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Curable copolymers of isobutylene and acrylic ester

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Curable copolymers of isobutylene and acrylic ester were successfully synthesized by incorporation of a third monomer into alternating copolymers of isobutylene and acrylic ester by means of complexed copolymerization catalysed with alkylboron halide. As the third monomer, acrylic ester including an unsaturated bond in the ester group (AEU), such as crotyl acrylate, or vinyl monomer including a chlorine atom (CVM), such as 2-chloroethyl vinyl ether, was effectively incorporated. The terpolymers containing AEU (AIDM) were easily vulcanized with sulfur. The terpolymers containing CVM (AICM) were sufficiently well cured with polyamine. The cured products of both AIDM and AICM had excellent properties in terms of oil resistance, water resistance and others. The blend of AIDM and ethylene–propylene–diene rubber was satisfactorily co-vulcanized with sulfur.

(Keywords: isobutylene; acrylic ester; curable copolymer)

INTRODUCTION

The authors have already found that alternating copolymers of isobutylene (IB) and acrylic ester (AE) were obtained by means of complexed copolymerization catalysed with alkylboron halide in much higher activities than with alkylaluminium halide[1].

The alternating copolymers of IB and AE have characteristic properties which cannot be expected from those of the corresponding homopolymers[2]. The alternating copolymers have higher thermal decomposition temperature than both homopolymers. Their hydrolysis resistance is excellent compared with the corresponding poly(acrylic ester)s and their weatherability is very good because of the lack of an unsaturated group. Their solubility parameter is about intermediate between the two homopolymers and they are expected to have good compatibility with both non-polar and polar polymers. Also the alternating copolymers are considered to have good oil resistance derived from the homogeneous distribution of polar ester groups.

Judging from the glass transition temperature and stress–strain curve, IB–ethyl acrylate and IB–n-butyl acrylate alternating copolymers have rubber-like properties. But the mechanical strengths of these copolymers are weak for practical uses (for example, their tensile strength is below $20\,\mathrm{kg\,cm^{-2}}$). Therefore if the alternating copolymers are made curable to become mechanically strong, they will afford new high-performance rubbers; especially, if an unsaturated bond is introduced into them they will be co-vulcanizable with commercial rubbers such as ethylene–propylene–diene rubber (EPDM) and others to give new rubbers. To make the alternating copolymers curable, it will be effective to incorporate a third monomer as curing sites.

In this paper the authors report the synthesis and the cured properties of the sulfur-vulcanizable terpolymers (AIDM) of IB, AE and diene, and the amine-curable terpolymers (AICM) of IB, AE and vinyl monomer including a chlorine atom.

EXPERIMENTAL

Materials

Ethylidene norbornene, dicyclopentadiene, 1,4-hexadiene and 4-vinylcyclohexene were commercial-grade samples used after distillation. Isopropenyl norbornene, methylene norbornene and chloromethyl norbornene were synthesized. Acrylic esters including an unsaturated bond in the ester group were synthesized by the ester interchange reaction between an alcohol with an unsaturated bond (R′OH) and methyl acrylate[3]:

$$\mathrm{CH_2{=}CHCOOCH_3 + R'OH}$$
$$\rightarrow \mathrm{CH_2{=}CHCOOR' + CH_3OH}$$

Vinyl monomers including a chlorine atom such as 2-chloroethyl vinyl ether, vinyl chloroacetate and 2-chloroethyl acrylate were commercial-grade samples used after drying with 4 Å molecular sieves. Other materials were described in the previous paper[1].

Polymerization

The polymerization was conducted following the method described in the previous paper[1] under a nitrogen atmosphere. In the case when diene was one

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component, a little antioxidant was added to the polymerization solution at the end of polymerization, and then the polymerization solution was poured into a rotating mixer containing an excess of methanol and the coagulated polymer was dried in a vacuum.

Curing method

Curing recipe. The components of the cure are as follows:

Component	AIDM (phr)	AICM (phr)
AIDM	100	
AICM		100
HAF carbon black	50	50
Stearic acid	1	1
Sulfur	1.5	1
Triethylenetetramine	–	2
Zinc oxide	5	
Tetramethylthiuram disulfide	1.5	
Mercaptobenzothiazole	0.5	

Compounding. Compounding was carried out using a Plasti-corder made by Brabender Ltd at 80°C.

Curing. The conditions for curing were:

Condition	AIDM	AICM
Temperature (°C)	160	120–150
Pressure (kg cm^{-2})	110	110
Time (min)	40	30

Measurements

Gel content was obtained as weight per cent of the insoluble part after shaking the flask containing 1 g of polymer and 100 ml of benzene at room temperature for 24 h. Iodine value was measured by a titrimetric method. Oil resistance tests were done in TSS test tube ageing testers made by Toyoseiki Manufacturing Co. at 70°C for 70 h using ASTM No. 3 oil from Japan Sun Petroleum Co. Water resistance tests were carried out by immersing samples in distilled water at 25°C for 10 days. Other measurements were described in the previous paper[1,2].

RESULTS AND DISCUSSION

Synthesis of the curable copolymers

The authors put two ideas into practice in order to incorporate diene into the alternating copolymers of IB and AE. They are the terpolymerization of (a) IB, AE and non-conjugated diolefin (NCD), and (b) IB, AE and acrylic ester including an unsaturated bond in the ester group (AEU).

NCD is considered to belong to the donor monomer in the present complexed copolymerization and is expected to replace part of the IB in the alternating sequences. On the other hand AEU is considered to belong to the acceptor monomer and is expected to replace part of the AE.

Terpolymerization of isobutylene, acrylic ester and non-conjugated diolefin. First the copolymerization of NCD and ethyl acrylate (EA) with ethylboron dichloride ($BEtCl_2$) was examined. The molar ratio of NCD/EA/$BEtCl_2$ in the feed was 30/20/1. The results are shown in *Table 1*. Isopropenyl norbornene (run No. 1) and methylene norbornene (run No. 2), which have a vinylidene group like IB, copolymerized in high yields. They will perhaps have *e* values near to that of IB. Norbornene derivatives such as dicyclopentadiene (run No. 4) and chloromethyl norbornene (run No. 7) gave low yields, i.e. the olefinic double bond in the norbornene ring did not have a high reactivity. Both 1,4-hexadiene (run No. 5) and 4-vinylcyclohexene (run No. 6) did not afford copolymers at all, i.e. the α-olefinic group and inner olefinic group hardly copolymerized. This will be derived from the higher *e* value (α-olefinic group) than for IB (in this connection, the *e* value[4] of hexene-1 is 0.92 and that of IB is -1.20) or steric hindrance (inner olefinic group). Ethylidene norbornene (run No. 3) showed a higher reactivity than dicyclopentadiene but the reason is not clear. In the cases of high yields, the gel contents were also high (run Nos. 1, 2 and 3) perhaps because both olefinic double bonds participated in the copolymerization. All copolymers were nearly equimolar composition except chloromethyl norbornene.

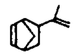
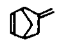
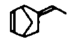
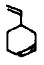
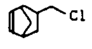
The results of the terpolymerization of IB, EA and NCD with $BEtCl_2$ are shown in *Table 2*. The molar ratio of IB/NCD/EA/$BEtCl_2$ in the feed was 40/4/20/1. Isopropenyl norbornene (run No. 1), which has a vinylidene group like IB, showed a comparatively similar reactivity to IB judging from both conversions. Methylene norbornene (run No. 2) also terpolymerized in a relatively high reactivity though inferior to isopropenyl norbornene. Ethylidene norbornene (run No. 3) and dicyclopentadiene (run No. 4) hardly terpolymerized in these conditions. Terpolymers in which isopropenyl norbornene or methylene norbornene was incorporated contained a high proportion of gels. All polymers contained about 50 mol% of EA. The feed monomer ratios were not so widely varied and the structure of polymers was not analysed; and therefore we cannot say clearly but perhaps isopropenyl norbornene or methylene norbornene reacted as donor monomer in the present complexed copolymerization to replace a part of the IB in the alternating sequences.

As mentioned above, NCDs having a vinylidene group were terpolymerized in good yields, but had the disadvantage of giving gelled polymers in the production process.

Terpolymerization of isobutylene, acrylic ester and acrylic ester including an unsaturated bond in the ester group. AEU including an unsaturated bond in the ester group was considered to be incorporated uniformly into the alternating sequences of IB and AE because the olefinic double bond in the conjugated position with the carbonyl group would have *Q* and *e* values near to those of AE.

The results of the terpolymerization are shown in *Table 3*. The molar ratio of IB/EA/AEU/$BEtCl_2$ in the feed was 100/20/2/1. All AEUs were terpolymerized in high yields. Methallyl acrylate (run No. 2) having a vinylidene group like IB polymerized at both acryloyl and methallyl groups judging from the high gel content and low iodine value. On the contrary in the cases of crotyl acrylate (run No. 3) and citroneryl acrylate (run No. 4) having an inner olefinic group, as expected, completely gel-free terpolymers were produced. This can be understood from the fact that the inner olefinic group

Table 1 Copolymerization of non-conjugated diolefin (NCD) and ethyl acrylate (EA)[a]

			Polymer					
	NCD		Polymerization yield	Gel content	Oxygen anal.	EA (mol%)	Conv. (%) on	
Run No.	Name[b]	Structure	(g)	(wt%)	(wt%)	in polymer	NCD	EA
1	IPNB		4.00	79	15.00	54.2	53	94
2	MNB		2.08	53	16.56	53.1	32	54
3	ENB		1.86	45	15.35	52.5	27	45
4[c]	DCPD		1.01	8	15.94	56.7	13	25
5	1,4-HD		0	–	–	–	–	–
6	VCH		0.06	–	–	–	–	–
7	CMNB		0.57	0	21.97 Cl 7.12	75.7	4	20

[a] Conditions: NCD, 30 mmol; EA, 20 mmol; $BEtCl_2$, 1 mmol; temp., −20°C; time, 3 h; order of addition, $BEtCl_2 \rightarrow$ the mixture of NCD and EA; under N_2 atmosphere; vessel, a glass tube

[b] IPNB, isopropenyl norbornene; MNB, methylene norbornene; ENB, ethylidene norbornene; DCPD, dicyclopentadiene; 1,4-HD, 1,4-hexadiene; VCH, 4-vinylcyclohexene; CMNB, chloromethyl norbornene

[c] Temp., 25°C; [η], 0.46 dl g^{-1}

Table 2 Terpolymerization of isobutylene (IB), ethyl acrylate (EA) and non-conjugated diolefin (NCD)[a]

			Polymer								
		Polymerization yield	Gel content	Iodine	Oxygen anal.	Composition (mol%)			Conv. (%) on		
Run No.	NCD	(g)	(wt%)	value	(wt%)	IB	NCD	EA	IB	NCD	EA
1	IPNB	12.4	87	13.5	18.53	49.7	4.2	46.1	48	41	90
2	MNB	12.5	70	5.3	19.16	52.2	1.6	46.2	53	16	94
3	ENB	12.1	39	1.6	20.62	48.9	0.5	50.6	47	5	97
4	DCPD	12.5	0	0	20.93	48.6	0	51.4	48	0	100
5	1,4-HD	1.8	–	0.3	20.52	–	–	–	–	–	–
6	VCH	12.2	–	0.6	20.16	–	–	–	–	–	–
7	CMNB	10.9	–	–	20.25 Cl 0.04	50.7	0.1	49.2	44	0.9	86

[a] Conditions: IB, 160 mmol; EA, 80 mmol; NCD, 16 mmol; $BEtCl_2$, 4 mmol; temp., −20°C; time, 3 h; order of addition, IB $\rightarrow$ $BEtCl_2$ $\rightarrow$ the mixture of NCD and EA; under N_2 atmosphere; vessel, a glass tube

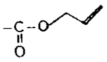
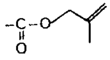
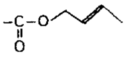
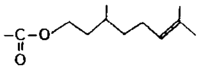
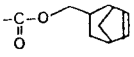
had hardly copolymerized with AE (*Table 1*). Norbornenylmethyl acrylate (run No. 5) having a norbornene ring gave a highly gelled polymer just like isopropenyl norbornene (*Table 2*). Allyl acrylate (run No. 1) gave a gelled polymer under these conditions. As for the gel formation in allyl acrylate, a few reasons are considered but not clear. As seen in *Table 3*, the conversions of AEUs were lower than EA. The propagation rate of AEU having a longer ester group than EA might be slower than EA due to steric hindrance.

Terpolymerization of isobutylene, acrylic ester and vinyl monomer including a chlorine atom. If a vinyl monomer that includes a chlorine atom in the molecule is incorporated as a third component into the alternating copolymers of IB and AE, the obtained terpolymers will be curable with polyamine.

2-Chloroethyl vinyl ether, vinyl chloroacetate and 2-chloroethyl acrylate were selected as vinyl monomers including a chlorine atom. 2-Chloroethyl vinyl ether and vinyl chloroacetate will be donor monomers and 2-chloroethyl acrylate will be an acceptor monomer in the present complexed copolymerization. The results of the terpolymerization are shown in *Table 4*. The reactivity of 2-chloroethyl vinyl ether (run No. 1) was higher than that of IB; on the contrary the reactivity of vinyl chloroacetate (run No. 2) was rather lower than that of IB and 2-chloroethyl acrylate showed reactivity near to EA. The *e* value of 2-chloroethyl vinyl ether is perhaps lower than IB.

Logothetis *et al.*[5] tried to incorporate 2-chloroethyl vinyl ether as cure sites into the alternating copolymer of ethylene and EA with boron trifluoride–azobisisobutyronitrile catalyst system, but they failed

Table 3 Terpolymerization of isobutylene (IB), ethyl acrylate (EA) and acrylic ester including an unsaturated bond in the ester group (AEU)[a]

			Polymer								
						Composition[b] (mol%)			Conv. (%) on		
Run No.	AEU ester group	Polymerization yield (g)	$[\eta]$ (dl g^{-1})	Gel content (wt%)	Iodine value	IB	EA	AEU	IB	EA	AEU
1[c]		26.3	0.75[d]	56	9.7	44.9	52.0	3.1	18	100	63
2		20.7		95	2.6	47.1	52.1	(0.8)	15	85	(13)
3[e]		26.7	1.16	0	12.1	47.5	48.7	3.8	20	100	79
4		27.1	1.88	0	9.4	44.1	52.7	3.2	18	100	64
5		24.7		91	3.4	45.8	53.1	1.1	18	100	21

[a] Conditions: IB, 800 mmol; EA, 160 mmol; AEU, 16 mmol; $BEtCl_2$, 8 mmol; temp., −20°C; time, 1 h; order of addition, IB → the mixture of EA and AEU → $BEtCl_2$; under N_2 atmosphere; vessel, a glass flask
[b] By iodine value and oxygen analyses
[c] Time, 0.25 h
[d] Benzene-soluble part
[e] Time, 2 h

Table 4 Terpolymerization of isobutylene (IB), ethyl acrylate (EA) and vinyl monomer including a chlorine atom (CVM)[a]

						Polymer					
						Composition[c] (mol%)			Conv. (%) on		
Run No.	CVM[b] (mmol)		Catalyst $BEtCl_2$ (mmol)	Polymerization yield (g)	$[\eta]$ (dl g^{-1})	IB	EA	CVM	IB	EA	CVM
1	CEVE	400	133	520	6.90	37.6	55.2	7.2	27	85	100
2	VCA	8	3.6	10.5	4.42	50.7	49.1	0.2	43	83	3
3	CEA	16	3.2	24.2	1.37	41.4	54.0	4.6	38	98	83

[a] Conditions: IB/EA/CVM molar ratio, 20/10/1; temp., −20°C; time, 3 h; order of addition IB → the mixture of EA and CVM → $BEtCl_2$; under N_2 atmosphere; vessel, a glass flask for run Nos. 1 and 3, a glass tube for run No. 2
[b] CEVE, 2-chloroethyl vinyl ether; VCA, vinyl chloroacetate; CEA, 2-chloroethyl acrylate
[c] By elemental analyses of chlorine and oxygen

Table 5 Vulcanization of AIDM

	Terpolymer					Cured product				
	Composition (mol%)									
Run No.	IB	EA	AEU[a]		$[\eta]$ (dl g^{-1})	Gel content (wt%)	Iodine value	Tensile strength (kg cm^{-2})	Elongation (%)	Hardness (shore A)
1	44.8	51.5	Allyl	3.7	2.86[b]	20	11.7	136	370	80
2	47.1	52.1	Methallyl	0.8		95	2.6	120	230	84
3	49.1	49.2	Crotyl	1.7	4.45	1	5.5	142	450	84
4	44.1	52.7	Citroneryl	3.2	1.88	0	9.4	140	290	83
5	45.8	53.1	Norbornenylmethyl	1.1	-	91	3.4	112	390	82

[a] Ester residue
[b] Benzene-soluble part

in the incorporation because of the cationic homopolymerization of 2-chloroethyl vinyl ether with boron trifluoride.

Cured properties of AIDM and AICM

AIDM could be vulcanized with sulfur by using its pendent unsaturated bonds. AICM could be cured with polyamine by using its pendent C–Cl bonds.

Vulcanization of AIDM. Concerning the curing recipe and curing conditions of AIDM, the examples of styrene–butadiene rubber (SBR), acrylonitrile–butadiene rubber (NBR), isobutylene–isoprene rubber (IIR) and ethylene–propylene–diene rubber (EPDM) were studied. The procedure for EPDM, which is a lowly unsaturated rubber like AIDM, became clear as the most suitable for AIDM. The appearance of

Table 6 Curing of AICM

	Terpolymer				Cured product			
	Composition (mol%)					Tensile		Modulus
Run No.	IB	AE[a]	CVM[b]	[η] (dl g^{-1})	strength (kg cm^{-2})	Elongation (%)	at 300% (kg cm^{-2})	Hardness (shore A)
1	47.5	EA 50.0	CEVE 2.5	4.95	141	510	120	74
2	37.6	EA 55.2	CEVE 7.2	6.90	143	300	143	71
3	43.2	BA 50.9	CEVE 5.9	3.55	102	370	67	72
4	50.7	EA 49.1	VCA 0.2	4.42	83	700	47	74
5	41.4	EA 54.0	CEA 4.6	1.37	97	280	–	82
Ref.[c]	–	EA 96.6	CEVE 3.4	3.90	129	340	111	70

[a] EA, ethyl acrylate; BA, n-butyl acrylate
[b] CEVE, 2-chloroethyl vinyl ether; VCA, vinyl chloroacetate; CEA, 2-chloroethyl acrylate
[c] A commercial acrylic rubber (Hycar 4021)

vulcanization was examined by a rheometer at 160°C and sufficient vulcanization was completed in 40 min judging from the time that the torque became flat. The vulcanization speed of AIDM was the same level as EPDM or IIR rubbers, and slower than general-purpose rubbers such as SBR and NBR. The curing recipe and curing conditions are shown in the 'Experimental' part. *Table 5* shows the results of vulcanization of AIDMs having various unsaturated bonds in the ester groups. All of them had enough tensile strength and elongation for practical uses. Especially in the case of crotyl acrylate, only 1–2 mol% of incorporation was enough for satisfactory mechanical properties (particularly good elongation). Terpolymers of methallyl acrylate or norbornenylmethyl acrylate also had good mechanical properties, though they were highly gelled.

Curing of AICM. Table 6 shows the results of curing of AICMs containing various vinyl monomers including a chlorine atom in comparison with a commercial acrylic rubber consisting of EA and a small amount of 2-chloroethyl vinyl ether. The mechanical properties of the terpolymers containing 2-chloroethyl vinyl ether were good enough for practical uses (run Nos. 1 and 2) and better than those of the commercial acrylic rubber (run No. Ref.). The incorporation of 2–3 mol% of 2-chloroethyl vinyl ether was sufficient. The terpolymer of n-butyl acrylate (run No. 3) showed lower tensile strength than EA but had better low-temperature performance. Terpolymers containing vinyl chloroacetate (run No. 4) or 2-chloroethyl acrylate (run No. 5) had a quite low tensile strength.

Oil resistance. AIDM and AICM contain about 50 mol% of polar AE, and therefore better oil resistance than for hydrocarbon rubbers is expected. *Figure 1* shows the results for the swelling tests of AIDM and AICM rubbers in ASTM No. 3 oil at 70°C for 70 h. As seen in the figure the oil resistance of AIDM and AICM rubbers had a critical point at about 43 mol% of IB. 2-Chloroethyl vinyl ether is an oil-resistant monomer having an ether bond and a chlorine atom, and it acts as a donor monomer to replace part of the IB in the polymer sequences. Therefore the swelling of AICM rubbers decreased in proportion to the content of 2-chloroethyl vinyl ether. The mechanical properties of AIDM rubbers were sufficient by the incorporation of 1–2 mol% of crotyl acrylate as mentioned before, but for high oil resistance an increased amount of crotyl acrylate, i.e. elevated crosslink density, was necessary as seen in *Figure 1*. However crotyl acrylate acts as an acceptor monomer to replace part of the EA in the polymer sequences, i.e. the content of IB is always nearly 50 mol% in AIDM rubbers, so the improvement of oil resistance by increasing the content of crotyl acrylate is limited. Therefore, for uses in which higher oil resistance is required, AICM rubbers are more suitable than AIDM rubbers.

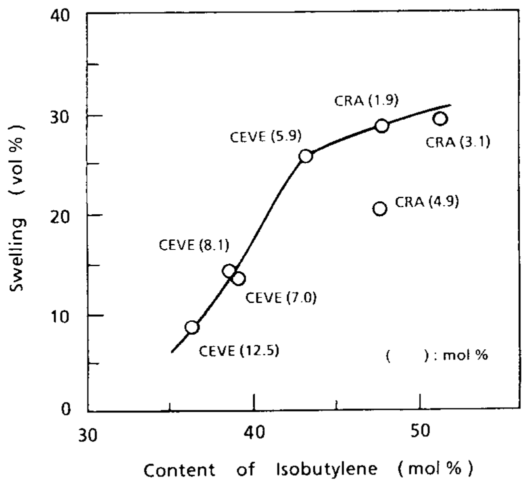


Figure 1 Relationship between content of isobutylene and oil resistance in AIDM and AICM rubbers. AIDM: isobutylene–ethyl acrylate–crotyl acrylate (CRA). AICM: isobutylene–ethyl acrylate–2-chloroethyl vinyl ether (CEVE). Conditions: ASTM No. 3 oil, at 70°C for 70 h

Table 7 shows the oil resistance of AIDM and AICM rubbers in comparison with various commercial rubbers. Hydrocarbon rubbers such as styrene–butadiene rubber (SBR), natural rubber (NR) and ethylene–propylene–diene rubber (EPDM) were highly swollen under these conditions. Acrylic rubber (ACM) is well known as a commercial oil-resistant rubber, especially at high temperature. The oil resistance of AICM rubbers was fairly close to that of ACM and acrylonitrile–butadiene rubber (NBR) and superior to such oil-resistant rubbers as polychloroprene rubber (CR) in spite of containing a

Table 7 Oil resistance of AIDM and AICM rubbers in comparison with various commercial rubbers

Rubber	Swelling[a] (wt%)	Swelling[a] (vol%)
AIDM[b]	14.4	20.2
AICM[c]	10.4	13.4
ACM[d]	5.3	7.3
NBR[e]	11.9	14.8
CR[f]	40.2	59.2
SBR[g]	73.3	93.2
NR[h]	94.2	116.7
EPDM[i]	110.8	136.2

[a] At 70°C for 70 h in ASTM No. 3 oil

[b] Terpolymer of isobutylene, ethyl acrylate and crotyl acrylate: molar composition, 47.8/47.3/4.9; iodine value, 15.4; [η], 4.44 dl g^{-1}

[c] Terpolymer of isobutylene, ethyl acrylate and 2-chloroethyl vinyl ether: molar composition, 37.6/55.2/7.2; [η], 6.90 dl g^{-1}

[d] Acrylic rubber, Hycar 4021

[e] Acrylonitrile–butadiene rubber, Hycar 1043

[f] Polychloroprene rubber

[g] Styrene–butadiene rubber

[h] Natural rubber

[i] Ethylene–propylene–diene rubber

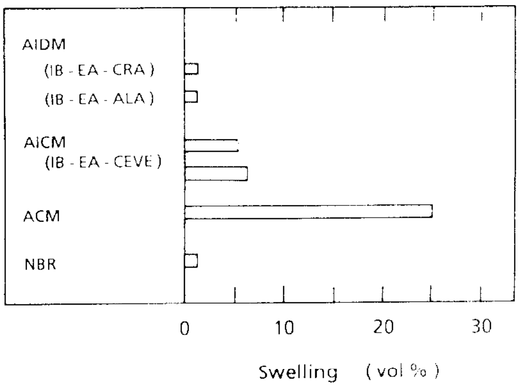


Figure 2 Water resistance of AIDM and AICM rubbers. IB, isobutylene; EA, ethyl acrylate; CRA, crotyl acrylate; ALA, allyl acrylate; CEVE, 2-chloroethyl vinyl ether; ACM, Hycar 4021; NBR, Hycar 1043. Conditions: at 25°C for 10 days

fair amount of IB. AIDM rubbers were a little inferior to AICM rubbers as mentioned above. The unexpectedly high oil resistance of AIDM and AICM rubbers might be derived from the uniformly distributed ester groups along the polymer chains.

Water resistance. Figure 2 shows the water resistance of AIDM and AICM rubbers. Both rubbers considerably improved the disadvantage of ACM rubber in water resistance. The properties of AIDM and AICM rubbers almost did not change after immersing in water. The water resistance of AIDM rubbers was superior to AICM rubbers (which was converse to oil resistance) and about equal to NBR.

Co-vulcanization of AIDM and commercial rubbers. Sulfur-vulcanizable AIDM rubbers can be used by themselves. Furthermore blends with other rubbers have the possibility to afford new high-performance rubbers if they can be co-vulcanized. By blending, the performances of AIDM rubbers are improved and at the same time the other rubbers are given the good performances of AIDM rubbers such as heat resistance, oil resistance, water resistance, weatherability and adhesion. The blends of AIDM and EPDM or IIR rubbers were satisfactorily co-vulcanized. *Figure 3* shows the results of the co-vulcanization of AIDM and EPDM rubbers. Additivity in tensile strength was nearly established and the elongation was sufficiently large. The solubility parameter of AIDM rubbers is relatively near to that of hydrocarbon rubbers by the incorporation of 50 mol% of IB, so that compatibility with EPDM or IIR rubber seems to be good. Moreover the curing recipe and curing conditions of AIDM rubbers closely resemble those of EPDM or IIR rubber. Therefore co-vulcanization was conceivably possible.

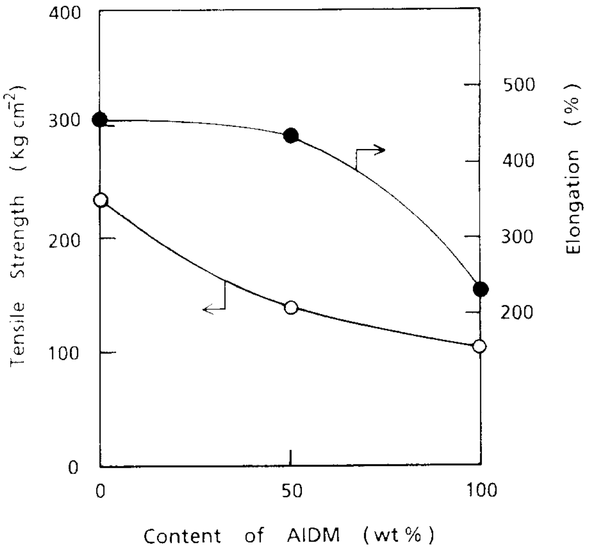


Figure 3 Co-vulcanization of the blend of AIDM and EPDM rubbers. AIDM: isobutylene–ethyl acrylate–allyl acrylate; molar composition, 46.9/50.8/2.3; iodine value, 6.8; [η], 2.13 dl g^{-1}. EPDM: ethylene–propylene–dicyclopentadiene; Royalene 301; iodine value, 8.0; [η], 1.62 dl g^{-1}.

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REFERENCES

1 Mashita, K., Yasui, S. and Hirooka, M. *Polymer* in press
2 Mashita, K. and Hirooka, M. *Polymer* in press
3 Rehberg, C. E. and Fisher, C. H. US Pat. 2456647, 1948 (US Secretary of Agriculture); *Chem. Abstr.* 1949, **43**, 4686b
4 Brandrup, J. and Immergut, E. H. 'Polymer Handbook', Wiley, New York, 1989, p. II-267
5 Logothetis, A. L. and McKenna , J. M. *J. Polym. Sci. (A)* 1977, **15**, 1441