Examination of Polychloroprene-Polyvinyl Chloride Blending

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The blending of polychloroprene (CR) and polyvinyl chloride (PVC) has been studied in order to obtain the lowpriced CR rubber of good processing properties. Of the two methods used, the latices blend gave better results than the dry blend on roll. The blend ratio of PVC/CR should be between 1/4 and 3/7, PVC of low polymerization degree and CR with ML_{1+4} 70~80 being preferably used. The fine structure of the PVC/CR latices blend was found to consist of CR, PVC, and leather phases.

1. INTRODUCTION

The price of polychloroprene (CR) has been yet high, though there is the difference between some grades, compared with the general purpose rubbers.

The demand of low-priced CR is very strong in a sales department. The applications are gasket, zipper, and window frame for architecture. The low-priced CR is naturally low in the cost and at the same time must be excellent in the various properties. In order to btain the low-priced CR, the following ofour techniques are considered.

1) Increasing the productivity,
2) Development of the better isolation process because the present freeze coagulation process is expensive (e. g., freeze coagulation → heat coagulation),
3) Blending or copolymerisation of CR with low-priced materials,
4) Improvement of polymerisation method (e. g., emulsion polymerisation → solution or/ and continuous polymerisation),

Since 1), 2), and 4) techniques were considered to required a lot of money and time, we were going to perform about 3) technique. In the investigation of 3) technique, we selected polyvinylchloride (PVC) as the low-priced material, which is related with the valid uitlization of vinylchloride monomer.

First, the blending technique of CR gum with PVC powder was studied to find the fundamental properties on blending of the both polymers. From the results, we investigated about the blending of CR latex with PVC latex.

2. RESULTS AND DISCUSSION

〔1〕 Blending of CR gum with PVC powder on roll

There was a little difference of solubility parameter between CR and PVC ($\Delta\delta=(\delta_{PVC}-\delta_{CR})\fallingdotseq 0.3\sim 0.5$), but when blended, CR and PVC showed the poor solubility. If PVC powder would have the plasticity, it would be dispersed homogeneously into CR gum.

Accordingly, it was considered that the physical properties of PVC/CR compound were greatly dominated with blending conditions. The blending conditions of CR with PVC were shown in **Table 1, 2,** and **Fig. 1.**

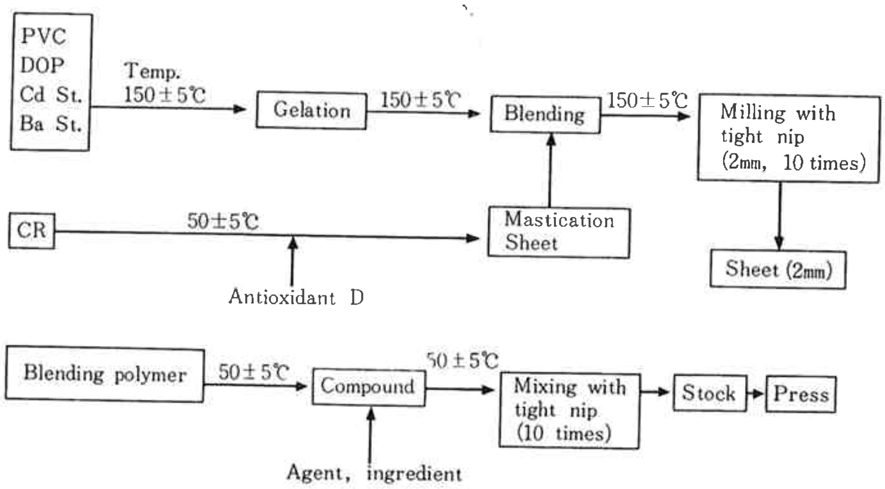

Fig. 1 Mixing condition of CR with PVC

Compound recipe

CR	75
Antioxidant D	0.75
MgO	3.0
Phenyl—naphthylamine	0.375
ZnO	0.75
Steanicacid(St)	0.75
PVC	25
DOP	12.5
Cd St	0.5
Ba St	0.25

Sample

Rubber : B-30, B-31, Y-30, R-22, W, WXJ
PVC : Degree of polymn. 450, 800, 1050
Compound : Gum mix (**Table** 1)

Examination item

1. CR-PVC blend condition (**Table** 1)
2. Degree of polymerisation and amount of PCV (**Table** 2 **and** 3)
3. Mooney viscosity of CR (the difference between CR grades) (**Table** 4)

Table 1 The results of processing and physical properties on PVC-PCR blending time

	B-30	VR-1	VR-2	VR-3	VR-4	VR-5
Mixing time of PVC-PCR blends		1′30″	2′10″	2′30″	4′00″	2′30″
ML_{1+4}						
raw	43	33	33	33	33	43
compound	43	35	30	33	30	43
Scorch time						
t_5	12′45″	13′20″	13′45″	14′00″	12′00″	11′30″
t_{10}	14′30″	16′30″	17′20″	17′25″	15′45″	14′50″
t_{35}	17′50″	24′15″	25′45″	25′55″	24′45″	23′40″
t	5′05″	10′55″	12′00″	11′55″	12′45″	12′10″
Processing properties						
W/L	1.8793			0.976		
Garvery rating	3			12		
T_B (kg/cm²)						
20′	155	79	84	92	108	90
30′	145	69	76	86	104	93
E_B (%)						
20′	710	740	750	770	820	540
30′	670	650	660	700	760	460
M_{300} (kg/cm²)						
20′	20	33	36	40	37	66
30′	22	37	42	47	45	76
Hs						
20′	45	53	54	54	53	64
30′	46	55	56	55	54	66

Table 2 Tensile properties of vulcanizates vs. blending ratio of PVC-PCR system

		B-10	VR-21	VR-22	VR-23	VR-24	VR-25	VR-26
Blend ratio			10	20	25	30	50	25
Mixing method				Mastication cycles 10 times				Mastication
Mooney viscosity								
	raw	43	39	32	33	33	31	32
	compd.	43	39	32	33	33	31	32
Scorch time								
	t_5	13′13″	11′50″	14′30″	15′25″	18′15″	21′45″	15′45″
	t_{10}	15′00″	14′50″	17′50″	19′25″	22′40″	28′00″	19′45″
	t_{35}	18′45″	19′35″	25′50″	29′10″	40′10″	105′30″	29′30″
	t	5′35″	7′45″	11′20″	13′45″	21′55″	83′45″	15′45″
T_B (kg/cm²)								
	20′	170	150	142	116	115	73	111
	30′	161	136	128	120	116	83	113
E_B (%)								
	20′	990	830	850	780	790	840	740
	30′	730	750	750	680	650	410	680
M_{300} (kg/cm²)								
	20′	19	25	38	44	47	62	45
	30′	16	28	42	52	58	71	51
Hs								
	20′	44	44	51	52	60	85	53
	30′	43	46	50	55	60	85	52

(1) Blending ratios of CR gum with PVC powder (PVC : Pn=1050, CR : B-30)

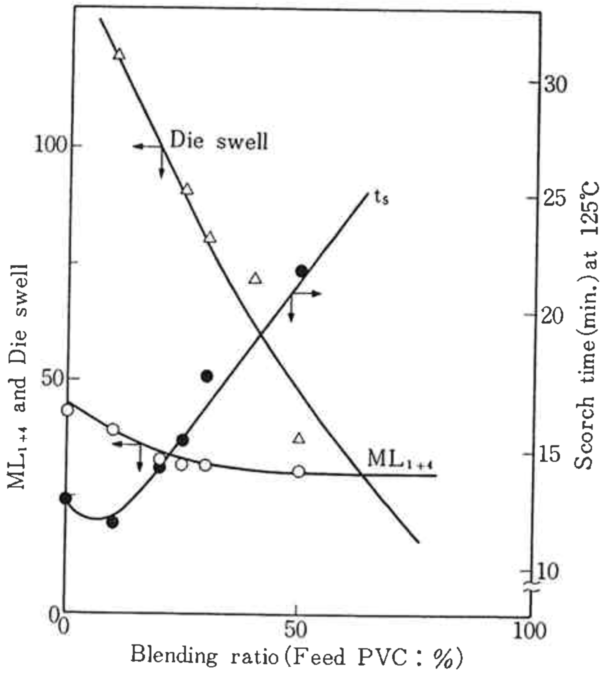

Fig. 2 The relationship between PVC/CR ratio and processing properties (PVC: Pn=1050, CR : B-30)

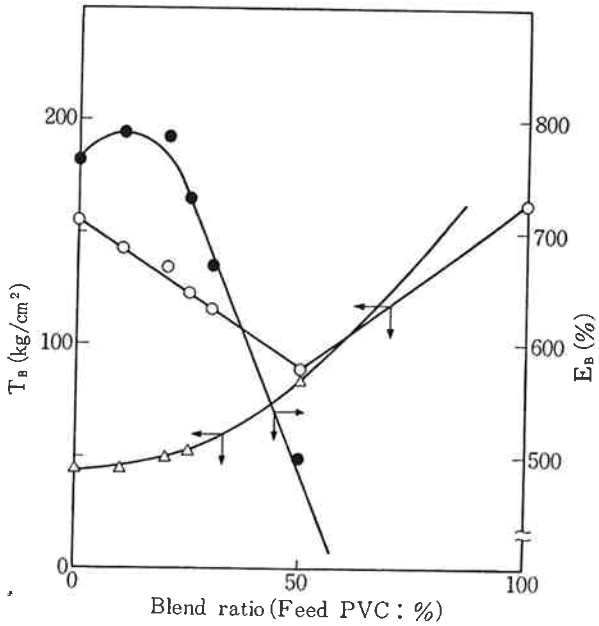

Fig. 3 The relationship of vulcanization properties on PVC/CR (PVC : Pn=1050, CR : B-30)

The relationship between the physical properties and the blending ratios were shown in **Fig. 2** and **3.** ML_{1+4}, T_B, and E_B decreased, M_{300} increased, and scorch time prolonged with increasing the amount of PVC.

As was evident from **Fig. 3**, the behavior of T_B was peculiar, that is, T_B had minimum at the ratio of PVC/CR=1/1. It might be considered that the behavior of T_B depended on the difference between two phenomena, or the dispersing state of plastic into rubber and rubber into plastic.

As seen from **Fig. 4**, W_R/W_T obtained from the cycle test of rubber decreased with increase of the amount of PVC. On the contrary, the processing properties were improved with increase in the amount of PVC.

As were evident from **Fig. 2, 3,** and **4,** the blending ratio of CR with PVC must be fixed when the cost or balance between the physical and processing properties were considered. In order to use PVC/CR compound as rubber, the ratio of PVC/CR should be 1/4 to 3/7, and the ratio of 1/3 was particularly desired.

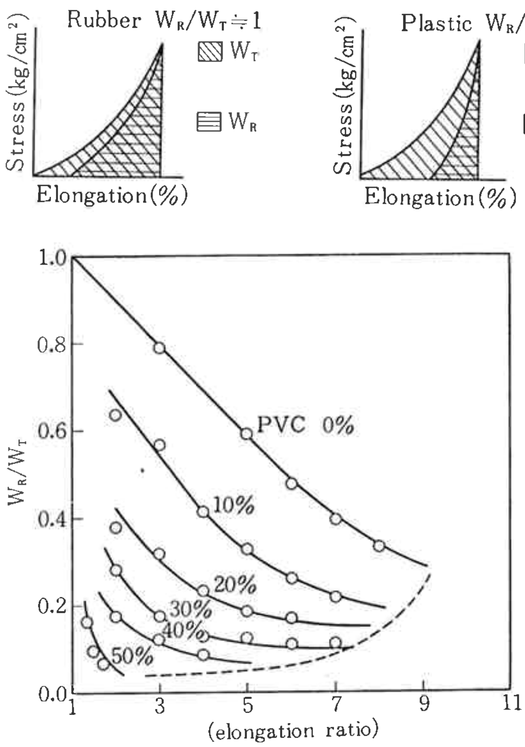

Fig. 4 The cycle test of CR rubber

(2) The effect of the degree of polymerisation (Pn) of PVC (CR : B-30, Blending ratio : PVC/CR=1/3)

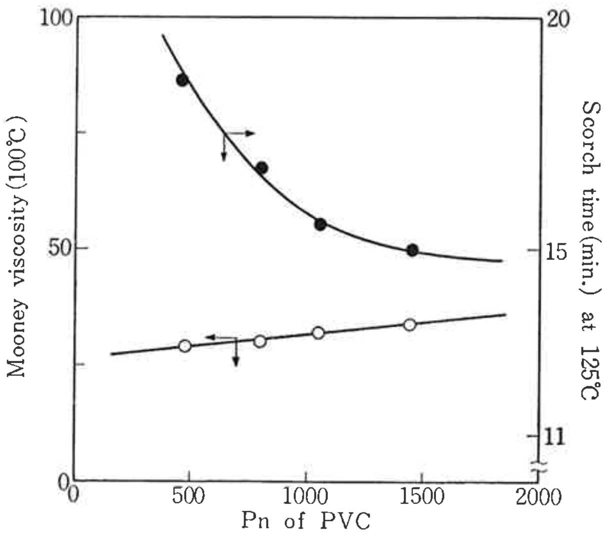

Fig. 5 The relationship between the properties of compound and degree of polymerisation on PVC (CR : B-30, PVC/CR=1/3)

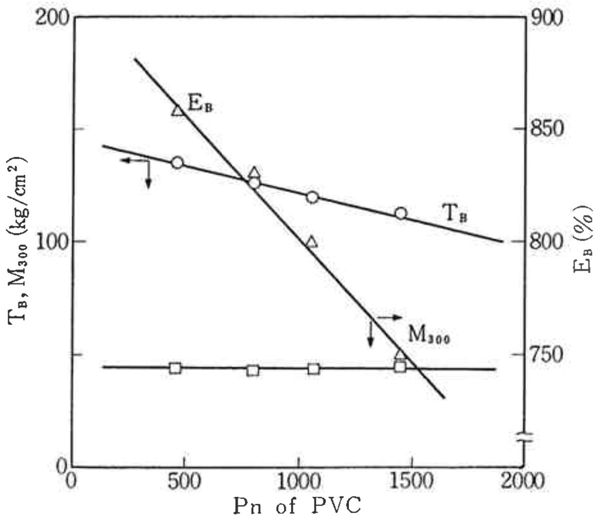

Fig. 6 The relationship between the physical properties of compound and degree of polymerisation of PVC (CR : B-30, PVC/CR=1/3)

The relationship between Pn of PVC and the properties of the compound were shown in **Fig. 5** and **6**.

What were evident from **Fig. 5** and **6** were as follows.

1) T_B and E_B decreased with increasing Pn of PVC,

2) Scorch time was shortened and M_{300} or ML_{1+4} was approximately constant.

From the results, PVC with the smaller Pn was desirable to employ.

(3) The effect of ML_{1+4} of CR upon the compound

The properties of the compound were estimated about the various ML_{1+4} of CR and the results were shown in **Fig. 7** and **8**. It was found that T_B, E_B, and Hs increased and die swell decreased with increase in ML_{1+4} of CR. Furthermore, when low ML_{1+4} of CR was used, ML_{1+4} of the compound became lower, so that the blending of CR was too difficult to blend. The most suitable ML_{1+4} of CR was 70 to 80, and if so, ML_{1+4} of the compound (PVC/CR=1/3) came to 40 to 50 which was ML_{1+4} of the general purpose grade.

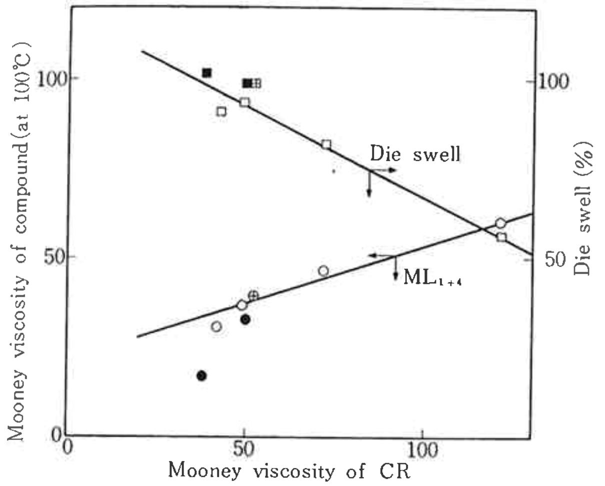

Fig. 7 The relationship between ML_{1+4} of CR and ML_{1+4} of compound or Die swell

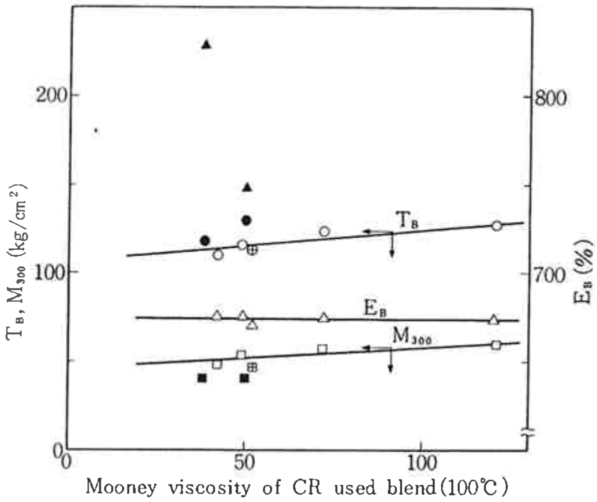

Fig. 8 The relationship between Mooney viscosity of CR and physical properties

〔2〕 Blending of CR latex with PVC latex

We investigated about the latex blending technique of CR latex with PVC latex on the basis of above results.

(1) Synthetic method of PVC latex

First, we developed the recipe of emulsion polymerisation of vinylchloride. The recipe

Table 3 The standard recipe on polymerisation of vinyl chloride

	Recipe 1	Recipe 2		Recipe 1	Recipe 2
Ingredient			Cat. system		
VC	100	95.0	KPS	0.2	0.2
n-BA		5.0	AQS	0.002	0.020
L.S	3.0	3.0	Condition		
NaH_2PO_4	0.231	0.231	Polymn. Temp.(°C)	50	50
Na_2HPO_4	0.252	0.252	Rotation (rpm)	150	150
H_2O	180	180	Polymn. time (hr)	Ca. 6	Ca. 6

was tabulated in **Table 3.** This recipe was employed for production of PVC latex for latex blending.

(2) Physical properties of PVC/CR compound

The results of physical and processing properties were tabulated in **Table 4.** The compound has been satisfactoried in processing and flow properties, but had the disadvantage of the high modulus and hardness compared with general purpose grade of CR.

Table 4 The basic properties of PVC/CR blend

	1	2	3	4	5	6
		Latices Blend				
	B-30	PVC/CR	PVC(DOP) /CR	PVC/CR (liq CR)	PVC-nBA /CR	Roll Blend
ML_{1+4}						
compd.	41	61	32	40	61	61
Scorch time						
t_5	10′18″	13′18″	17′16″	10′10″	13′06″	17′06″
t_{35}	15′00″	20′06″	25′36″	15′15″	18′48″	28′30″
t	4′42″	6′48″	7′30″	5′45″	5′42″	11′28″
Die swell (%)	175	59	67	87	109	94
Garvey rating	5	8	12	12	9	9
T_B (kg/cm²)						
Aver.	159	155	128	139	151	88
E_B (%)						
Aver.	780	580	730	610	560	510
M_{300} (kg/cm²)						
Aver.	16	81	43	50	63	69
Hs						
Aver.	44	78	72	73	67	69

(3) Fine structure of compound

The structure of the compound was investigated by means of theory which we had been

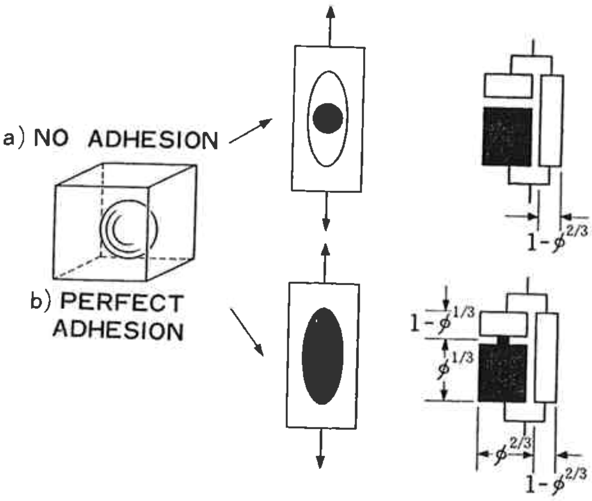

Fig. 9 Schematic two-component models and corresponding numerical models in cases of no and perfect adhesion between the phases.

a) No adhesion between the phases:

$$\sigma(\alpha)=(1-\phi^{2/3})\sigma_R(\alpha) \quad (1)$$

b) Perfect adhesion between the phases:

$$\sigma(\alpha)=(1-\phi^{2/3})\sigma_R(\alpha)+\phi^{2/3}\sigma_p(\alpha_p) \quad (2)$$

$$\sigma_p(\alpha_p)-\sigma_R(\alpha_R) \quad (3)$$

$$\alpha=(1-\phi^{1/3})\alpha_R+\phi^{1/3}\alpha_p \quad (4)$$

where $\sigma(x)$ is the stress of a blend an an elongation ratio of α, $\sigma_R(\alpha)$ the stress of a rubber matrix at α, $\sigma_p(\alpha_p)$ the stress of PVC component at α_p, $\sigma_R(\alpha_R)$ the seress of a rubber matrix at α_R, ϕ the volume fraction of PVC

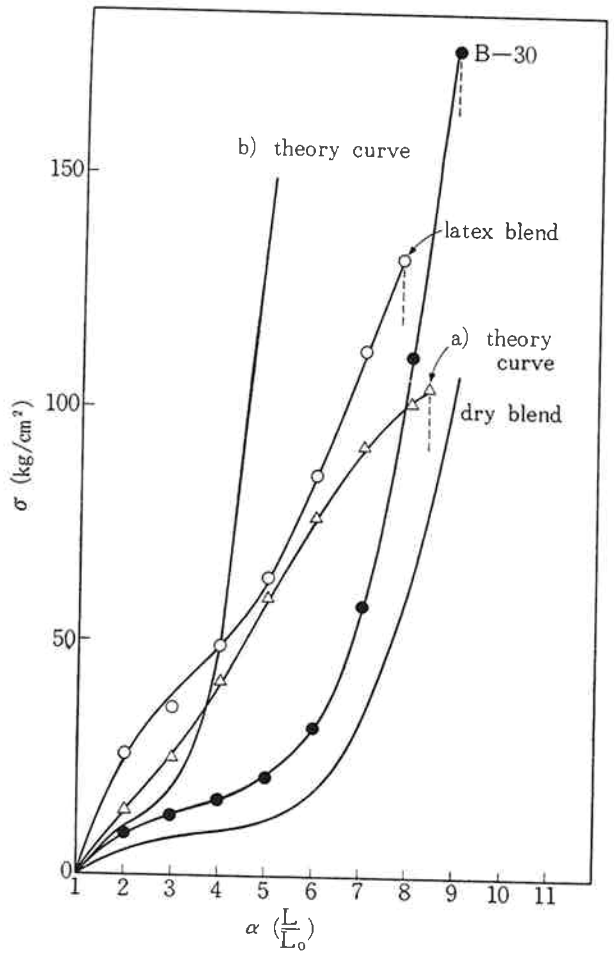

Fig. 10 Stress-strain curve of valucanized PVC-CR rubber. PVC/CR ratio : 1/3

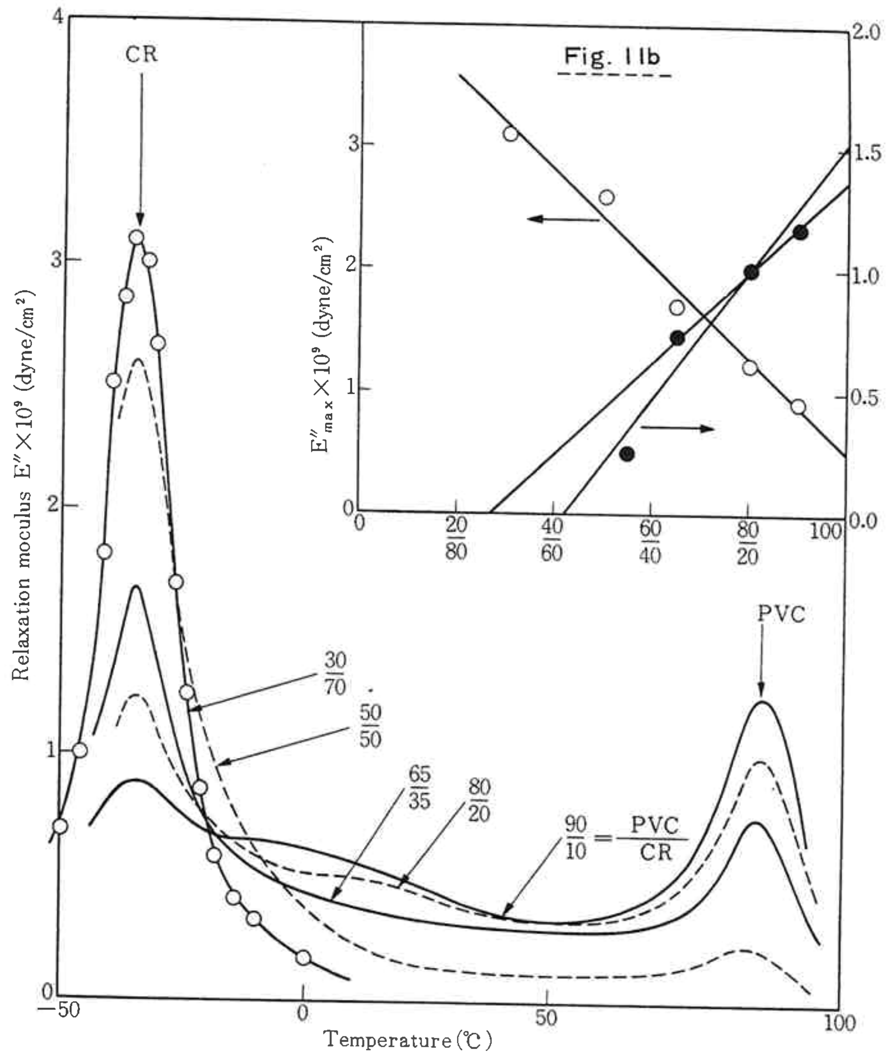

Fig. 11 Dispersion on temperature of dynamic loss modulus, E″, (**Fig. 11a**), and relation of E_{max} on composition of TS-100 (**Fig. 11b**)

once estimated in the case of perfect or no adhesion between phases in easy processing grade. The model was illustrated in **Fig. 9**.

Fig. 10 showed the theoretical and experimental stress-strain curves of the compound and CR only. The stress-strain curves of latex blending compound was fairly resemble to that of the compound adhering perfectly between the phases, and especially the very high stress was showed under the elongation ratio. Next, the dynamic viscoelastic behavior of the compound was measured by using a Vibron DDV–II in order to find the reason for the peculiar properties,and the results were shown in **Fig. 11a**.

As seen from **Fig. 11 a**, the glass temperature of PVC and CR were 90 and −35°C, respectively. In addtion, the new peak to the right side of CR peak appeared according to the change of the blending ratio. On the other hand, we estimated the relationship between the blending ratio and the magnitude (E″ max) of PVC or CR, and these values were plotted against the blending ratio in **Fig. 11 b**.

The E″ max curve of CR was reasonable but the E″ max curve of PVC came to 0 at about 30% in PVC. These results indicated that the disappearance part of PVC appeared as the new peak to the right side of CR peak. From these results, it was found that the fine structure of PVC/CR compound consisted of three phases of PVC, CR, and leather phase. The schematic model of the compound was illustrated in **Fig. 12**.

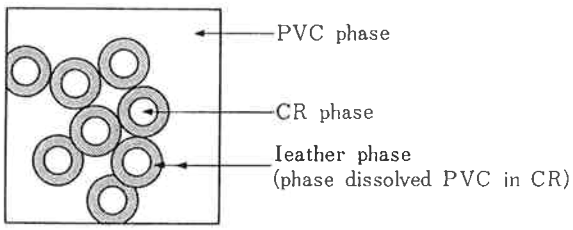

Fig. 12 Schematic model of PVC/CR compound