecular weight 934 was supplied by Cochin Refineries, Balmer Lawrie Ltd Ambalamugal, Kerala. Oleic acid supplied by Godrej Soaps, Mumbai. Paraffinic oil from Indian Oil Corporation, Chennai. Wax from Gujarat Paraffins, Ahmedbad, Phenol Formaldehyde resin (PF resin) 6414 supplied by Indian Plastics, Mumbai. Compounding ingredients, zinc oxide, stearic acid, and carbon black (HAF, N 330) were commercial grade. Dibenzthiazyl disulphide (MBTS) Tetramethylthiuram disulfide (TMTD) were rubber grade supplied by Bayer India, Mumbai Ltd. Accinox TQ (Polymerised 1,2 dihydro 2,2,4 - Trimethyl Quinoline) was supplied by ICI India Ltd. West Bengal. Pifflex-13 (substituted paraphenylene diamine) was supplied by Poly Olefins Ltd, India. Methanol, dioxan, triethylamine, acetone, methyl ethyl ketone and toluene were of reagent grade and used as such.

2.2. Preparation of polyisobutylene-bound paraphenylene diamine

Polyisobutylene-bound-paraphenylenediamine (PIB-PD) [12] of molecular weight 2300 was prepared by the condensation reaction between chlorinated polyisobutylene and paraphenylene diamine (PD).

2.3. Preparation of chlorinated paraffin wax-bound paraphenylene diamine

Chlorinated paraffin wax-bound paraphenylene diamine (CPW-PD) [13] of molecular weight 1050 was prepared by the condensation reaction between chlorinated paraffin wax and PD.

The newly prepared oligomer-bound antioxidants (Table 1) were added to NR, SBR, NBR, IIR and blends of NR/BR and NR/SBR as per formulations given in the Tables 2–4. The amount of plastciser can be reduced by the use of liquid polymer bound antioxidants as shown in the Tables 2–4.

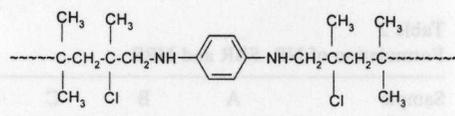
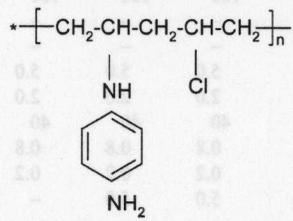
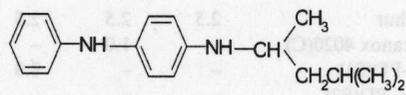
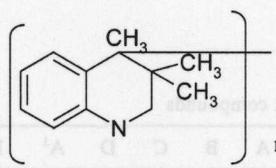
The optimum cure times (time to reach 90% of the maximum torque) of compounds were determined on a Göttfert Elastograph, model 67.85, as per ASTM D-1646 (1981). NR, SBR, NBR NR/SBR and NR/BR mixes were moulded in an electrically heated laboratory hydraulic press at 150 °C up to their optimum cure time. While IIR (resin cure) and IIR(sulphur cure) mixes were moulded in an electrically heated laboratory hydraulic press at 190 and 170 °C respectively up to their optimum cure time.

Rubber compounds were moulded in an electrically heated laboratory hydraulic press at 150 °C up to their optimum cure time. Dumbbell shaped tensile test pieces were punched out of these compression moulded sheets along the mill grain direction. The tensile properties of the vulcanizates were evaluated on a Zwick Universal Testing machine using a cross head speed of 500 mm/min according to ASTM D-412-87, method A. Tear resistance of the vulcanizates was evaluated as per ASTM D-624-86 using un-nicked 90° angled test specimens.

The ageing resistance of the vulcanizates were studied by ageing for 24, 48 and 72 h at 100 °C, then measuring the retention in tensile properties. The compression set of the samples was determined as per ASTM D-395:89, method B. The hardness (shore A) of the moulded samples was tested using a Zwick 3115 hardness tester in accordance with ASTM D-2240. Flex resistance of the samples was tested using a Demattia flexing machine as per ASTM D-813-95. Abrasion resistance was measured using a DIN abrader as per DIN 53516. Resilience of the samples was determined by vertical rebound as per ASTM D 2632-96.

Crosslink density ($1/2M_c$) was determined by the equilibrium swelling method using toluene as solvent for NR, SBR, IIR vulcanizates and for NR/SBR and NR/BR blends. For NBR, methyl ethyl ketone was used, as it swells better in the polar solvent. Samples of ~1 cm diameter, 0.2 cm thickness and 0.2 g weight were punched out from the central portion of the vulcanizate. These were allowed to swell in the solvent for 24 h. The swollen samples were taken out of the solvent and dried in vacuum oven and samples weighed again.

Table 1
Antioxidants used

Name	Formula
<i>Prepared antioxidants</i>	
1. Polyisobutylene-bound-paraphenylenediamine (PIB-PD)	
2. Chlorinated paraffin wax bound-paraphenylenediamine (CPW-PD)	
<i>Conventional antioxidants</i>	
3. Vulkanox 4020	
4. Accinox TQ	

The volume fraction of rubber (V_r) in the swollen network was then calculated by the method reported by Ellis and Welding from the following equation [15].

$$V_r = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_0\rho_s^{-1}}$$

where T —weight of the test specimen, D —deswollen weight of the test specimen, F —weight fraction of insoluble components, A_0 —weight of the absorbed solvent corrected for the swelling increment, ρ_r —density of rubber and ρ_s —density of solvent.

In the case of vulcanizates containing HAF black, the value of V_r obtained as above, was converted into V_{r0} , by means of the following equation which was derived by Porter [16]

$$\frac{V_{r0}}{V_r} = 0.56 \times e^{-z} + 0.44$$

where z —weight fraction of filler.

The crosslink density $1/2 M_c$ was determined from V_{r0} using the Flory–Rehner equation [17].

$$1/2 M_c = - \frac{[\ln(1 - V_{r0}) + V_{r0} + \chi V_{r0}^2]}{2\rho_r V_s (V_{r0})^{1/3}}$$

where ρ_r is the density of rubber; V_s is the molar volume of solvent; χ is the parameter characteristics of the interaction between rubber and solvent; M_c is the number average molecular weight of the rubber chains between crosslinks; and V_{r0} is volume fraction of rubber in swollen network.

Ozone ageing studies under static conditions were conducted according to ASTM D 518 Method B in a Mast Model 700-1 ozone test chamber at 40 °C. Ozone concentration in the chamber was adjusted to 50 parts per hundred million (pphm).

Photographs were taken using an optical microscope Carl Zeiss Stemi 2000 C with magnification 2.5.

3. Results and discussion

Table 5 shows the flex resistance of NR, SBR, NBR, IIR and elastomer blends of NR/BR and NR/SBR. The flex resistance is dependent on the network structure and the nature of the antidegradant present in the sample. The vulcanizates of NR, SBR, NBR and IIR containing new oligomer-bound antioxidants possess significantly superior flex resistance compared to that containing conventional antioxidant even at pin hole crack formation level. The same trend is shown during medium crack growth and deep crack formation. NR/

Table 2
Formulation of NR, SBR and NBR

Sample	A	B	C	D	A1	B1	C1	D1	A2	B2	C2	D2
NR	100	100	100	100	–	–	–	–	–	–	–	–
SBR	–	–	–	–	100	100	100	100	–	–	–	–
NBR	–	–	–	–	–	–	–	–	100	100	100	100
ZnO	5.0	5.0	5.0	5.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
HAF N330	40	40	40	40	40	40	40	40	40	40	40	40
MBTS	0.8	0.8	0.8	0.8	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
TMTD	0.2	0.2	0.2	0.2	0.15	0.15	0.15	0.15	0.5	0.5	0.5	0.5
Aromatic oil	5.0	5.0	–	–	5.0	5.0	–	–	–	–	–	–
DOP	–	–	–	–	–	–	–	–	5.0	5.0	–	–
Sulphur	2.5	2.5	2.5	2.5	2.0	2.0	2.0	2.0	1.5	1.5	1.5	1.5
Vulkanox 4020(C)	–	1.0	–	–	–	1.0	–	–	–	1.0	–	–
PIB-PD(S1)	–	–	8.0	–	–	–	8.0	–	–	–	8.0	–
CPW-PD(S2)	–	–	–	6.0	–	–	–	6.0	–	–	–	6.0

Table 3
Formulation of IIR compounds

Sample	A	B	C	D	A ¹	B ¹	C ¹	D ¹
IIR	95	95	95	95	100	100	100	100
Neoprene	5	5	5	5	–	–	–	–
HAF N330	60.0	60.0	60.0	60.0	55.0	55.0	55.0	55.0
ZnO	5.0	5.0	5.0	5.0	4.0	4.0	4.0	4.0
Stearic acid	1.0	1.0	1.0	1.0	2.0	2.0	2.0	2.0
Oleic acid	3.0	3.0	3.0	3.0	–	–	–	–
Wax	1.0	1.0	1.0	1.0	–	–	–	–
PF resin	10.8	10.8	10.8	10.8	–	–	–	–
Paraffinic oil	4.0	4.0	–	–	15	15	7.0	8.0
MBTS	–	–	–	–	1.0	1.0	1.0	1.0
Sulphur	–	–	–	–	2.0	2.0	2.0	2.0
Vulkanox 4020(C)	–	1.0	–	–	–	1.0	–	–
PIB-PD(S1)	–	–	8.0	–	–	–	8.0	–
CPW-PD(S2)	–	–	–	6.0	–	–	–	6.0

BR blends show superior flex crack resistance compared to NR/SBR blends as expected. Here also blends containing bound antioxidants show better resistance to crack formation. This improved performance is obviously due to the polymeric nature of the bound antioxidants.

Table 6 shows the ozone resistance of NR, SBR, NBR, IIR and elastomer blends of NR/BR and NR/SBR. The NR, SBR and NBR are vulnerable to ozone attack but when bound antioxidants are used the extent of cracking is reduced. Butyl rubber has good ozone resistance. IIR resin cured vulcanizates display better ozone resistance than sulphur cured ones. Here also the vulcanizates containing bound antioxidants are superior to the conventional one. NR/SBR blend is less susceptible to ozone attack than NR/BR.

Table 7 shows the variation in mechanical properties of the vulcanizates with and without antioxidant. The variation in tensile strength, elongation at break, modulus, crosslink density, tear strength and abrasion resistance before and after ageing at 100 °C for 72 h is given

Table 4
Formulation of NR/BR and NR/SBR blends

Sample	A4	B4	C4	D4	A5	B5	C5	D5
NR	70	70	70	70	70	70	70	70
BR	30	30	30	30	–	–	–	–
SBR	–	–	–	–	30	30	30	30
ZnO	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Stearic acid	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
HAF N330	45	45	45	45	45	45	45	45
Aromatic oil	7.5	7.5	0	0	7.5	7.5	0	0
Accinox TQ(C)	–	1.0	–	–	–	1.0	–	–
MOR	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
TMTD	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Sulphur	2.1	2.1	2.1	2.1	2.2	2.2	2.2	2.2
PIB-PD(S1)	–	–	8.0	–	–	–	8.0	–
CPW-PD(S2)	–	–	–	6.0	–	–	–	6.0

in Table 7. Retention in properties is improved by the addition of new oligomer-bound antioxidants for rubber vulcanizates and blends. A similar trend was shown for crosslink densities and abrasion resistance. From this we could infer that bound and antioxidants have better retention of properties compared to vulcanizates containing conventional antioxidants.

Figs. 1–7 show the various optical micrographs of ozone-cracked samples of NR, SBR, NBR, IIR (S-cure), IIR (resin cure), NR/SBR and NR/BR vulcanizates respectively. Fig. 1(a)–(d) show the photographs of ozone cracked surface of NR vulcanizates on crack initiation. Fig. 1(a¹)–(d¹) show the photographs of ozone-cracked surface of NR vulcanizates after 19 h in an ozone chamber. The photographs clearly show that vulcanizates without antioxidants develop severe cracks [Fig. 1(a) and (a¹)], vulcanizates with conventional antioxidant show less cracking [Fig. 1(b) and (b¹)], while fewest cracks are observed for samples containing bound antioxidants [Fig. 1(c) and (d) and (c¹) and (d¹)]. So it may be concluded that the ozone resistance of the

Table 5
Flex cracking (kilocycles)

Samples	Pin holes				Small cracks				Medium cracks				Deep cracks			
	W	C	S1	S2	W	C	S1	S2	W	C	S1	S2	W	C	S1	S2
NR	35	40	50	55	40	60	80	90	66	82	100	102	80.7	104	181	185
SBR	150	180	220	240	180	235	290	295	230	270	325	330	260	300	350	360
NBR	55	75	100	105	85	99	124	136	100	152	163	170	113	183	194	196
IIR (S-cure)	58	65	75	68	75	82	85	87	78	88	90	94	82	92	100	110
IIR (resin cure)	465	509	748	800	512	589	785	980	582	685	813	1052	718	808	989	1200
NR/BR	200	310	351	378	422	462	421	428	462	500	555	560	500	550	600	620
NR/SBR	72	109	138	164	110	150	216	219	150	186	232	245	184	233	284	290

Table 6
Ozone resistance of the samples W, without antioxidant, C, conventional antioxidant, PIB-PD and CPW-PD (bound antioxidants)

Samples	Crack initiation time (h)				Nature of ozone crack of samples after 19 h in ozone chamber			
	W	C	PIB-PD	CPW-PD	W	C	PIB-PD	CPW-PD
NR	2	2.5	3	3	Deep	Deep	Moderate	Moderate
SBR	3	4	5	5.5	Deep	Deep	Moderate	Moderate
NBR	3	4	4.5	5	Deep	Deep	Moderate	Moderate
IIR (S-cure)	5	6	10	12	Deeper	Deep	Shallow	Shallow
IIR (resin cure)	5	7	9	14	Deep	Moderate	Shallow	Shallow
NR/BR	2.5	3	5	6	Deep	Deep	Moderate	Moderate
NR/SBR	3.5	6	8	9	Deep	Deep	Shallow	Shallow

Table 7
Mechanical properties before and after ageing for 100 °C

Samples	Properties										
	TS (N/mm ²)		EB (%)		M (200%, N/mm ²)		C.D × 10 ⁻⁵	Tearstr. (N/mm)		Ab. Re. (cc/h)	
	RT	Aged, 72 h at 100 °C	RT	Aged, 72 h at 100 °C	RT	Aged, 72 h at 100 °C	RT	RT	Aged, 72 h at 100 °C	RT	
NR	W	28	5.5	500	170	8.4	–	6.45	77	26.1	3.8
	C	28.3	10.7	500	220	8.7	10.7	7.6	79	36	3.6
	S1	29	13.5	490	270	8.8	11.5	7.9	81	45	3.5
	S2	27	12	510	290	8.9	11.6	8.33	82	49	3.3
SBR	W	23.4	7.02	420	140	6.2	–	4.1	67	20	3.1
	C	24.6	10	418	200	6.4	8.6	6.66	68	31	3.0
	S1	24	12.1	419	180	6.5	9.5	7.12	68	42	2.9
	S2	24.3	13.1	410	140	6.9	8	7.34	71	43	2.8
NBR	W	22	8	580	201	5.86	8	12	55	20	3.1
	C	22.5	11	570	241	6.2	9	14	54	24	2.8
	S1	23	14	555	310	6.3	10.5	16	55	30	2.7
	S2	23	17	550	280	6.4	10.6	18	56	33	2.7
IIR (S-cure)	W	14.3	7	612	300	5.2	6.5	1.43	55	21	8.5
	C	14.5	11	572	410	5.8	6.8	1.45	56.2	29	8.0
	S1	14.6	12.5	570	480	5.9	7.5	1.65	56.5	34.5	7.9
	S2	14.8	13.6	568	505	6	8.5	1.67	56.6	35	7.9
IIR (PF-resin cure)	W	15.2	9	660	400	6.6	8.12	2.5	55.2	22	6.5
	C	15.3	11.7	695	498	6.65	8.4	2.3	56	30	6.2
	S1	15.8	12	695	590	6.7	8.7	2.5	56.5	34	6.1
	S2	15.5	12.2	690	600	6.75	8.9	2.6	57	35.8	5.9
NR/BR blend	W	20.5	6	580	130	7.2	–	7.2	67	23	2.9
	C	20.8	8.4	584	200	7.5	8.4	7.5	68	32	2.8
	S1	21	12	578	280	8.0	9.0	8	70	45	2.6
	S2	21.5	13	572	320	8.2	9.2	8.26	71	48	2.6
NR/SBR blend	W	21.6	7	530	160	5.9	–	6.24	65	19	3.5

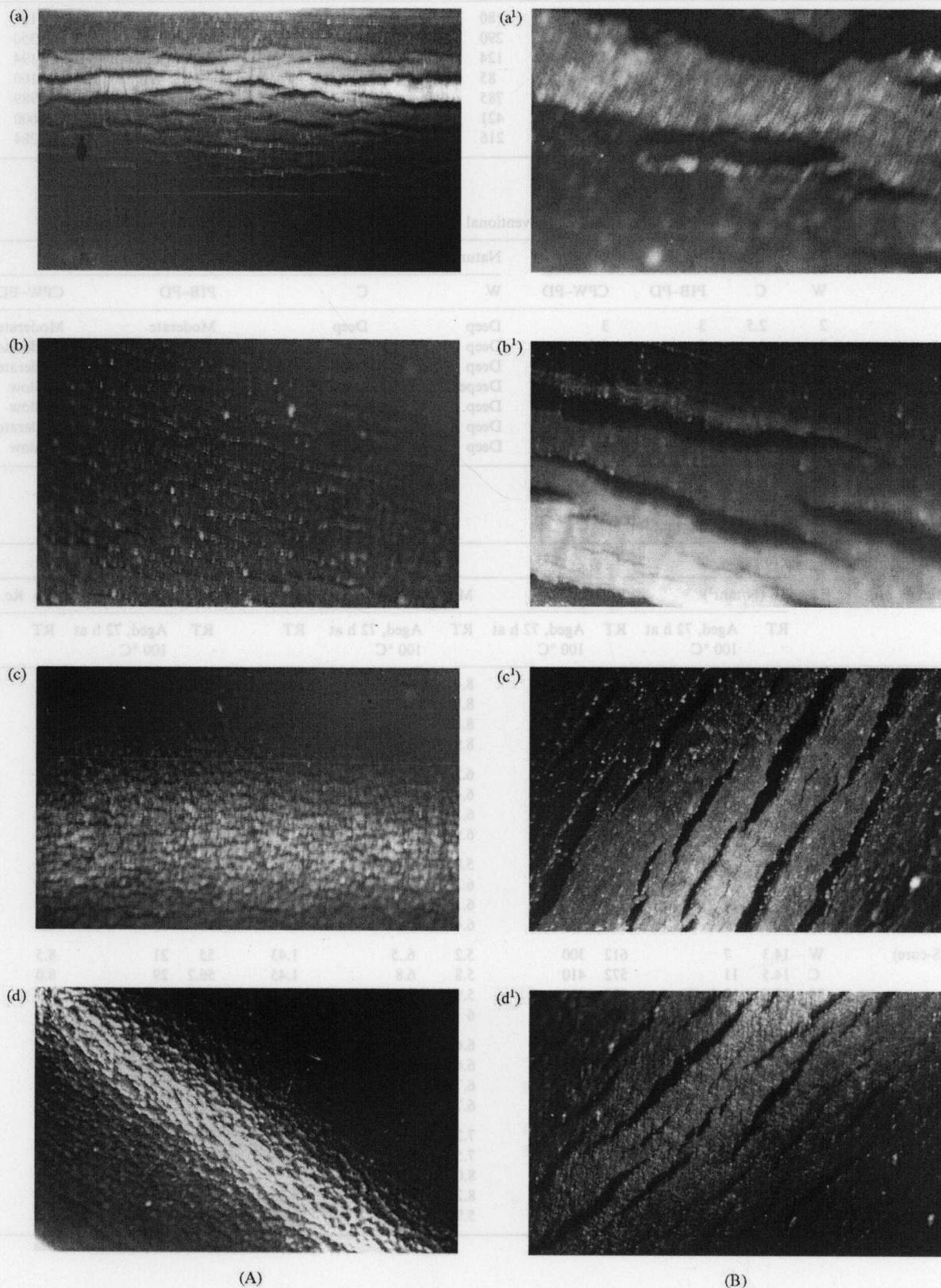


Fig. 1. (A) Ozone crack initiation of NR vulcanizates (a) without antioxidant, (b) with vulkanox 4020, (c) with PIB-PD, (d) with CPW-PD; (B) ozone crack growth after 19 h (a') without antioxidant, (b') with vulkanox 4020, (c') with PIB-PD, (d') with CPW-PD.

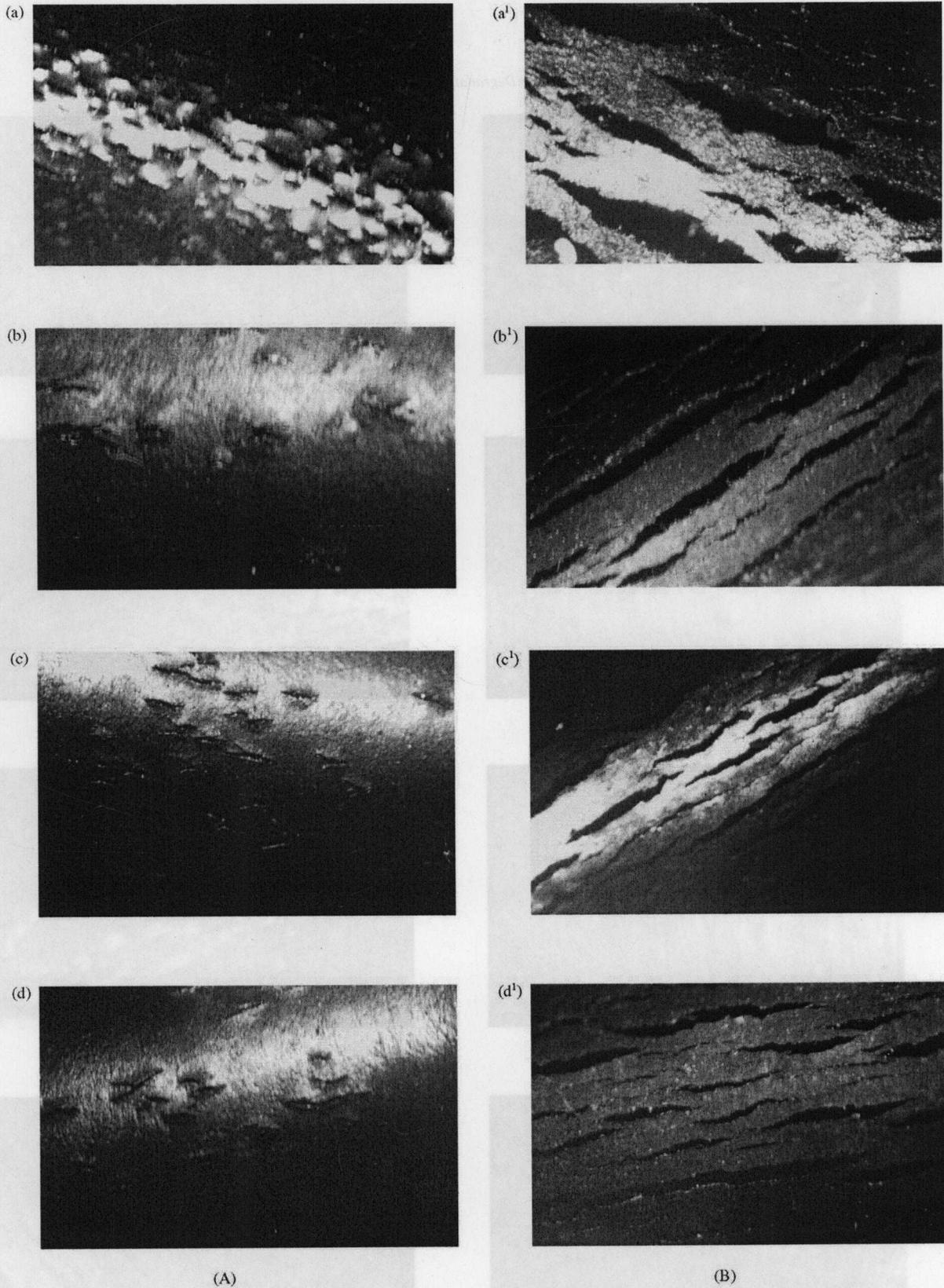


Fig. 2. (A) Ozone crack initiation of SBR vulcanizates (a) without antioxidant, (b) with vulkanox 4020, (c) with PIB-PD, (d) with CPW-PD; (B) ozone crack growth after 19 h (a') without antioxidant, (b') with vulkanox 4020, (c') with PIB-PD, (d') with CPW-PD.

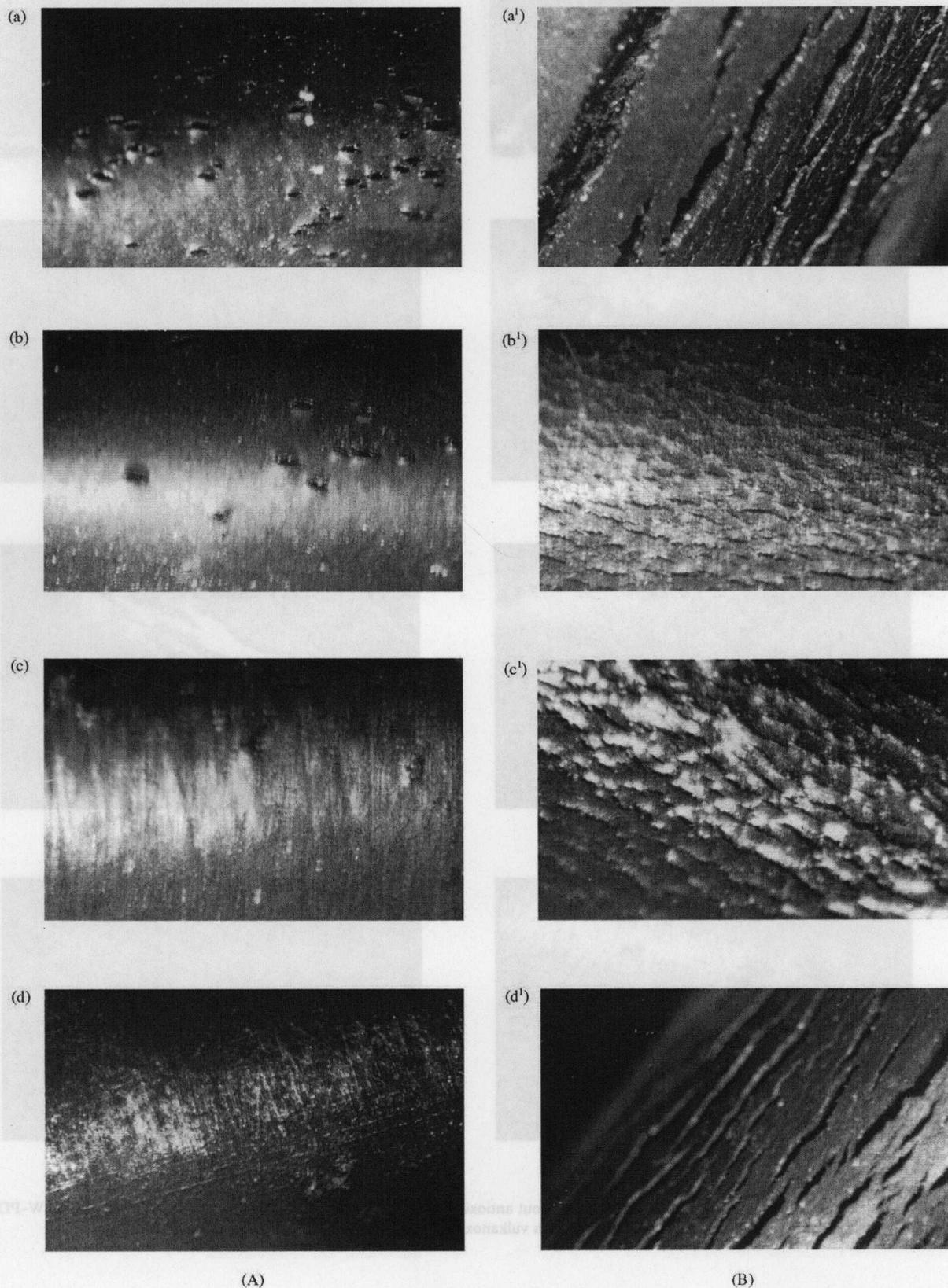


Fig. 3. (A) Ozone crack initiation of NBR vulcanizates (a) without antioxidant, (b) vulkanox 4020, (c) with PIB-PD, (d) with CPW-PD; (B) ozone crack growth after 19 h (a') without antioxidant, (b') with vulkanox 4020, (c') with PIB-PD, (d') with CPW-PD.

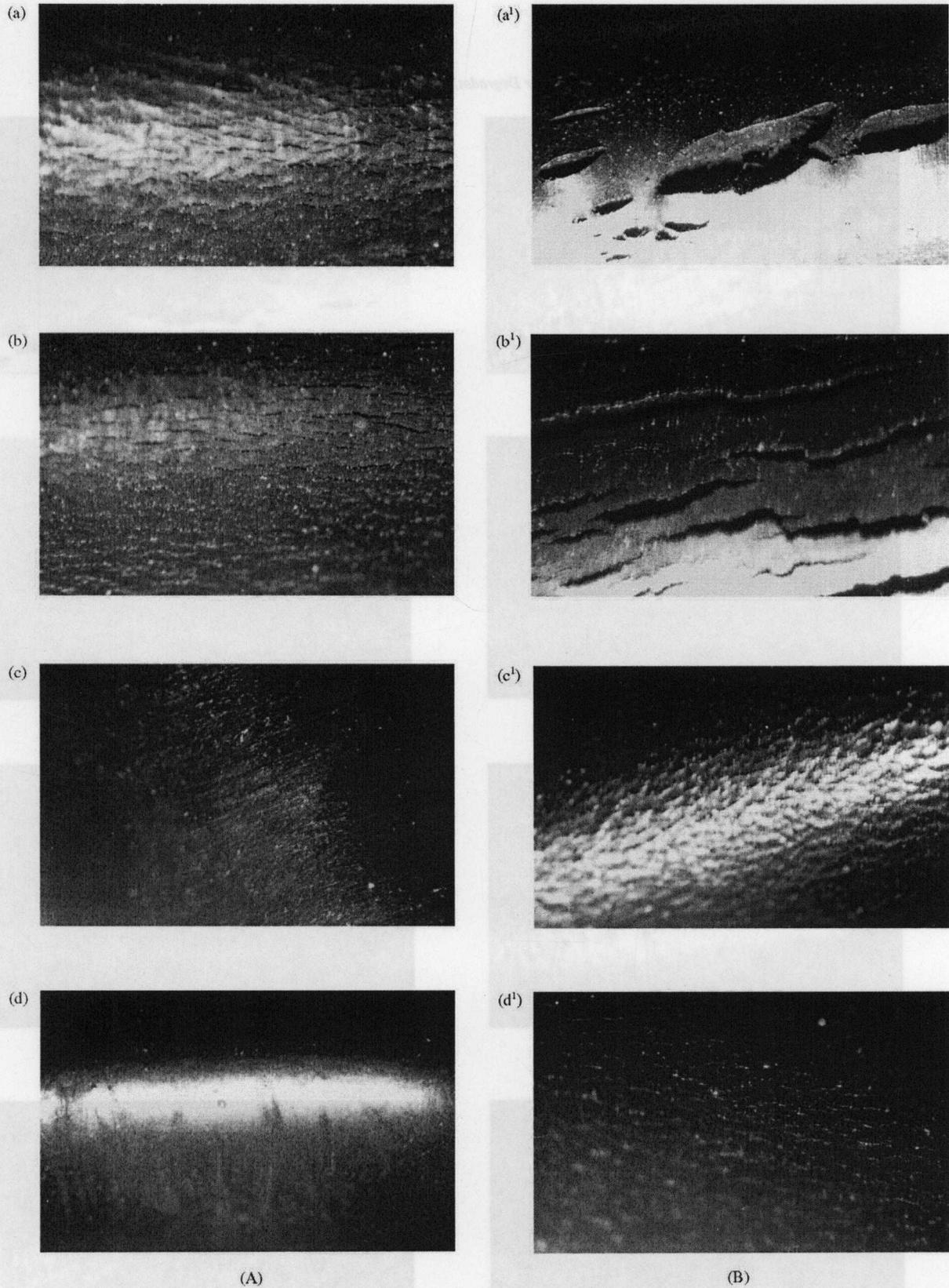


Fig. 4. (A) Ozone crack initiation of IIR (S-cure) vulcanizates (a) without antioxidant, (b) with vulkanox 4020, (c) with PIB-PD, (d) with CPW-PD; (B) ozone crack growth after 19 h (a') without antioxidant, (b') with vulkanox 4020, (c') with PIB-PD, (d') with CPW-PD.

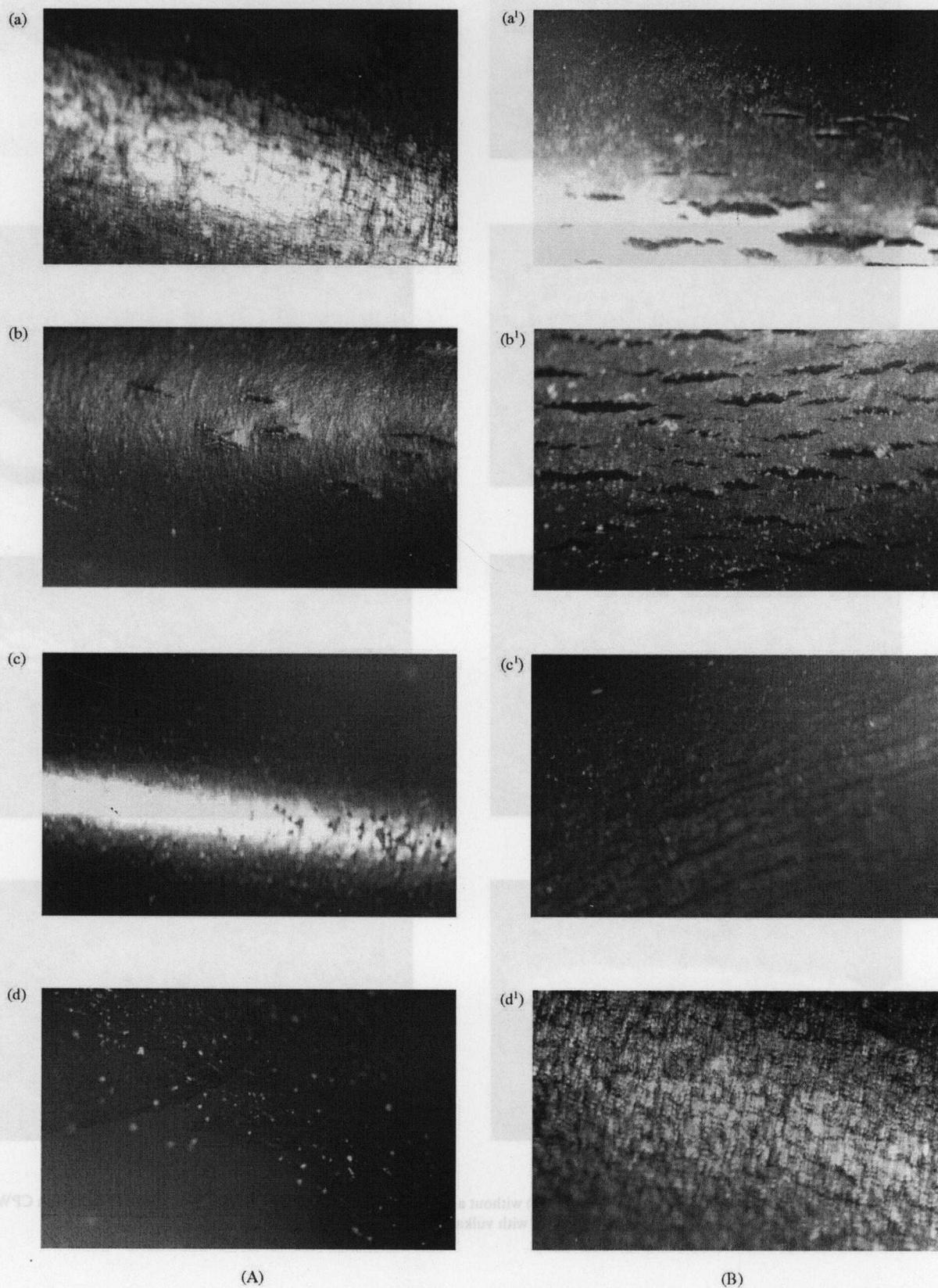


Fig. 5. (A) Ozone crack initiation of IIR (resin cure) vulcanizates (a) without antioxidant, (b) with vulkanox 4020, (c) with PIB-PD, (d) with CPW-PD; (B) ozone crack growth after 19 h (a') without antioxidant, (b') with vulkanox 4020, (c') with PIB-PD, (d') with CPW-PD.

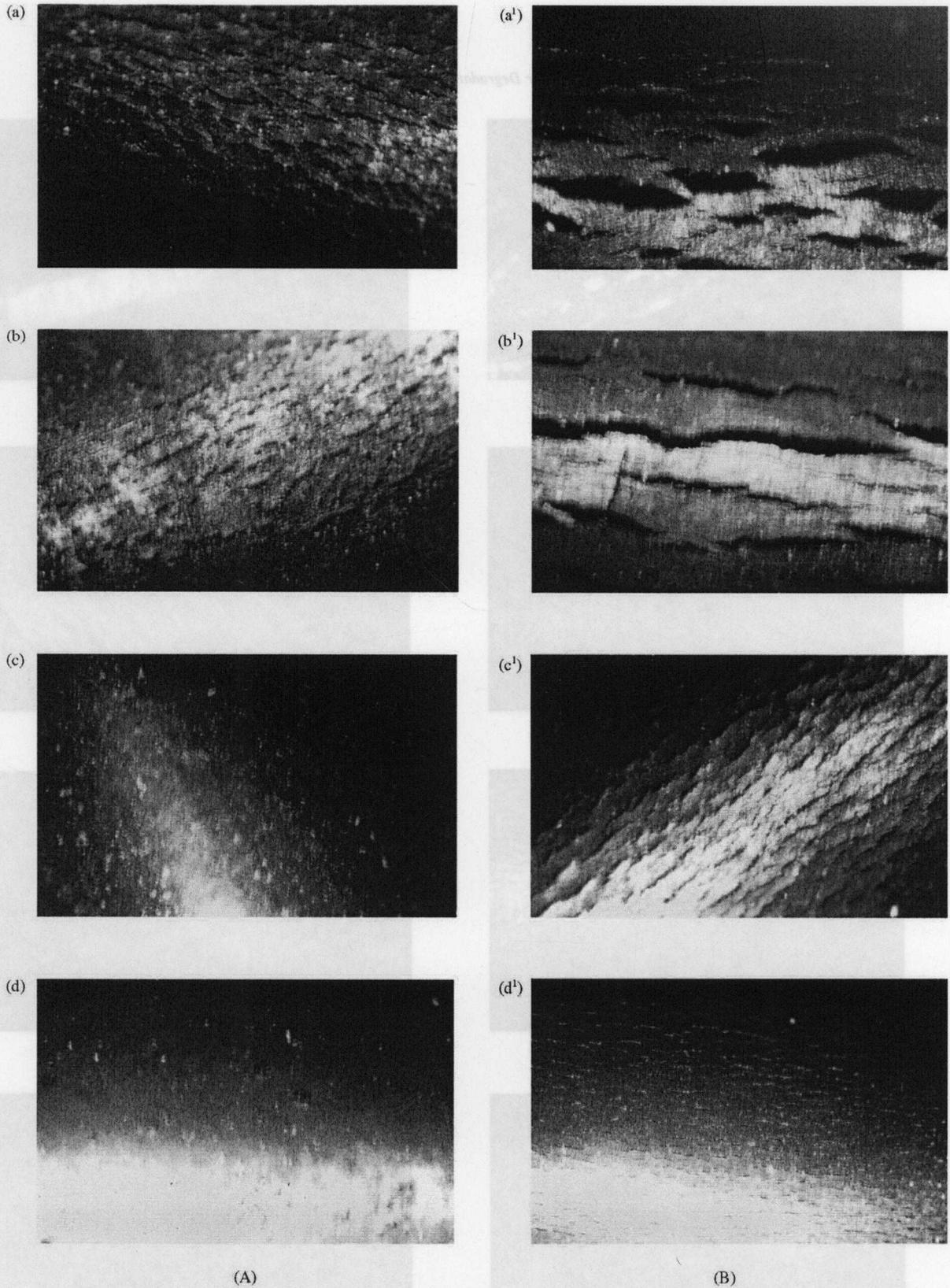


Fig. 6. (A) Ozone crack initiation of NR/SBR blends (a) without antioxidant, (b) with accinox TQ, (c) with PIB-PD, (d) with CPW-PD; (B) ozone crack growth after 19 h (a') without antioxidant, (b') with accinox TQ, (c') with PIB-PD, (d') with CPW-PD.

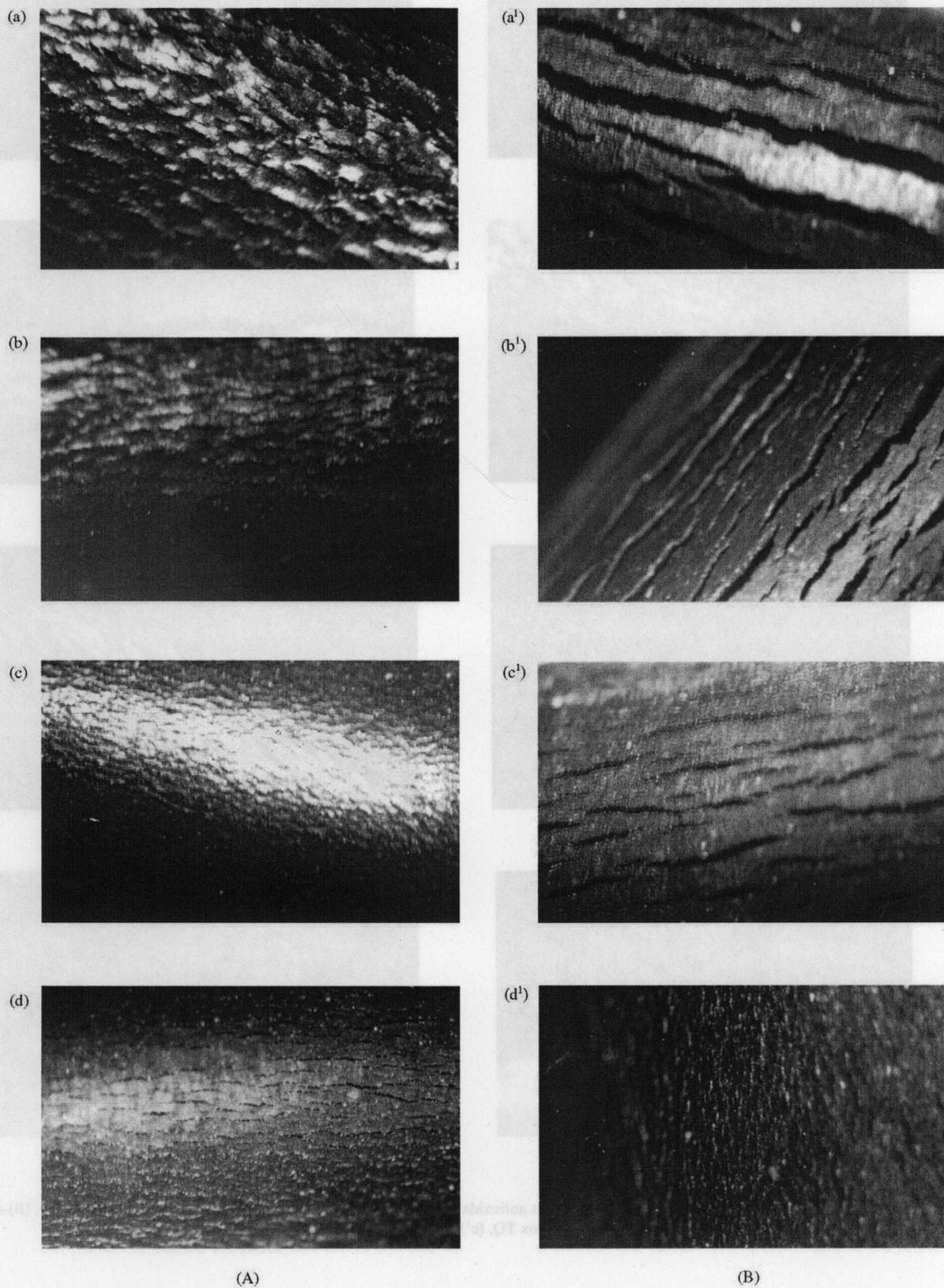


Fig. 7. (A) Ozone crack initiation of NR/BR blends (a) without antioxidant, (b) with accinox TQ, (c) with PIB-PD, (d) with CPW-PD; (B) ozone crack growth after 19 h (a') without antioxidant, (b') with accinox TQ, (c') with PIB-PD, (d') with CPW-PD.

vulcanizates containing bound-antioxidants is superior to the vulcanizates containing conventional antioxidant.

Fig. 2(a)–(d) shows the photographs of ozone cracked surface of SBR vulcanizates on crack initiation. Fig. 2(a¹)–(d¹) shows the photographs of ozone-cracked surface of SBR vulcanizates after 19 h in an ozone chamber. The photographs clearly show that vulcanizates without antioxidants develop severe cracks [Fig. 2(a) and (a¹)], vulcanizates with conventional antioxidant show fewer cracks [Fig. 2(b) and (b¹)], while fewest cracks are again observed for samples containing bound antioxidants [Fig. 2(c) and (c¹) and (d) and (d¹)]. This further proves that the ozone resistance of the vulcanizates containing bound antioxidants is superior compared to the vulcanizate containing conventional antioxidant.

Fig. 3(a)–(d) shows the photographs of ozone cracked surface of NBR vulcanizates on crack initiation. Fig. 3(a¹)–(d¹) shows the photographs of ozone-cracked surface of NBR vulcanizates after 19 h in an ozone chamber. The photographs clearly show that vulcanizates without antioxidants develop severe cracks [Fig. 3(a) and (a¹)], vulcanizates with conventional antioxidant show fewer cracks [Fig. 3(b) and (b¹)], while fewest cracks are observed for samples containing bound antioxidants [Fig. 3(c) and (c¹) and (d) and (d¹)]. Even though the resistance to ozone degradation is less compared to other vulcanizates, the ones containing bound antioxidant are superior in ozone resistance compared to that containing conventional antioxidant (Table 6) as in the previous case.

Fig. 4(a)–(d) shows the photographs of ozone cracked surface of IIR (S-cured) vulcanizates on crack initiation. Fig. 4(a¹)–(d¹) shows the photographs of ozone-cracked surface of IIR (S-cured) vulcanizates after 19 h in an ozone chamber. The photographs clearly show that vulcanizates without antioxidants develop intense cracks [Fig. 4(a) and (a¹)], vulcanizates with conventional antioxidant show fewer cracks [Fig. 4(b) and (b¹)], while lowest level of cracking is observed for samples containing bound antioxidants [Fig. 4(c) and (c¹) and (d) and (d¹)]. This again shows that the ozone resistance of the vulcanizates containing bound antioxidants is superior to the vulcanizates containing conventional antioxidant.

Fig. 5(a)–(d) shows the photographs of ozone cracked surface of IIR (resin cured) vulcanizates on crack initiation. Figs. 5(a¹)–(d¹) shows the photographs of ozone-cracked surface of IIR vulcanizates after 19 h in an ozone chamber. The photographs clearly show that vulcanizates without antioxidants develop severe cracks [Fig. 5(a) and (a¹)], vulcanizates with conventional antioxidant show fewer cracks [Fig. 5(b) and (b¹)], while fewest cracks are observed for samples containing bound antioxidants [Fig. 5(c) and (c¹) and (d) and (d¹)]. The same trend is noticed as in the above cases.

The resin-cured butyl rubber has superior inhibition against ozone cracking than sulphur-cured ones as expected.

Fig. 6(a)–(d) shows the photographs of ozone cracked surface of NR/SBR blends on crack initiation. Fig. 6(a¹)–(d¹) shows the photographs of ozone-cracked surface of NR/SBR blends after 19 h in an ozone chamber. The photographs clearly show that the blends without antioxidants develop deeper cracks [Fig. 6(a) and (a¹)] and the blends with conventional antioxidant show fewer cracks [Fig. 6(b) and (b¹)] whereas fewest cracks are observed for samples containing bound antioxidants [Fig. 6(c) and (c¹) and (d) and (d¹)]. So improved ozone resistance of the blends containing bound antioxidants is demonstrated. NR/SBR blends show excellent results, which may be due to the higher ozone resistance of SBR present.

Fig. 7(a)–(d) shows the photographs of ozone cracked surface of NR/BR blends on crack initiation. Fig. 7(a¹)–(d¹) shows the photographs of ozone-cracked surface of NR/BR blends after 19 h in an ozone chamber. The photographs clearly show that blends without antioxidants develop severe cracks [Fig. 7(a) and (a¹)], blends with conventional antioxidant show less cracking [Fig. 7(b) and (b¹)], while least cracking is observed for samples containing bound antioxidants [Fig. 7(c) and (c¹) and (d) and (d¹)]. This shows the superiority of the bound antioxidants in elastomer blends as in the case of the individual elastomers.

The greater resistance to ozone ageing for polymers containing bound antioxidants may be due to their appreciably higher molecular weight, which lessens their volatility. The saturated backbone prevents network formation, which helps blooming to the surface and acting as a good barrier for ozone attack.

When the efficiency of bound antioxidants CPW–PD and PIB–PD compared, it may be observed that the former imparts higher resistance. This may be due to its lower molecular weight, which helps blooming to the surface of rubber products to form a thin inert protective film to prevent direct contact with the atmospheric air.

4. Conclusions

1. Ozone and flex resistance of the vulcanizates containing bound antioxidants are superior to those containing conventional antioxidants.
2. The bound antioxidant is effective in elastomer blends of NR/SBR and NR/BR.
3. The vulcanizate containing oligomer-bound antioxidants is found to give superior ageing resistance compared to that containing conventional antioxidants.

4. The mechanical properties are improved by the use of oligomer-bound antioxidants.

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