

## Preparation of Sulfur Crosslinkable EVA and Blend With Rubbers

Sei Young Choi<sup>†</sup> and Je Yong Jin

Department of Chemistry, Chongju University, Chongju 360-764, Korea

(Received June 3, 1999)

### 황가황형 EVA의 제조 및 고무와의 블렌드

최 세 영<sup>†</sup> · 진 제 용

청주대학교 이공대학 화학과

(1999년 6월 3일 접수)

**ABSTRACT** : In this study, double bond, unsaturated group was introduced to the main chain of EVA by chemically treating EVA, nondiene polymer. Benzene sulfonic acid, ENB and DCPD were used as a third element. Also, from blending CR and SBR, conventional synthetic rubber we prepared vulcanizates and examined their physical properties. The datum lead to the following conclusion that some problems were modified; limited temperature in use and mechanical properties like hardness, tensile strength, tensile stress, and elongation rate of thermoplastic EVA, keeping the following advantages of original EVA; green strength, injection molding by pressure, adhesion, tackiness, dimensional stability, and ozone resistance, etc.

It is expected that continuous research of the modification between nondiene and diene polymer will improve what were shown disadvantages in synthetic polymer; processing, oxidation resistance, and adhesion. In addition, it will be possible to continue process of rubber products by utilizing possible fluidity for fusion of EVA.

**요약** : 본 연구에서는 제3의 성분으로 벤젠 술폰산계열 반응성 화합물과 ENB 및 DCPD를 사용하여 비diene계 고분자인 EVA를 특수 화학적 처리에 의하여 EVA의 주쇄에 불포화기 즉, 이중결합을 도입시켰다. 또한 이중결합도입 EVA와 diene계 범용합성고무인 CR, SBR과의 블렌드를 통하여 황가황체를 제조하여 황가체들의 물리적 특성을 비교 검토하였다. 검토결과 원래의 EVA가 갖고 있는 green strength, 사출·압출 성형성, 접착성, 점착성, 치수안정성, 오존저항성 등의 장점은 그대로 살리면서도 황가황이 가능하여 열가소성의 EVA가 갖는 사용온도의 한계 문제와 기계적 특성 즉, 경도, 인장강도, 인장 응력, 신장율 등을 향상시켰다. 비diene계 고분자와 diene계 고분자의 블렌드에 있어서 개질에 대한 연구가 더 수행되어진다면 합성고무에서 나타나는 부족한 가공성, 내산화 안정성, 접착성 등을 크게 향상시킬 수 있을 것이며 아울러 EVA의 용해유동성을 이용한 고무제품 가공공정의 연속화가 가능하게 될 것이다.

<sup>†</sup>대표저자(e-mail : sychoi@chongju.ac.kr)

*Keywords* : EVA, modification, sulfur, vulcanization, synthetic rubber.

## I. Introduction

As polymer industry involving plastic, synthetic rubber, paint and adhesive, etc has been rapidly developed, materials for synthetic polymer has faced many complicated requirements; ozone-resistance, heat-resistance, wear-resistance and weather-resistance, etc. According to this trend, not a few ways to improve properties of polymeric materials have been in a broad study because it was difficult to meet the requirements with straight polymer polymerized from single monomers.

### ※ Modification Methods

- 1) Chemical treatment by acid and alkali solution.
- 2) Chemical reaction, flame-treating, IR-injection, electron injection, ion-beam injection, corona discharge, and plasma process, etc.

It is necessary for polymer to be vulcanized when is blended with the diene polymer. That is because some of unfavorable properties can be overcome by crosslinking; poor compatibility and different vulcanization rate between the two polymers which are blended each other, and unfavorable dispersion of filler.

In this study, we modified the double bond-introduced EVA with elasticity between plastic and rubbers by using a third material. Blending the EVA treated with a third material to diene rubber, we examined their physical, vulcanization and surface properties in the following ways.

Firstly, Introduction of unsaturated group to EVA by a third material secondly, Blend of unsaturated group-introduced EVA and diene synthetic rubber, and thirdly, Examination of EVA vulcanizates by sulfur

## II. Experiment

### 1. Experimental materials and reagents

- ① Ethylene Vinylacetate copolymer (EVA)  
vinyl content ; 28wt%
- ② Styrene butadiene rubber (SBR)  
bonding styrene ; 23.5wt%
- ③ Chloroprene rubber (CR)  
mooney viscosity ;  $48 \pm 5$ (ML1+4, 100°C)
- ④ Benzenesulfonic acid
- ⑤ Ethylidene norbonene(ENB)
- ⑥ Dicyclopentadiene(DCPD)
- ⑦ Other additives  
; carbon black for filler, first-class sulfur for vulcanizing agent, stearic acid for processing agent, and TT, M, CZ and Na-22 for vulcanization accelerator

### 2. Experimental methods

#### 2.1 Preparation of double bond-introduced EVA

EVA was mastified with three ingredients, benzene sulfonic acid, ENB and DCPD in an open roll for about 1 hour as in the recipe given in Table 1, separately.

After then, the acetoxyl group of the EVA was distracted by acetic acid, and the double bond-introduced EVA was prepared, as shown in Fig. 1.

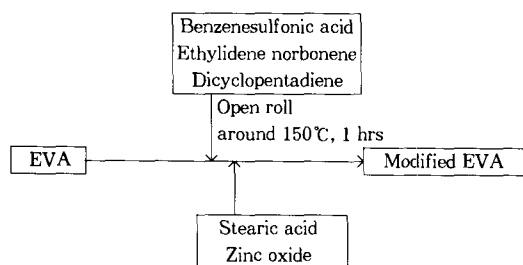


Fig. 1. Flow diagram for modified EVA.

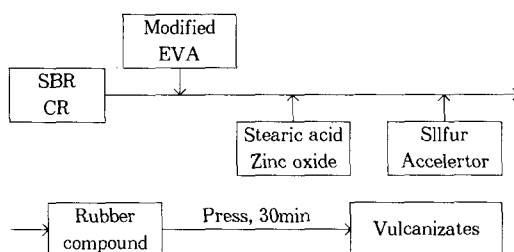


Fig. 2. Flow diagram for preparation of vulcanizates.

Table 1. Recipe for Modified EVA.

Recipe no.	E-1	E-2	E-3	E-4	E-5	E-6	E-7	E-8
EVA	100	100	100	100	100	100	100	100
A	2	-	-	-	-	-	-	-
B	-	2	-	-	-	-	-	-
C	-	-	2	-	-	-	-	-
D	-	-	-	2	-	-	-	-
E	-	-	-	-	2	-	-	-
F	-	-	-	-	-	2	-	-
G	-	-	-	-	-	-	2	-
H	-	-	-	-	-	-	-	2
Stearic acid	1	1	1	1	1	1	1	1
Zinc oxide	3	3	3	3	3	3	3	3

※ A ; 2,5-dichlorobenzene sulfonic acid

B ; 2,4,5-trichlorobenzene sulfonic acid

C ; *p*-chlorobenzene sulfonic acid

D ; 2,4-dimethylbenzene sulfonic acid

E ; 2,4,6-trimethylbenzene sulfonic acid

F ; *p*-methylbenzene sulfonic acid

G ; Ethylidene norbonene

H ; Dicyclopentadiene

## 2.2 Preparation of vulcanizates from double bond-introduced EVA and synthetic rubber

We prepared the double bond-introduced EVA in the same way as in the first by using the most favorable benzene sulfonic acid, ENB and DCPD.

As the next step, the modified EVA was blended with synthetic rubber as in the recipe given in Table 2.

Fig. 2 shows the compounding of the modifier

Table 2. Recipe for EVA Compounds

Recipe no.	unit : phr									
Ingredient	S0	S11	S12	S13	S21	S22	S23	S31	S32	S33
Modified EVA	-	75	50	25	75	50	25	75	50	25
SBR	100	25	50	75	25	50	75	25	50	75
Zinc oxide	9	9	9	9	9	9	9	9	9	9
Stearic acid	1	1	1	1	1	1	1	1	1	1
HAF	40	40	40	40	40	40	40	40	40	40
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TT	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
M	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
CZ	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

Recipe no.	unit : phr									
Ingredient	C0	C11	C12	C13	C21	C22	C23	C31	C32	C33
Modified EVA	-	75	50	25	75	50	25	75	50	25
CR	100	25	50	75	25	50	75	25	50	75
Zinc oxide	9	9	9	9	9	9	9	9	9	9
Stearic acid	1	1	1	1	1	1	1	1	1	1
HAF	40	40	40	40	40	40	40	40	40	40
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TT	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
M	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Na-22	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

※ S ; Styrene butadiene rubber

C ; Chloroprene rubber

with SBR, CR in different amounts, separately.

Also, in Table 2 S-1, S-2 and S-3 series present the vulcanizates made from blending each benzene sulfonic acid, ENB and DCPD with SBR respectively; and C-1, C-2 and C-3 series present the vulcanizates made from blending each benzene sulfonic acid, ENB and DCPD with CR respectively.

3. Test methods

3.1 Test of cure characteristics

We did the testing of their cure characteristics by four criteria; maximum torque( $M_{max}$ ), minimum torque( $M_{min}$ ),  $t_{10}$  and  $t_{90}$  by using rheometer.

3.2 Test of physical properties

We did the testing of their physical properties, we used hardness tester called shore A and also, used universal tensile testing machine to measure the modulus of 50, 100 and 200% and the elongation of each of them.

3.3 Analysis of FT-IR spectra

FT-IR was used to see if the double bonds were introduced to the EVA.

3.4 Analysis of surface properties

Scanning electron microscopy(SEM) was used to find the state of dispersion between the double bond-introduced EVA and the vulcanizates of the synthetic rubber.

III. Test Results

1. Test of cure characteristics

In Fig. 3, 4, 5 and 6 S-1, S-2 and S-3 series present the vulcanizates made from blending each benzene sulfonic acid, ENB and DCPD with SBR respectively;

and C-1, C-2 and C-3 series present the vulcanizates made from blending each benzene sulfonic acid, ENB and DCPD with CR respectively.

2. Test of physical properties

First, as the content of the double bond-introduced EVA increases, all the three groups go up in

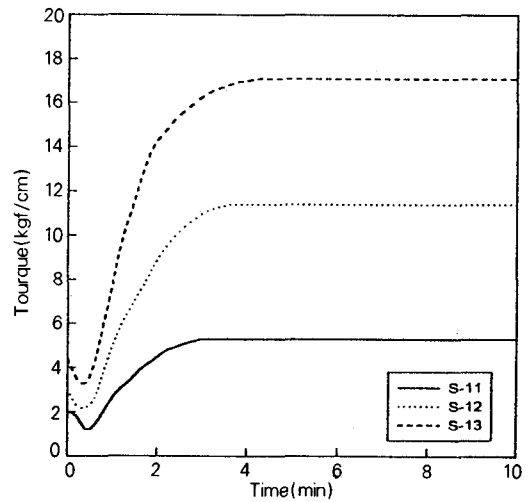


Fig. 3. Cure characteristics of the vulcanizates mixed to SBR with benzene sulfonic acid treated EVA.

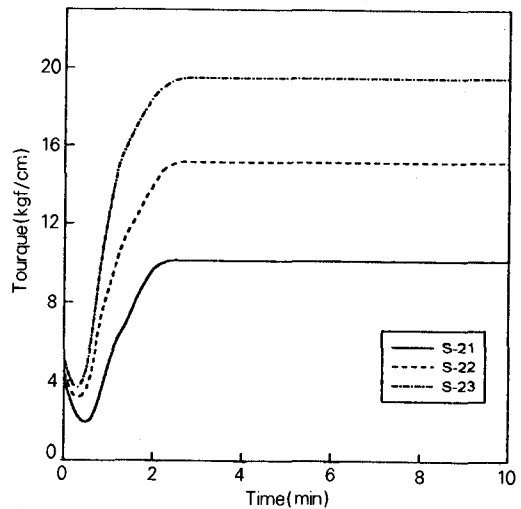


Fig. 4. Cure characteristics of the vulcanizates mixed to SBR with ENB-treated EVA.

hardness. The vulcanized group from blending the double bond-introduced EVA with CR is little higher than that with SBR in hardness.

As the synthetic rubber contents went up, all the three groups became increased in tensile strength.

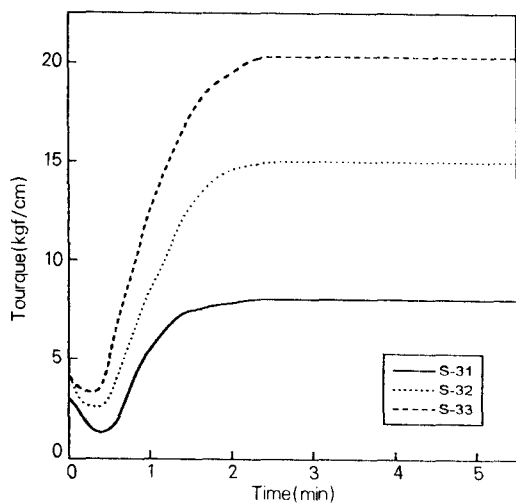


Fig. 5. Cure characteristics of the vulcanizates mixed to SBR with DCPD-treated EVA.

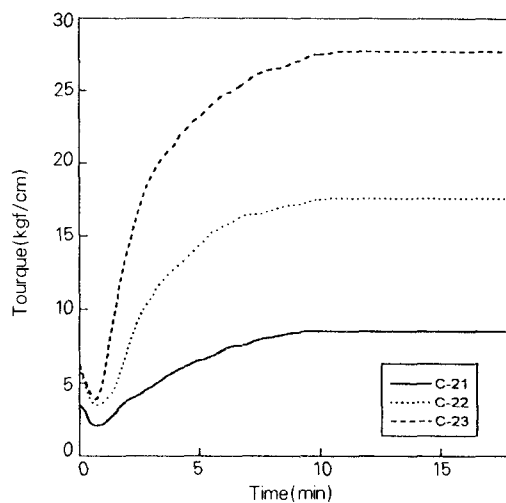


Fig. 7. Cure characteristics of the vulcanizates mixed to CR with ENB-treated EVA.

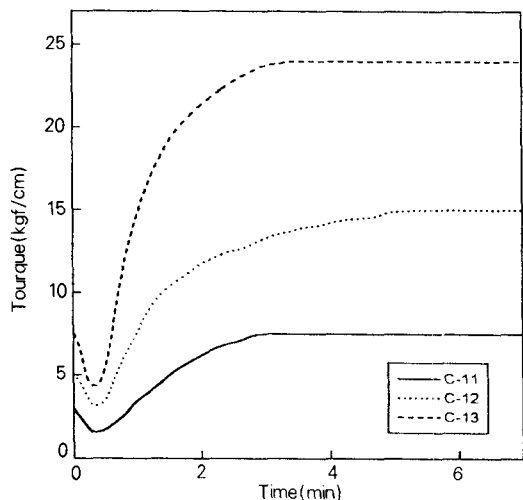


Fig. 6. Cure characteristics of the vulcanizates mixed to CR with benzene sulfonic acid treated EVA.

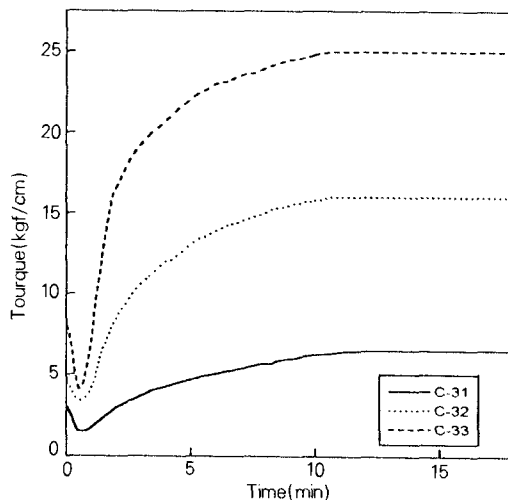


Fig. 8. Cure characteristics of the vulcanizates mixed to CR with DCPD-treated EVA.

In the case of modulus of 100%, S-2 and C-2 groups made from ENB showed a higher modulus than S-1, S-3 and C-1, C-3 groups prepared from benzene sulfonic acid and DCPD respectively.

### 3. Analysis of FT-IR spectra

Showing the FT-IR spectrum of the EVA before treatment, Fig. 17 helped us to find that there was C=O peak of acetoxy group of the EVA in the range of wave number ( $1750\sim 1730\text{cm}^{-1}$ ).

Fig. 18, 19 and 20 provide us the FT-IR spectra

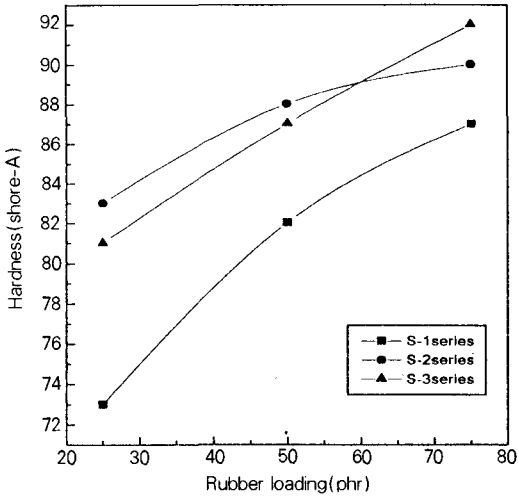


Fig. 9. Hardness of SBR sulfur vulcanizates.

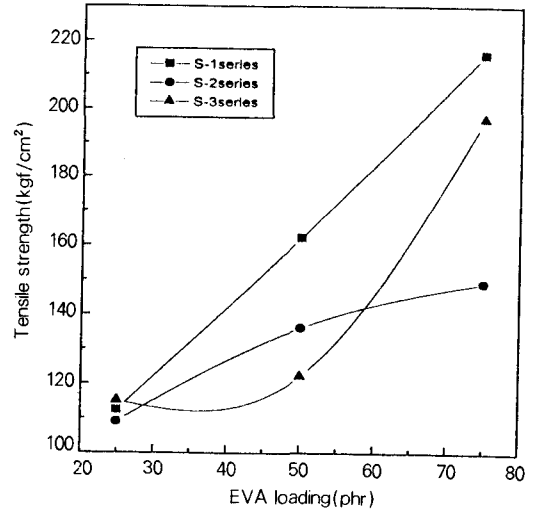


Fig. 11. Tensile strength of SBR sulfur vulcanizates.

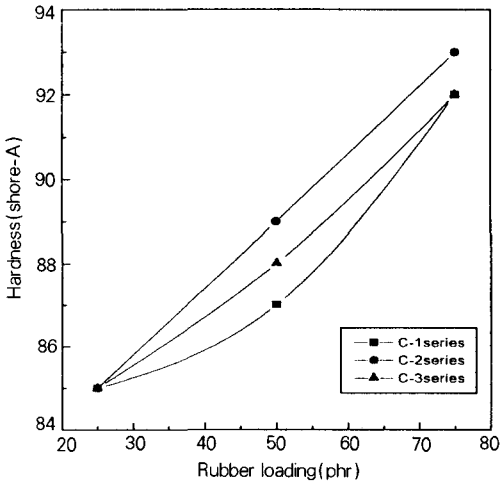


Fig. 10. Hardness of CR sulfur vulcanizates.

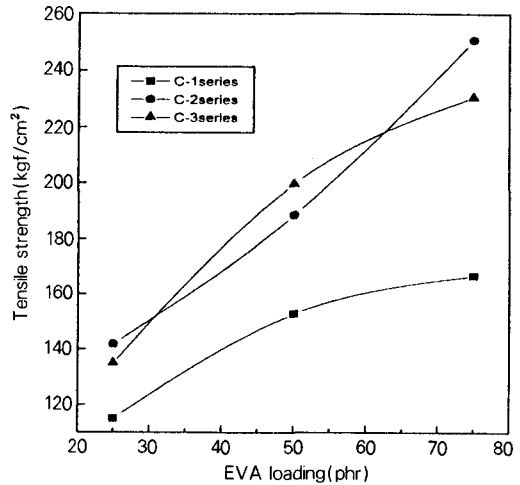


Fig. 12. Tensile strength of CR sulfur vulcanizates.

of the EVA treated with benzene sulfonic acid, ENB, and DCPD. In the range of  $1660\sim 1650\text{cm}^{-1}$ , we could find the double bond( $\text{C}=\text{C}$ )peak of the treated EVA.

#### 4. Analysis of surface properties

Fig. 21 concerns the vulcanizate from blending benzene sulfonic acid with SBR and CR separately; and Fig. 22 for the vulcanizates from blending

ENB with SBR and CR respectively. At the end, Fig. 23 for the vulcanizates from blending DCPD with SBR and CR respectively.

All of them are vulcanizates blended with the double bond-introduced EVA by 50phr, and it also shows that the additions as well as the filler are evenly dispersed.

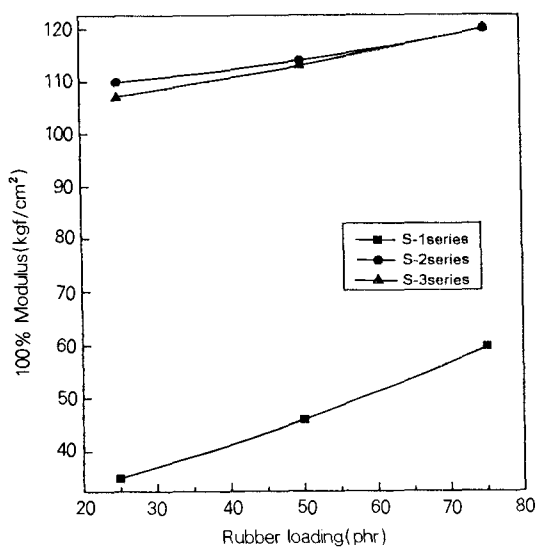


Fig. 13. 100% modulus of SBR sulfur vulcanizates.

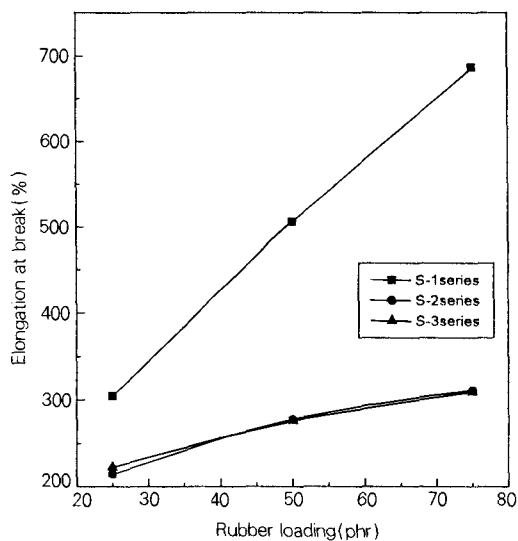


Fig. 15. Elongation at break of SBR sulfur vulcanizates.

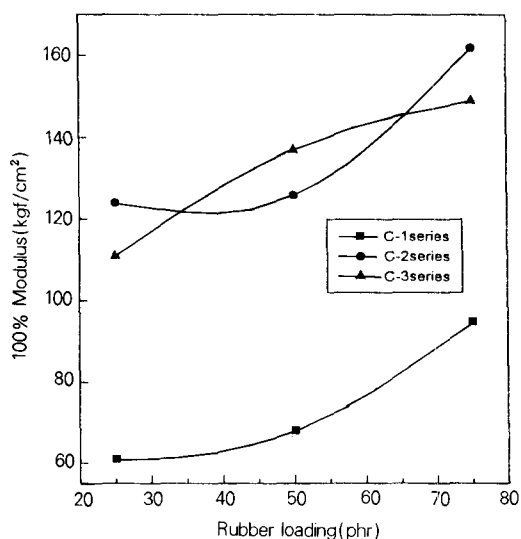


Fig. 14. 100% modulus of CR sulfur vulcanizates.

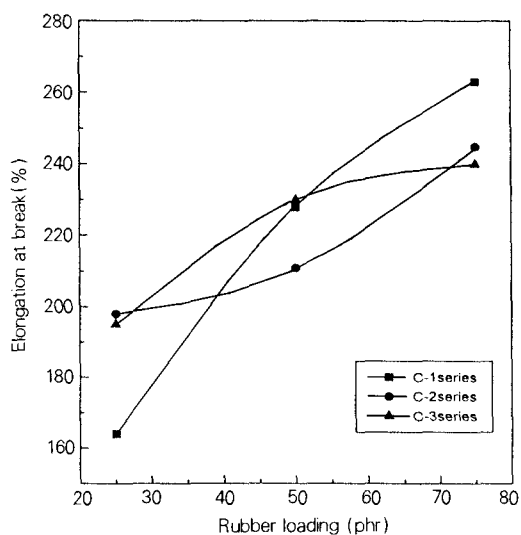
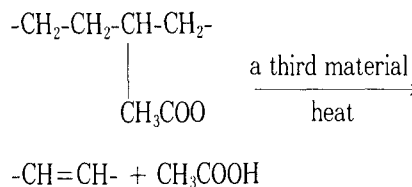


Fig. 16. Elongation at break of CR sulfur vulcanizates.

#### IV. Conclusions

In this study, we introduced double bonds to the main chain of the EVA with elasticity between plastic and rubber by using benzene sulfonic acid, ENB and DCPD. Mechanism is as follows;



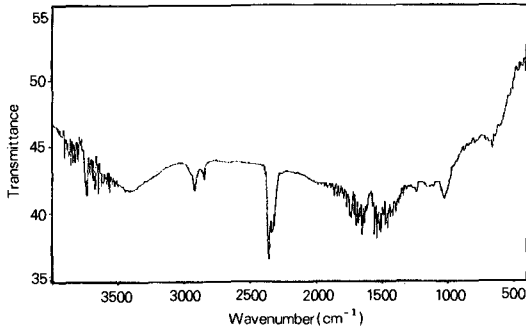


Fig. 17. FT-IR spectra of untreated EVA.

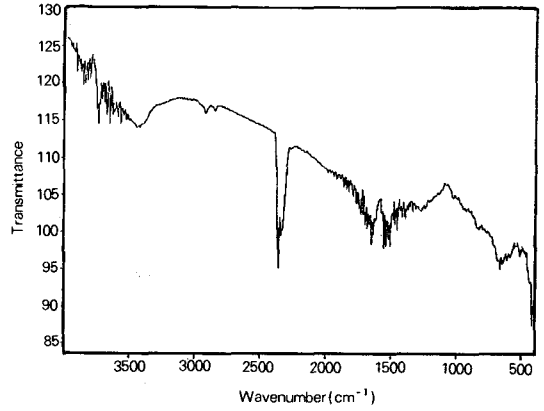


Fig. 20. FT-IR spectra of the EVA treated by DCPD.

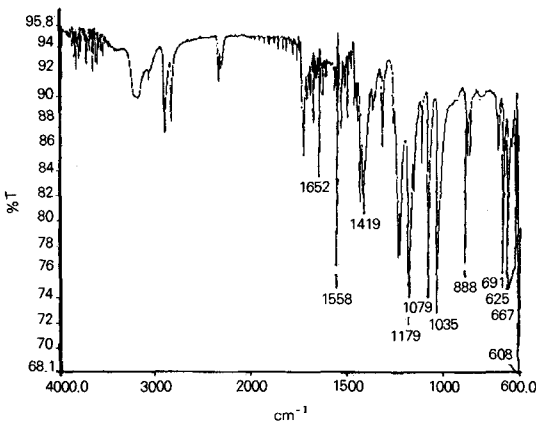


Fig. 18. FT-IR spectra of the EVA treated by benzene sulfonic acid.

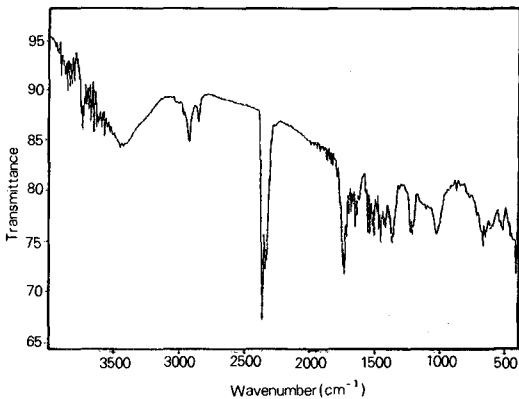
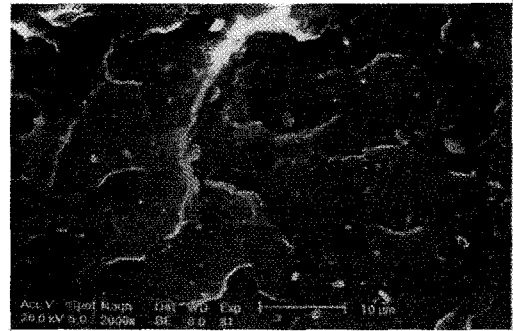
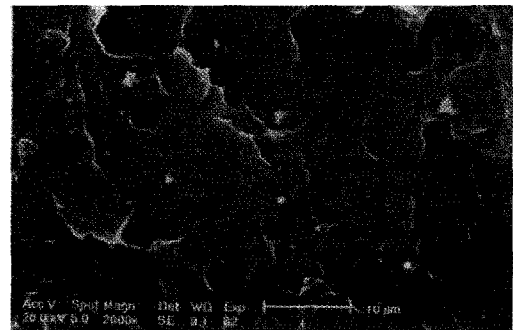


Fig. 19. FT-IR spectra of the EVA treated by ENB.



(a) S-11



(b) C-11

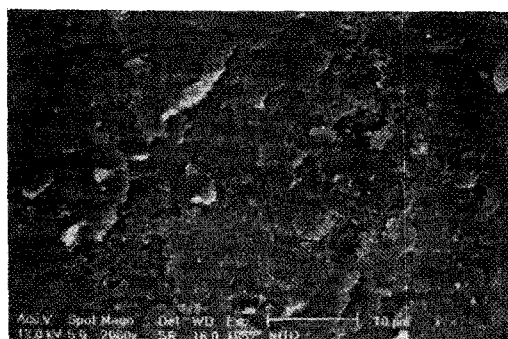
Fig. 21. SEM micrographs of the benzene sulfonic acid-treated EVA.

Moreover, blending the double bond-introduced EVA with the synthetic rubbers, we prepared

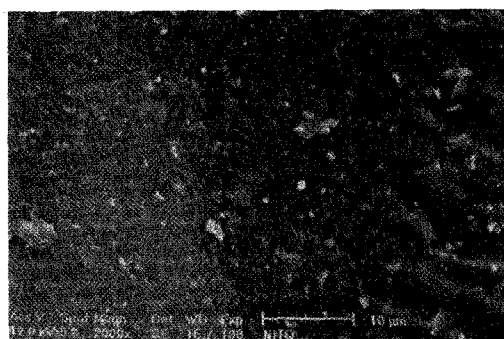
vulcanizates, and examined their physical vulcanization and surface properties.

The results are as follows.

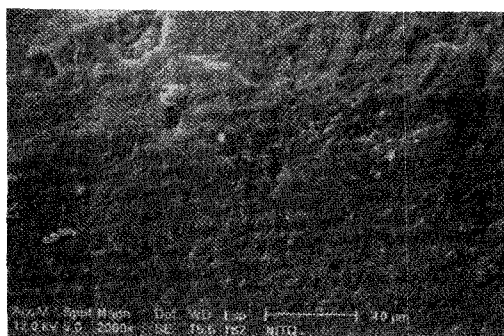




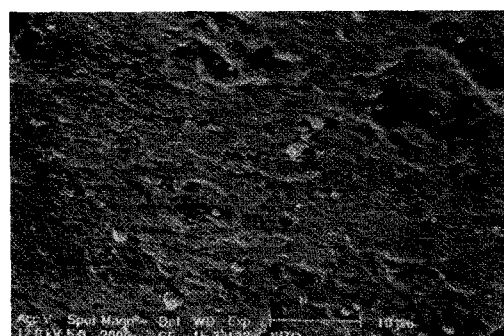
(a) S-21



(a) S-31



(b) C-21



(b) C-31

Fig. 22. SEM micrographs of the ENB-treated EVA.

Fig. 23. SEM micrographs of the DCPD-treated EVA.

1. All of them showed the characteristics of flat curing, and the double bond-introduced vulcanizate with benzene sulfonic acid had a little higher torque value than the vulcanizates with ENB or DCPD.

2. From FT-IR spectra, we could find that double bonds were introduced to the EVA with benzene sulfonic acid, ENB and DCPD.

3. We examined the tensile and elongation of the vulcanizates from the double bond-introduced EVA by using an universal tensile testing machine.

4. We found the state of even dispersion of the vulcanizates from the double bondintroduced EVA utilizing SEM.

From this study, we found it possible to intro-

duce double bonds to the EVA which has been impossible to vulcanize because of no existence of unsaturated group like double bond by using a third material.

### Acknowledgments

This work was supported by grant NO.(971-1102-011-2) from the Basic Research program of the KOSEF.

### References

1. A. Legros, P. J. Carreau and B. D. Favis, *Polymer*, **38**, 5085 (1997).
2. D. M. Brewis and D. Briggs, *Polymer*, **22**, 7

- (1981).
3. Sujit K. Datta, A. K. Bhowmick and T. K. Chaki, *Polymer*, **37**, 45 (1996).
  4. C. Lacroix, M. Bousmina and P. J. Carreau, *Polymer*, **37**, 2949 (1996).
  5. Jin Wen Qian, Xiaohui Wang, Guo Rong Qi and Chi Wu, *Macromolecules*, **30**, 3283 (1997).
  6. 小坂勇次郎, 高分子, **18**, 310 (1969).
  7. 齊藤光高, 小坂勇次郎, 日本ゴム協會誌, **43**, 192 (1970).
  8. 渡辺修三, 東曹研報, **10**, 79 (1966).
  9. I. O. Salyer, H. M. Leeper : *Rubber Age*, June and July (1971).
  10. 宇佐元輝義, 沖田泰介, 吉田誠志, *Plastics Age*, **85** (1969).