ภาคผนวก ก

สูตรยางธรรมชาติอิพ๊อกซิไดซ์และผลการทดสอบยางอิพ๊อกซิไดซ์

ตารางที่ 1 สูตรยางธรรมชาติอิพ๊อกซิไดซ์ ชนิด Epoxyprene® 25 และ ชนิด Epoxyprene® 50

สารเคมี	สูตรที่ 1*	สูตรที่ 2	สูตรที่ 3	สูตรที่ 4	สูตรที่ 5
Epoxyprene® 25	100	100	-	-	-
Epoxyprene® 50	-	-	100	100	100
Calcium stearate	3.0	-	3.0	3.0	-
Sodium carbonate	-	0.25	-	-	0.25
ZnO	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0
Wingstay® L	1.0	-	1.0	1.0	-
CBS	1.5	2.4	0.6	1.5	1.0
TMTD	-	1.6	-	-	-
Sulfur	1.5	0.3	2.5	1.5	2.8
Struktol® 60 NS	-	-	1.5	-	-

หมายเหตุ * เป็นสูตรที่นำไปใช้ในยางผสม (หน่วยเป็น phr)

ตารางที่ 2 ความทนต่อแรงดึงและค่าการยืด ณ จุดขาดของยางอิพ๊อกซิไดซ์สูตรต่างๆ

สูตร	ความทนต่อแรงดึง (MPa)	ค่าการยืด ณ จุดขาด (%)
สูตรที่ 1	23.01 ± 0.70	905 ± 17
สูตรที่ 2	17.03 ± 1.55	880 ± 18
สูตรที่ 3	18.70 ± 2.20	768 ± 38
สูตรที่ 4	21.24 ± 1.97	848 ± 25
สูตรที่ 5	19.45 ± 1.24	662 ± 20

ภาคผนวก ข

สูตรยางผสมระหว่างยางธรรมชาติอิพ๊อกซิไดซ์กับยางคลอโรซัลโฟเนตเตตพอลิเอทธิลีน
และผลการทดสอบยางผสมระหว่างยางธรรมชาติอิพ๊อกซิไดซ์กับยางคลอโรซัลโฟเนตเตต-
พอลิเอทธิลีน

ตารางที่ 3 สูตรยางผสมระหว่างยางธรรมชาติอิพ๊อกซิไดซ์และยางคลอโรซัลโฟเนตเตตพอลิ-
เอทธิลีน

สารเคมี	สูตรที่ 1	สูตรที่ 2
Epoxyprene® 25	80 - 60	-
Epoxyprene® 50	-	80 - 60
CSM	20 - 40	20 - 40
Calcium stearate	3.0	3.0
Sodium carbonate	-	-
ZnO	5.0	5.0
Stearic acid	2.0/1.0*	2.0/1.0*
Wingstay® L	1.0	1.0
CBS	1.5	1.5
TMTD	-	-
Sulfur	1.5	1.5
Struktol® 60 NS	-	-
MgO	4.0	4.0
PE-200®	3.0	3.0
Tetrone® A	2.0	2.0
MBTS	1.5	1.5

หมายเหตุ * เลขตัวหน้าเป็นปริมาณที่ใช้กับยางธรรมชาติอิพ๊อกซิไดซ์ และเลขตัวหลังเป็น
ปริมาณที่ใช้กับยางคลอโรซัลโฟเนตเตตพอลิเอทธิลีน (หน่วยเป็น phr)

ตารางที่ 4 ความทนต่อแรงดึงและค่าการยืด ณ จุดขาดของยางผสมระหว่างยางธรรมชาติอิพ๊อกซิ-
           ไดซ์และยางคลอโรซัลโฟเนตเตตพอลิเอทิลีน

สูตร	ความทนต่อแรงดึง (MPa)		ค่าการยืด ณ จุดขาด (%)	
	คำนวณ	ผลที่ได้	คำนวณ	ผลที่ได้
Epoxyprene® 25 (ENR25)	-	23.01 ± 0.70	-	905 ± 17
Epoxyprene® 50 (ENR50)	-	21.24 ± 1.97	-	848 ± 25
CSM (C4)	-	23.38 ± 1.09	-	854 ± 26
ENR25/CSM (20/80)	23.08	24.10 ± 0.85	894.8	849 ± 12
ENR25/CSM (70/30)	23.12	23.83 ± 2.36	889.7	756 ± 21
ENR25/CSM (60/40)	23.16	21.45 ± 1.39	884.6	692 ± 16
ENR50/CSM (80/20)	21.67	16.70 ± 1.72	849.2	654 ± 23
ENR50/CSM (70/30)	21.88	16.76 ± 1.53	849.8	670 ± 17
ENR50/CSM (60/40)	22.10	6.82 ± 0.48	850.4	442 ± 18

ภาคผนวก ค

ผลการทดสอบยางผสมระหว่างยางธรรมชาติ ยาง ENR และยางคลอโรซัลโฟเนตเตตพอลิเอทิลีน

ตารางที่ 5 ความทนต่อแรงดึงและค่าการยืด ณ จุดขาดของยางผสม 3 ชนิด

สูตร	Stress (MPa)		Strain (%)	
	คำนวณ	ผลที่ได้	คำนวณ	ผลที่ได้
NR/ENR25/CSM (100/0/0)	-	24.13 ± 1.93	-	950 ± 26
NR/ENR25/CSM (0/100/0)	-	23.01 ± 0.70	-	905 ± 17
NR/ENR25/CSM (0/0/100)	-	23.38 ± 1.09	-	854 ± 26
NR/ENR25/CSM (70/10/30)	26.21	23.78 ± 0.92	1012	863 ± 21
NR/ENR25/CSM (65/5/30)	23.85	24.92 ± 0.89	919	845 ± 15
NR/ENR25/CSM (60/10/30)	23.79	24.33 ± 1.04	917	826 ± 10
NR/ENR25/CSM (50/20/30)	23.68	22.51 ± 1.97	912	778 ± 26
NR/ENR25/CSM (40/30/30)	23.57	19.33 ± 1.99	908	734 ± 18

หมายเหตุ สูตรยางธรรมชาติที่ใช้ คือ สูตร NR5

สูตรยาง ENR ที่ใช้ คือ สูตรที่ 1

สูตรยางคลอโรซัลโฟเนตเตตพอลิเอทิลีนที่ใช้ คือ สูตร C4

ภาคผนวก ง

วิธีการหาค่าความหนาแน่นและค่า Volume fraction

<u>วิธีการหาค่าความหนาแน่น</u>

ตัดชิ้นตัวอย่างให้มีขนาด 10 x 10 mm แล้วนำไปชั่งน้ำหนักชิ้นตัวอย่างในอากาศ และชั่งน้ำ
หนักในน้ำ โดยใช้ตาชั่งความหนาแน่น ในกรณีที่ชิ้นตัวอย่างลอยน้ำ จะใช้ที่หนีบกระดาษหนีบชิ้น
ตัวอย่างไว้ในขณะที่นำไปชั่งในน้ำ จากนั้นจึงนำค่าที่ได้มาคำนวณหาความหนาแน่น ตามสมการดัง
นี้

$$Density = W_1 /(W_1 - W_2) \qquad \text{(ก)}$$

$$\text{หรือ} \quad Density = W_1 /(W_1 + W_3 - W_4) \qquad \text{(ข)}$$

เมื่อ W_1 เป็นมวลที่ชั่งในอากาศ มีหน่วยเป็น g

      W_2 เป็นมวลที่ชั่งในน้ำ มีหน่วยเป็น g

      W_3 เป็นมวลของที่หนีบกระดาษ มีหน่วยเป็น g

      W_4 เป็นมวลของที่หนีบกระดาษและชิ้นตัวอย่างที่ชั่งในน้ำ มีหน่วยเป็น g

<u>วิธีหาค่า Volume fraction</u>

1. ตัดชิ้นตัวอย่างให้เป็นแผ่นกลมมีขนาดเส้นผ่าศูนย์กลาง 8 mm มีความหนา 1.5 mm แล้วนำ
   ชิ้นตัวอย่างไปชั่งน้ำหนัก

2. นำชิ้นตัวอย่างไปแช่ในคลอโรฟอร์ม ที่อุณหภูมิห้อง เป็นเวลา 7 วัน (คลอโรฟอร์มมีความ
   หนาแน่น 1.5 g/ml)

3. นำชิ้นตัวอย่างออกจากคลอโรฟอร์ม ซับชิ้นตัวอย่างให้แห้ง แล้วนำไปชั่งน้ำหนัก

4. นำชิ้นตัวอย่างไปอบในตู้อบความดัน ที่อุณหภูมิ 60°C เป็นเวลา 48 ชั่วโมง จากนั้นนำชิ้นตัว
   อย่างมาชั่งน้ำหนัก

5. คำนวณหาค่า Volume fraction ตามสมการดังนี้

$$Volume fraction(V_r) = \frac{(W_2 / \delta_r)}{(W_2 / \delta_r) + [(W_1 - W_2)/ \delta_s]} \qquad \text{(ค)}$$

เมื่อ W_1 เป็นน้ำหนักหลังจากแช่ในคลอโรฟอร์ม มีหน่วยเป็น g

 W_2 เป็นน้ำหนักหลังจากอบในตู้อบความดัน มีหน่วยเป็น g

      δ_r, δ_s เป็นความหนาแน่นของชิ้นตัวอย่างและคลอโรฟอร์มตามลำดับ มีหน่วยเป็น g/ml

ตารางที่ 6 ค่าความหนาแน่นและค่า Volume fraction ของยางธรรมชาติ ยาง ENR ยางคลอโร-ซัล
โฟเนตเตตพอลิเอทธิลีน และยางผสม

สูตร	ความหนาแน่น (g/ml^3)	Volume fraction
NR1	0.9383	0.2587
NR2	0.9788	0.2758
NR5	0.9497	0.2471
C1	1.1968	0.2607
C4	1.1984	0.2347
ENR (สูตรที่ 1)	0.9814	0.2115
B4-20	0.9817	0.2533
B4-30	0.9733	0.2793
B4-40	1.0053	0.2798
B4-50	1.0402	0.2831
B4-60	1.0714	0.2695
B4-70	1.1166	0.2534
B4-80	1.1416	0.2617
B4-30 (ENR 1.0 phr)	1.0067	0.2728
B4-30 (ENR 3.0 phr)	1.0030	0.2627
B4-30 (ENR 5.0 phr)	0.9896	0.2629
B4-30 (ENR 10.0 phr)	0.9897	0.2756
NR/ENR25/CSM (65/5/30)	0.9932	0.2839
NR/ENR25/CSM (60/10/30)	0.9837	0.2808
NR/ENR25/CSM (50/20/30)	1.0022	0.2884
NR/ENR25/CSM (40/30/30)	1.0072	0.2695

ภาคผนวก จ

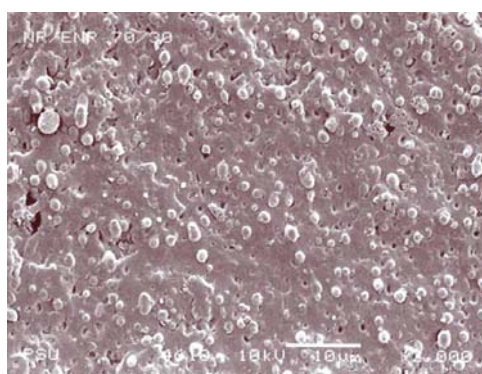**รูป SEM ของยางผสม ENR/CSM และยางผสม NR/ENR**
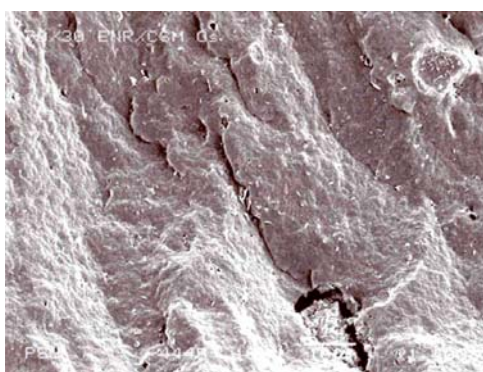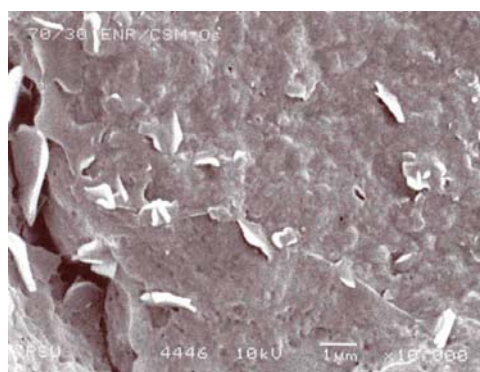
a (1) a (2)
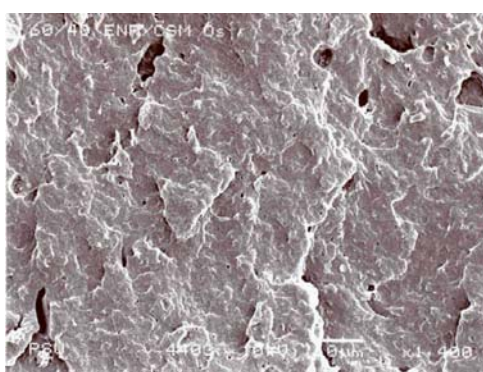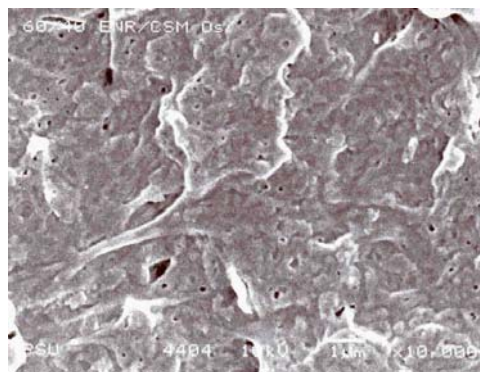
b (1) b (2)

c

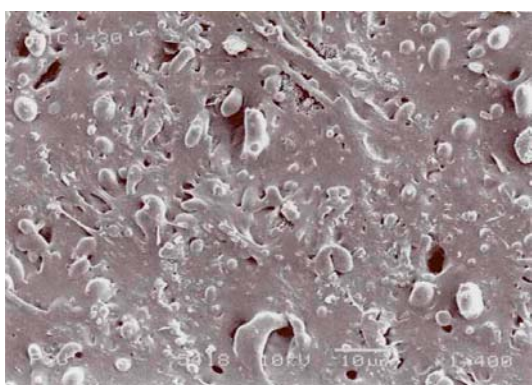รูปที่ 1 SEM ของยางผสม ENR/CSM และยางผสม NR/ENR

หมายเหตุ : a) ENR25/CSM (70/30) (1) กำลังขยาย 1,400 เท่า และ (2) กำลังขยาย 10,000 เท่า

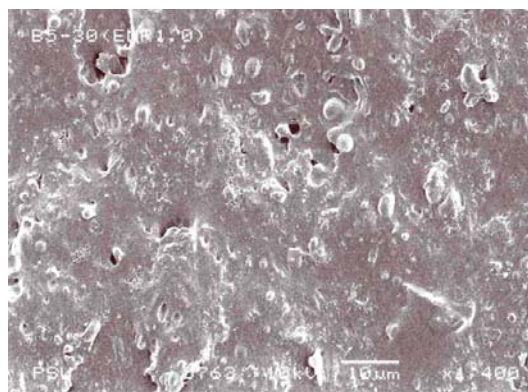b) ENR25/CSM (60/40) (1) กำลังขยาย 1,400 เท่า และ (2) กำลังขยาย 10,000 เท่า
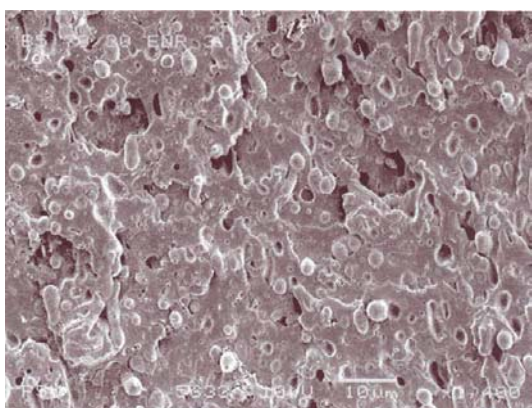
c) NR/ENR25 (70/30) กำลังขยาย 1,400 เท่า

ภาคผนวก ฉ

รูป SEM ของยางผสมสูตร B1 ที่อัตราส่วน 70/30 เมื่อเติมยาง ENR ที่ปริมาณต่างๆ
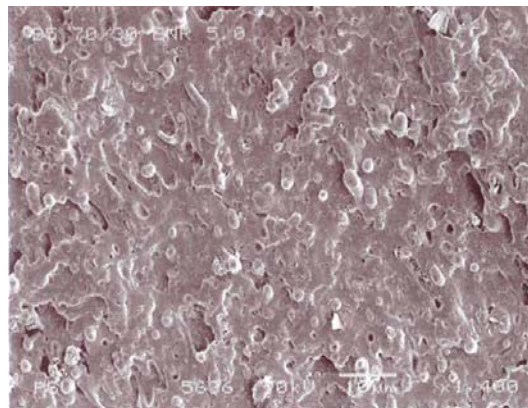

(a)

(b)

(c)

(d)

รูปที่ 2 SEM ของยางผสมสูตร B1 ที่อัตราส่วน 70/30 เมื่อเติมยาง ENR ที่ปริมาณต่างๆ

หมายเหตุ : (a) 0 phr, (b) 1 phr, (c) 3 phr และ (d) 5 phr (กำลังขยาย 1,400 เท่า)

ภาคผนวก ฌ

บทความต่างๆที่ได้รับการตีพิมพ์

Mechanical Properties and Blend Compatibility of Natural Rubber –Chlorosulfonated Polyethylene Blends

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ABSTRACT: Natural rubber (NR) was blended with chlorosulfonated polyethylene (CSM) with various formulation and blend ratios (NR/CSM: 80/20 –20/80, wt/wt). Rubber blends were prepared by using a two-roll mill and vulcanized in a compression mold to obtain the 2 mm-thick sheets. Tensile properties, tear resistance, thermal aging resistance, ozone resistance, and oil resistance were determined according to ASTM. Compatible NR/CSM blends are derived from certain blends containing 20–30% CSM without adding any compatibilizing agent. Tensile and tear strength of NR-rich blends for certain formulations show positive deviation from the rule of mixture. Thermal aging resistance depends on formulation and blend ratio, while ozone and oil resistance of the blends increase with CSM content. Homogenizing agents used were Stuktol®60NS and Epoxyprene®25. Stuktol®60NS tends to decrease the mechanical properties of the blends and shows no significant effect on blend morphology. Addition of 5–10 phr of epoxidized natural rubber (ENR, Epoxyprene® 25) increases tensile strength, thermal aging resistance, and ozone resistance of the blends. It is found that ENR acts as a compatibilizer of the NR/CSM blends by decreasing both CSM particle size diameter and α transition temperature of CSM. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 127–140, 2005

Key words: chlorosulfonated polyethylene; epoxidized natural rubber; Hypalon; natural rubber; rubber blends

INTRODUCTION

It is well established that elastomers do not exhibit all of the properties that are desired, and elastomeric blends are frequently used in the rubber industry to obtain the best compromise in compound mechanical/physical properties, processability, and cost. Therefore, there is a need to know which polymers can be successfully blended and what factors influence the final blend properties. Natural rubber (NR) is deteriorated by ozone and thermal attack due to a highly unsaturated backbone, and it also shows low oil and chemical resistance due to nonpolarity. Improvement in the poor ozone, aging, and oil resistance of NR can be achieved by blending it with low/saturated rubbers and chlorinated rubbers, such as NR/EPDM blend,[1–8] NR/SBR blend,[9–12] NR/NBR blend,[13–15] NR/BR blend,[9] NR/CR blend,[11,16] NR/CPE blend,[17–20] and NR/ULDPE blend.[21]

Chlorosulfonated polyethylene (CSM) is an important synthetic rubber. Hypalon® is the registered trademark for a series of CSM manufactured by DuPont Dow Elastomers. The vulcanizate of CSM is highly resistant to the deteriorating effects of ozone, oxygen, weather, heat, oil, and chemicals. It can be compounded to give high mechanical properties—for example, high tensile strength and abrasion resistance. The main applications of CSM are in electric cables, hose for liquid chemicals, waterproof cloth, floor tiles, and oil resistant seals. CSM coatings are used for inflated fabric structure, diaphragms, gloves, garments, light colored roof coatings, and coatings on chemical tanks and equipment. Recently, there have been many publications reporting the thermal aging behavior of CSM,[22–30] whose applications include electric cables used in nuclear power facilities[25,26,30] and geomembranes.[31] There are a few publications that have discussed rubber blends based on CSM, including CSM/EVA,[32–34] CSM/EPR,[35,36] CSM/NBR,[37–40] and CSM/ENR.[41–43] To the best of our knowledge, the NR/CSM blend has not yet been reported in the literature. Owing to the presence of the polarity of the chlorine group in CSM, NR/CSM blends should be resistant to ozone, oil, heat, flame, and nonpolar chemicals.

Based on chemical structure, the NR/CSM blend becomes incompatible due to the difference in polarity. One way to improve the compatibility of immiscible blends is the use of a compatibilizer with segments chemically (or physically) identical to the individual homopolymers. The compatibilizer is claimed to: (1) reduce the interfacial energy between phases,

(2) permit a finer dispersion during mixing, (3) provide a measure of stability against gross segregation, and (4) result in improved interfacial adhesion. It is known that CSM could be crosslinked by polyfunctional alcohols.[39] De et al.[38–43] reported that blends of CSM/ENR and CSM/carboxylated nitrile rubber behaved as "self-vulcanizable rubber blends" since the blends without curative got vulcanized during molding. The mechanism of crosslinking between CSM and ENR in CSM/ENR blends was proposed by De et al.[43] The miscibility of CSM/ENR blends depended on the epoxy content and the blend ratio.

The purpose of this work was to investigate mechanical and thermal aging properties, as well as ozone and oil resistance of NR/CSM blends. ENR, Epoxyprene®25, and a homogenizer, Struktol®60NS, were introduced to the system, and their effect on properties of the blends was examined. We focused on NR-rich blends due to the higher cost of CSM.

EXPERIMENTAL

Materials

The natural rubber used in this study was STR60CV, constant viscosity grade, produced in Thailand. Its Mooney viscosity is 66 [ML(1 + 4) at 100°C]. The chlorosulfonated polyethylene used was Hypalon® 40, with Mooney viscosity of 63 [ML(1 + 4) at 100°C], which appears in Structure.

$$\{[(-CH_2-CH_2)_x -CH_2-\underset{\underset{Cl}{|}}{CH-}]_y -CH_2-\underset{\underset{SO_2Cl}{|}}{CH-}\}_n$$
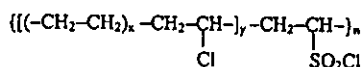
It contains 34.40% chlorine and 0.98% sulfur, by weight. The sulfonyl chloride group is a reactive site for crosslink reaction. Struktol®60NS and epoxidized natural rubber (Epoxyprene® 25) were used as a homogenizing agent. All chemicals for rubber compounding were commercial grade and used as received.

TABLE I
Formulation of Rubber Compounds

Chemical	NR1	NR2	NR3	CSM1	CSM2
NR	100	100	100	—	—
Stearic acid	1	2	2	—	1
ZnO	5	10	5	—	—
Wingstay L	1	3	1	—	—
MBTS	0.75	—	—	—	1.5
TMTD	0.3	—	—	—	—
CBS	—	0.6	1.5	—	—
Sulfur	1.5	2.8	1.5	—	—
Hypalon® 40	—	—	—	100	100
MgO	—	—	—	4	4
PE (200 mesh)	—	—	—	3	3
Tetrone® A	—	—	—	2	2

TABLE II
Formulation of Rubber Blends

Compound no.	Formulation
B1	NR1/CSM1 + 3 phr Struktol® 60NS
B2	NR1/CSM2
B3	NR2/CSM2
B4	NR3/CSM2
B5	NR1/CSM1

Preparation of blends

Rubber compounds were mixed on a two-roll mill. NR was masticated prior to blending with CSM, then the rubbers were mixed together until homogenization before adding chemicals. The 2 mm thick slabs were then press cured at 150°C. Vulcanization time was determined by using a moving die rheometer (MDR2000). Formulations of the rubber compounds are shown in Tables I and II. Calcium stearate (3 phr of ENR) was added to the blends containing ENR. Blend composition was in the range of 80/20–20/80 (NR/CSM), by weight.

Measurement of mechanical properties

Tensile testing and tear resistance were conducted at a speed of 500 mm/min according to ASTM D412 and ASTM D813, respectively. Thermal aging was operated at 70°C for 7 days by using a gear oven and calculated changes in tensile properties according to ASTM D573. The aging resistance is expressed as a percentage of the change in tensile properties calculated as follows:

$$P = [(A - O)/O] \times 100$$

where P is the percentage change in the property, O is the original value, and A is the value after aging. Increases are indicated as positive and decreases as negative. Testing of the oil resistance of vulcanized blends was carried out in ASTM oil no. 1 and IRM903 oil (equivalent to ASTM oil no. 3) at room temperature (27–30°C) for 7 days. Specimen dimension was 2 mm × 8 mm (thickness × diameter). Swelling volume was calculated similarly to the above equation. Ozone resistance measurement was carried out in a Toyoseiki® EG2001 under an ozone concentration of 50 parts per hundred million (pphm) and a temperature of 40°C for 96–168 h (4–7 days). The rectangular-shaped specimens (2 mm × 10 mm, thickness × width) were extended for 20% strain (grip length = 70 mm) and maintained this way during 48 h in the absence of light, prior to testing. The ozone attack was examined in the specimens performed under the same deformation of 20%. Crack observation was determined by using a magnifying glass and recorded by a digital camera.
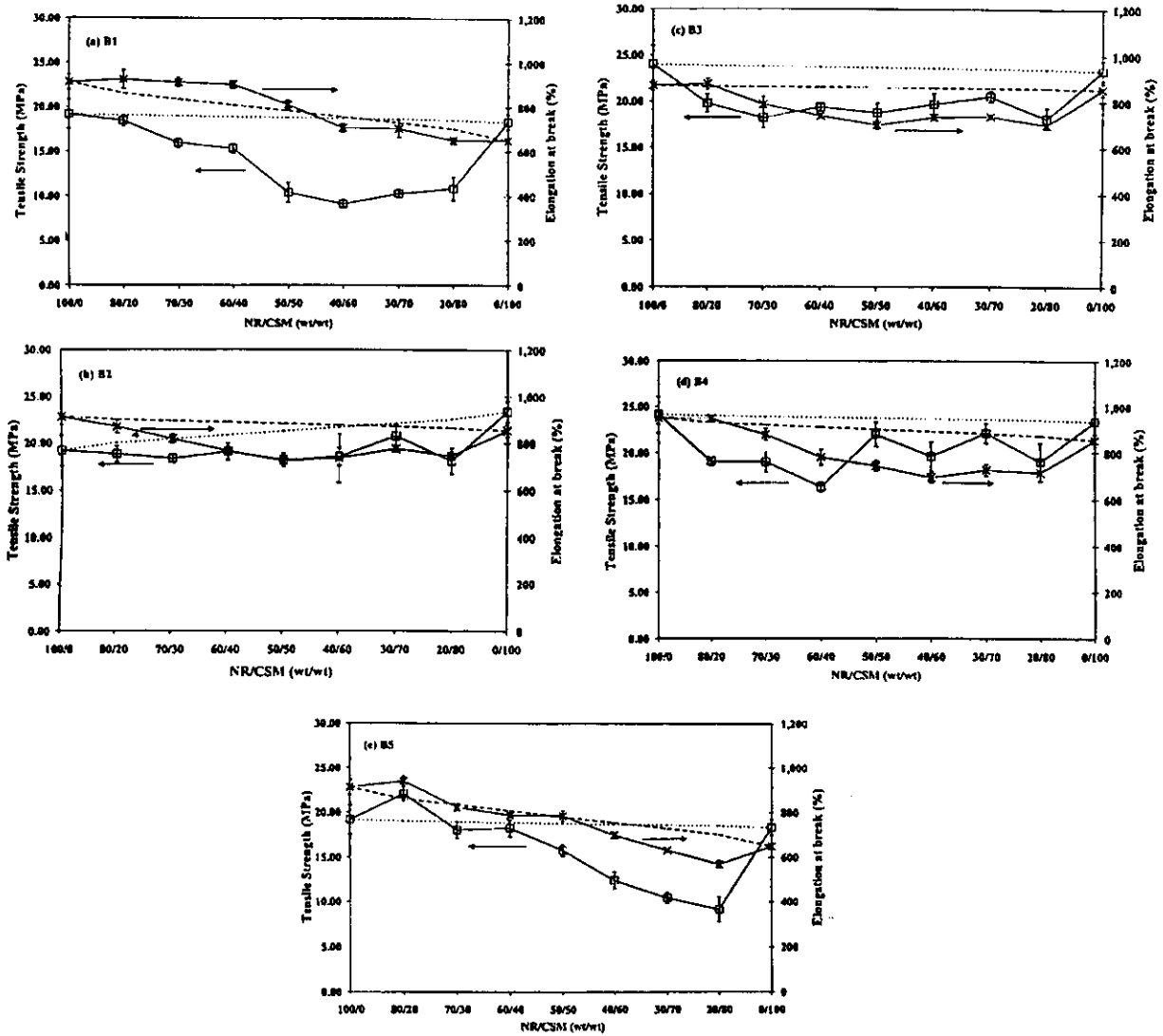
Figure 1 Tensile strength and elongation at break of blends at various compositions: (a) B1, (b) B2, (c) B3, (d) B4, and (e) B5. □ = stress, × = strain. Dot and dash lines represent additivity.
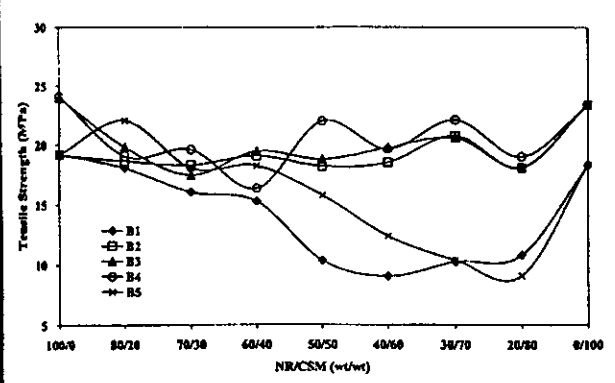

Figure 2 Tensile strength of NR/CSM blends.

Blend characterization

Fractured surfaces of tensile tested specimens were coated with gold prior to observation by using a scanning electron microscope. Transition temperature was investigated by using the Rheometric Scientific® DMTA V, at a frequency of 3.5 Hz and a strain control of 0.16%. Testing was operated in tension mode at a heating rate of 2°C/min within the temperature range between −120°C and 50°C.

RESULTS AND DISCUSSION

Rubber blends without the compatibilizer

Mechanical properties

We believe that chemical compositions affect mechanical properties of rubber blends; therefore, we em-
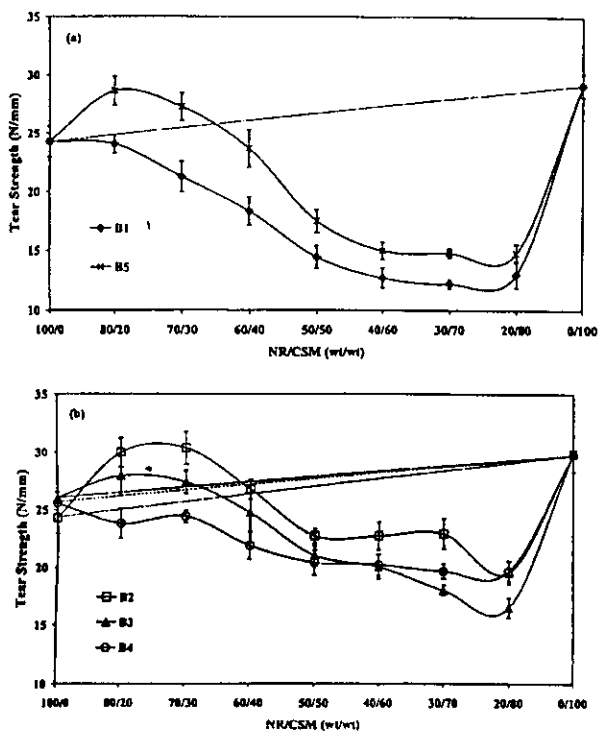
Figure 3   Tear strength of NR/CSM blends: (a) B1 and B5; (b) B2, B3, and B4.

ployed various blend formulations as listed in Tables I and II. Actually, B1 and B5 consisted of the same chemical composition except for the presence of 3 phr-Struktol®60NS in B1. Tensile strength and elongation at break of rubber blends are shown in Figures 1(a–e) for B1–B5, respectively. The dot and dash lines represent the additive line calculated from the rule of mixture. Synergistic properties (above or on the additive line) and slightly negative deviation (< 10%) from the additive line are derived from certain blend compositions, indicating compatibility of the blends. Tensile strength of the 80/20 B5 blend exhibits positive deviation (+16%), while the 70/30 and 60/40 B5 blends show slightly negative deviation, −5% and −3%, respectively. Increasing CSM content decreases tensile strength of B5. The presence of Struktol® (B1) decreases tensile strength, as shown in Figure 1(a). By adding 3 phr of Struktol®, tensile strength of the 80/20 blend is changed from +16% (above the additive line) to −3% (below the additive line), and the 70/30 and 60/40 blends of B1 become much lower than the additive line (−16%). Similar to B5, increasing CSM content decreases the tensile strength of B1. Tensile strength of B2–B4 is below the additive line, and only the 80/20 and 70/30 blends of B2 show little negative deviation, ≤ 10%. The synergistic behavior of elongation at break is also derived from the blends. Positive deviation and little negative deviation (≤ 10%) from

the additive line are obtained from the NR-rich blends of all formulations. The comparison of tensile strength of each blend is exhibited in Figure 2. B1 seems to be the worst blend, while B4 seems to be the best one for the CSM-rich blends. B5 is the best blend for the 80/20 blends, while B4 and B3 become the best one for the 70/30 and 60/40 blends, respectively. Although B5 displays more compatibility than other formulations, its tensile strength was lower than others.

Tear strength of the NR-rich blends of B5 shows positive deviation from the additive line, as shown in Figure 3(a). The presence of Struktol® decreases tear strength of the blends. The 80/20 and 70/30 blends of B2 and B3 also provide synergistic behavior in tear strength, as illustrated in Figure 3(b), while B4 showed nonsynergy for all blend ratios. Tear strength of all blends decreases as CSM content increases.

These results elucidate that mechanical properties of the NR/CSM blends depend on blend ratio and blend formulation; incorporation of 3 phr of Struktol® into the blends deteriorates mechanical properties. Compatible blends from NR blended with CSM without the compatibilizer could be prepared by choosing the right chemical composition and right blend ratio.

Physical properties

In the present study, the thermal aging resistance of NR seems to be better than that of CSM, as shown in
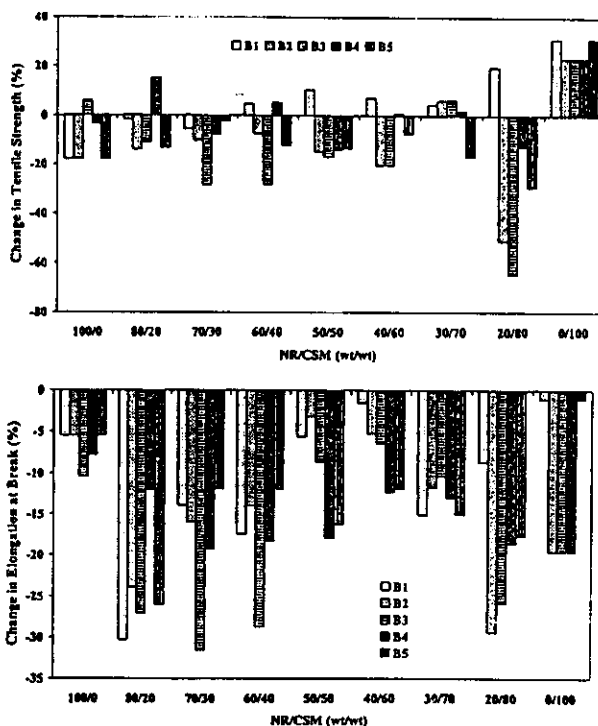

Figure 4   Thermal aging resistance of NR/CSM blends: (a) changes in tensile strength; (b) changes in elongation at break.

TABLE III
Ozone Test Results of NR/CSM Blends

Rubber	T1 (hrs)	T2 (hrs)	Appearance after exposed for 96 hrs*/Other comments	Rank
NR1	8	72	Broke into 2 pieces after exposed for 168 hrs.	6
NR2	4	48	Broke into 2 pieces after exposed for 72 hrs.	6
NR3	8	72	Very deep cracks were observed.	5
ENR	24	—	Crack length was 1 mm*.	4
CSM1	—	—	No crack was observed after exposed for 168 hrs.	—
CSM2	—	—		
B1: 80/20	16	48	Very deep cracks were observed.	5
70/30	16	72	Specimen broke into 2 pieces*.	
60/40	16	72		
50/50	96	—	Very tiny cracks were observed and no crack growth	
40/60	96	—	was observed.	
30/70	120	—		
20/80	—	—	No crack after exposed for 168 hrs.	
B2: 80/20	24	—	Surface-crack length was ~ 2 mm*.	2
70/30	24	—	Surface-crack length was ~ 1 mm*.	
60/40	72	—		
50/50	—	—	No crack was observed after exposed for 168 days.	
40/60–20/80	—	—	No crack was observed after exposed for 168 days.	
B3: 80/20	16	—	Crack length was ~ 2 mm*.	3
70/30	16	—	Crack length was ~ 2 mm*.	
60/40	—	—	No crack was observed after exposed for 168 hrs.	
50/50–20/80	—	—	No crack was observed after exposed for 168 hrs.	
B4: 80/20	8	—	Crack length was ~ 2 mm*.	3
70/30	16	—	Crack length was ~ 1 mm*.	
60/40	—	—	No crack was observed after 96 hrs.	
50/50	—	—		
40/60–20/80	—	—	No crack was observed after 168 hrs.	
B5: 80/20	16	—	Deep-crack length was ~ 2 mm*.	4
70/30	16	—	Deep-crack length was ~ 3 mm*.	
60/40	16	—		
50/50	—	—	Crack length was ~ 1 mm*.	
40/60–20/80	—	—	No crack was observed after 168 hrs.	
NR/ENR/CSM				
70/10/30	24	—	Surface-crack length was ~ 1 mm*.	2
70/5/30	24	—	Surface-crack length was ~ 0.5 mm*.	
65/5/30	—	—	Very tiny cracks on the surface were observed after	1
60/10/30	—	—	120 hrs and no change was observed after 168 hrs.	
50/20/30	—	—		
40/30/30	—	—		

Note. T1 = time for crack initiation. T2 = time for crack growth of 5 mm length. Rank #1 = the best ozone resistance, #6 = the worst ozone resistance, comparison made on 30% CSM concentration.

Figure 4. It is known that crosslinking could be occurring in CSM under thermal aging. As a result, its tensile strength increases and elongation at break decreases. Crosslinking and molecular scission could be occurring in thermal aging of NR. Thermal degradation of CSM has been reported.[23,24,27,37,38] During thermal oxidation, partial removal of –SOCl$_2$ and dehydrochlorination takes place. Chlorine loss gives C=C in the main chain. These cause local stiffening and become preferential sites for thermo-oxidation and crosslinking. In our system, crosslinking may be the dominant mechanism in CSM and chain scission may be the dominant one in NR. Consequently, virgin CSM shows an increase in tensile strength and NR shows a decrease after thermal aging. Nevertheless, most of the blends show a decrease in this property, including the CSM-rich blends. The most change is for the 20/80 blend. However, some formulation and blend ratios perform synergistic behavior, with lesser change in tensile strength than the original rubbers. Small changes (≤ ±10%) are obtained from many blends. All specimens show a decrease in elongation at break, and most of them change less than 15%. B1 seems to be better than B5, indicating the positive influence of Struktol®. Similar to mechanical properties, thermal aging resistance depends upon formulation and blend ratio, and the improvement in the thermal aging resistance of NR is accomplished by blending with CSM.

Ozone concentrations of less than 1 ppb can severely attack nonresistance elastomers if they are in the strained condition; therefore, ozone attack is often the most important effect of exposure to the atmo-
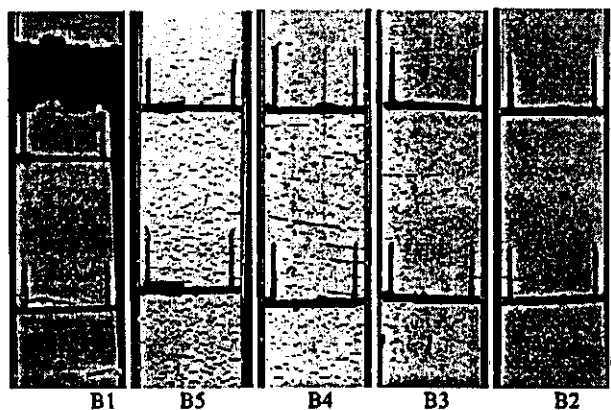
Figure 5 Photographs of the 70/30 blends after ozone testing for 96 h at 40°C under 50 pphm of ozone concentration. Specimens are ranked in order of severity; B1 is the least ozone resistant and B2 is the most. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

sphere. Test samples having 20% strain were exposed to ozonized air of 50 pphm ozone concentration. Ozone test results are summarized in Table III. Observation with a magnifying glass has been done every 1 h. Time for crack initiation is referred to as T1, and time for crack propagation to 5 mm is referred to as T2. Cracks developed on the surface of NR, which had no antiozonant, at 4–8 h of exposure time. Some re-
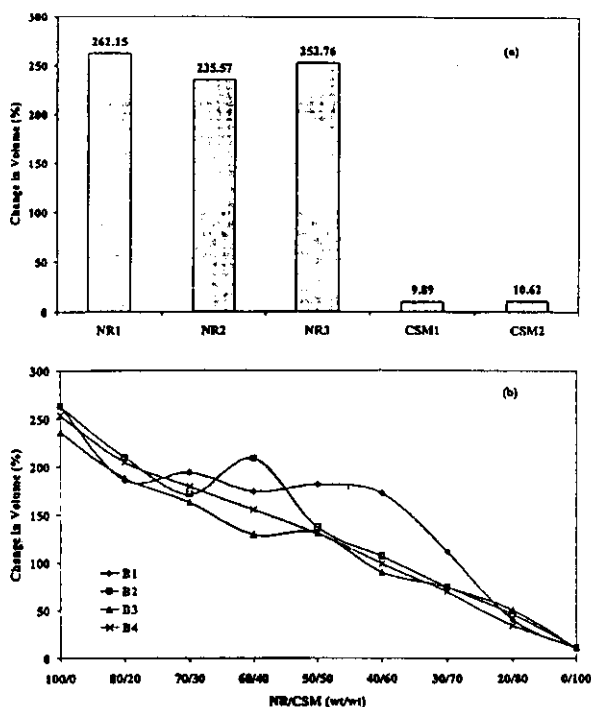
Figure 7 Changes in volume after immersion in ASTM oil no. 1 for 7 days at room temperature: (a) NR and CSM; (b) NR/CSM blends: B1–B4.
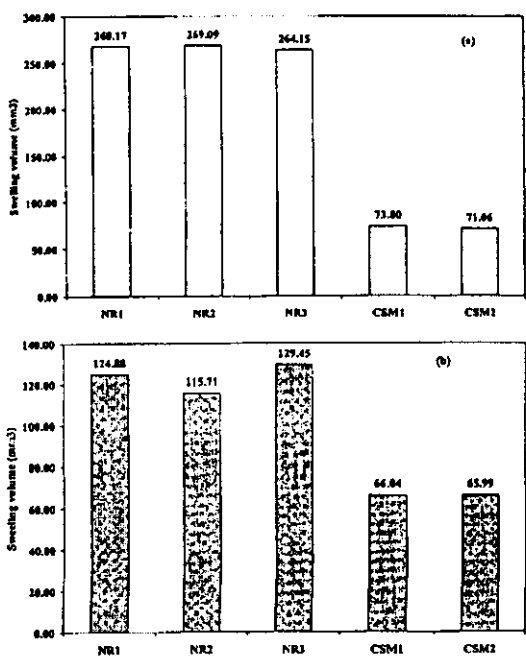

Figure 6 Swelling volume of NR and CSM after swelling for 7 days at room temperature: (a) ASTM oil no. 1; (b) IRM903 oil.
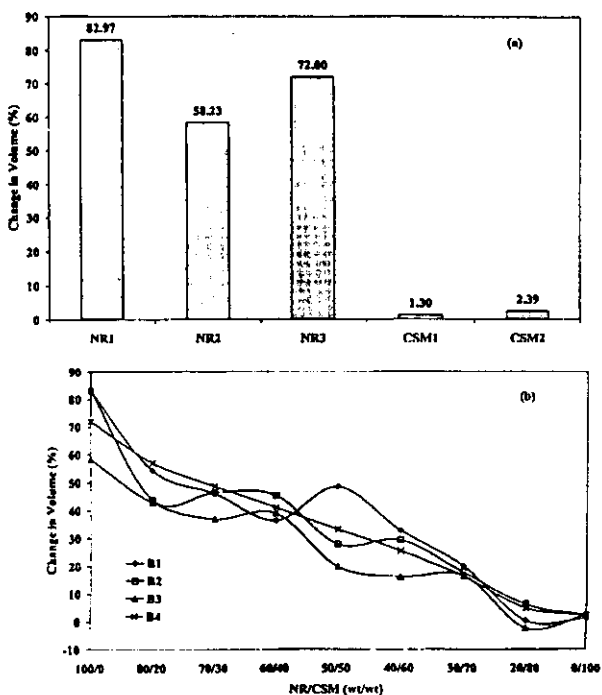

Figure 8 Changes in volume after immersion in IRM903 oil for 7 days at room temperature: (a) NR and CSM; (b) B1–B4.

TABLE IV
Tensile Properties of NR/CSM (80/20) Blends Showing Effect of Struktol®60NS

Rubber	σ_b (MPa)		ε_b (%)	
	Experiment	Calculation*	Experiment	Calculation*
NR1	19.17 ± 1.63	—	912 ± 33	—
NR2	24.00 ± 2.04	—	868 ± 22	—
NR3	24.13 ± 1.93	—	950 ± 26	—
CSM1	18.34 ± 0.86	—	649 ± 13	—
CSM2	23.38 ± 1.09	—	854 ± 26	—
B5	22.03 ± 0.78	19.00	938 ± 22	859
B5 + 1 phr Struktol®60NS	17.55 ± 0.74	19.00	889 ± 19	859
B1 (3 phr Struktol®60NS)	18.40 ± 0.62	19.00	922 ± 42	859
B2	18.80 ± 0.87	20.01	870 ± 28	900
B2 + 1 phr Struktol®60NS	19.87 ± 0.56	20.01	887 ± 17	900
B2 + 3 phr Struktol®60NS	18.99 ± 0.85	20.01	874 ± 26	900
B3	19.80 ± 1.01	23.88	875 ± 24	865
B3 + 1 phr Struktol®60NS	21.83 ± 0.94	23.88	871 ± 17	865
B4	19.04 ± 0.45	23.98	947 ± 12	931
B4 + 1 phr Struktol®60NS	21.41 ± 0.86	23.98	934 ± 19	931

* Rule of mixture: (Property)$_{blend}$ = (wt)$_1 \cdot P_1$ + (wt)$_2 \cdot P_2$, where wt is weight fraction; P is property; 1 and 2 are rubber1 and rubber2, respectively.

searchers reported that crack initiation in NR took place within 2 h. ENR shows better ozone resistance; it took 24 h for crack initiation. Undoubtedly, CSM performs with excellent ozone resistance, as expected. The nature and intensity of cracks are different for various blends. Deep cracks and surface cracks as well as micro-cracks are observed in specimens. CSM greatly increases the ozone resistance of NR, and ozone resistance of the blends increases with increasing CSM content. We did rank the ozone resistance of the blends based on specimen appearance after testing as described in Table III. Lower rank number indicates higher ozone resistance. Ozone resistance can be ranked in the following order: B2 > B3, B4 > B5 > B1 > NR. Figure 5 represents tested specimens after exposure for 96 h. Although the cracks in B5 are shorter than those in B3 and B4, these shorter cracks are much deeper and look more severe. To improve ozone resistance of NR by CSM, it is essential to have enough CSM content and get the right formulation. In our case, CSM content should be more than 30%, similar to

NR/EPDM blends that need 35–40% of EPDM to improve the ozone resistance of NR.[1]

The swelling volume of virgin NR and CSM are shown in Figure 6. NR displays much less resistance in ASIM oil no. 1 than IRM903 oil, whereas CSM shows a slight difference between both oils. Oil resistance of CSM is higher than that of NR, about 2–3.5 times; and dimension stability after immersion for 7 days of CSM is much better than that of NR, about 25–70 times, as shown in Figures 7(a) and 8(a). Changes in volume of the blends are shown in Figures 7(b) and 8(b) for ASTM oil no. 1 and IRM903 oil, respectively. Oil resistance of the blends increases with CSM content.

Effect of Stuktol®

Compatible blends could be obtained from NR/CSM blends in the present study, that is, the increase in

Scheme 1

TABLE V
Tensile Properties of NR/ENR/CSM Blends (B4)

Rubber	σ_b (MPa)		ε_b (%)	
	Experiment	Calculation*	Experiment	Calculation*
100/0/0	24.13 ± 1.93	—	950 ± 26	—
0/100/0	23.01 ± 0.70	—	905 ± 17	—
0/0/100	23.38 ± 1.09	—	854 ± 26	—
70/30/0	25.21 ± 1.35	23.79	963 ± 28	936
0/70/30	23.83 ± 2.36	23.12	756 ± 21	889
70/0/30	19.01 ± 1.10	23.91	879 ± 25	921
70/5/30	24.33 ± 0.94	23.75	861 ± 16	920
70/10/30	23.78 ± 0.92	23.82	863 ± 21	919
65/5/30	24.92 ± 0.89	23.85	845 ± 15	919
60/10/30	24.33 ± 1.04	23.79	826 ± 10	917
50/20/30	22.51 ± 1.97	23.68	778 ± 26	912
40/30/30	19.33 ± 1.99	23.57	734 ± 18	908

* Rule of mixture.
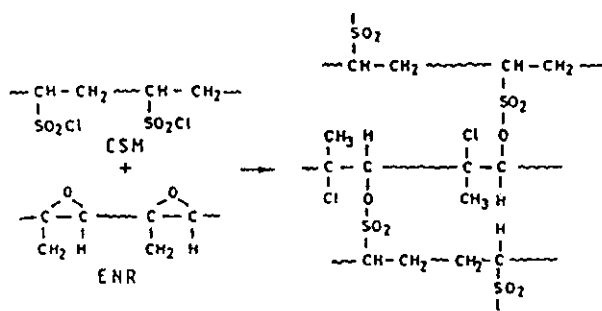
TABLE VI
Changes in Tensile Properties After Thermal Aging of NR/ENR/CSM Blends (B4)

Rubber	σ_b (MPa)		ε_b (%)	
	Experiment	Calculation*	Experiment	Calculation*
70/0/30	−7.87	4.35	−19.33	−11.07
70/5/30	2.71	4.50	−18.12	−10.65
70/10/30	−2.19	4.63	−23.99	−10.39
65/5/30	−0.92	4.92	−19.76	−15.61
60/10/30	−7.56	5.48	−20.34	−10.65
50/20/30	−4.80	6.57	−22.49	−10.16
40/30/30	−2.22	7.66	−16.21	−9.77

* Rule of mixture.

TABLE VII
Tear Resistance of NR/ENR/CSM Blends (B4)

Rubber	Tear strength (N/mm)	
	Experiment	Calculation*
70/0/30	24.41 ± 0.51	26.83
70/5/30	22.77 ± 0.92	26.80
70/10/30	22.11 ± 0.49	26.79
65/5/30	23.04 ± 0.79	26.79
60/10/30	23.70 ± 0.66	26.75
50/20/30	24.30 ± 1.30	26.66
40/30/30	22.78 ± 0.80	26.58

* Rule of mixture.

Figure 10   Photographs of the NR/ENR/CSM blends after ozone testing for 96 h at 40°C under 50 pphm of ozone concentration. Specimens are ranked in order of severity, showing an improvement in ozone resistance by the addition of ENR. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tensile strength of the 80/20 blend of B5 and the increase in tear strength of the 80/20 and 70/30 blends of B2, B3, and B5. Compatibility is dependent of blend

formulation, blend ratio, and properties. The addition of 3 phr of Struktol® decreases tensile and tear strength of the blends. However, this does not mean that Struktol® is not a good homogenizer. We found that only 1 phr of Struktol® could increase tensile strength of the 80/20 blends of B2, B3, and B4, but it is still lower than the rule of mixture, as shown in Table IV. Based on properties of the blends stated earlier, Struktol® seems to be not a good compatibilizer for the
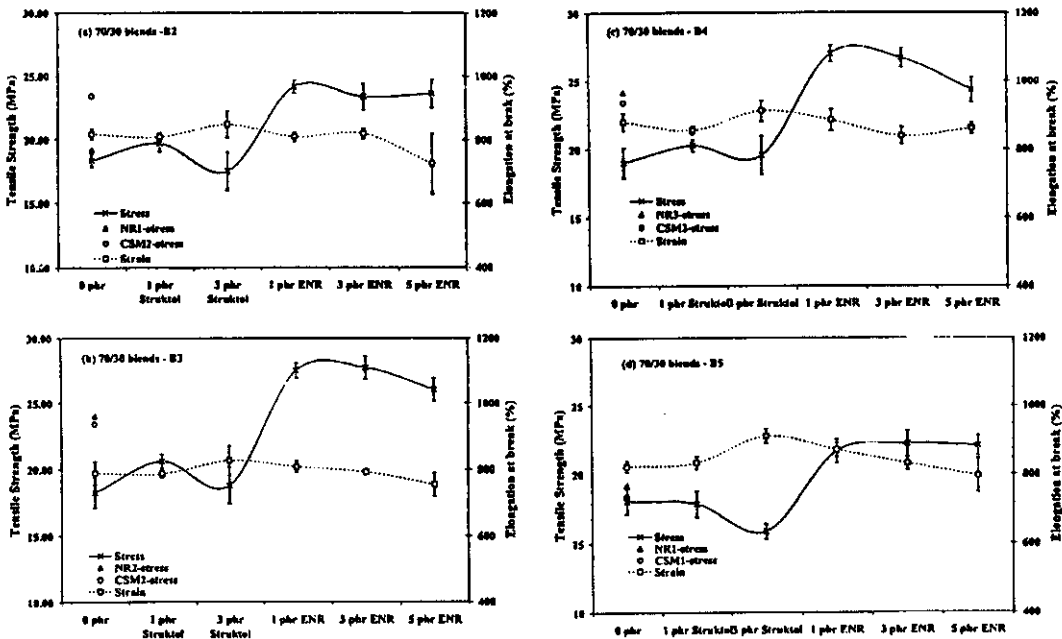

Figure 9   Effect of ENR and Struktol® on tensile properties of the blends containing 30% CSM: (a) B2, (b) B3, (c) B4, and (d) B5. The 0 phr represents the blend without a homogenizer; B5 with 3 phr Struktol was B1.

TABLE VIII
Particle Size of CSM in the Blends Determined by using SEM

| Rubber	Average diameter (μm)	Minimum diameter (μm)	Maximum diameter (μm)
B1*: 20% CSM	2.00 ± 0.78	0.80	4.81
30% CSM	1.71 ± 0.74	0.68	4.55
40% CSM	1.89 ± 0.74	0.69	4.25
50% CSM	1.89 ± 0.67	0.75	3.79
B2: 20% CSM	2.17 ± 0.78	0.89	4.85
30% CSM	2.32 ± 1.04	0.41	5.30
40% CSM	2.40 ± 0.86	0.77	5.63
50% CSM	2.22 ± 0.80	0.65	4.74
B3: 20% CSM	2.04 ± 0.83	0.70	4.92
30% CSM	2.45 ± 1.02	0.90	5.43
40% CSM	2.25 ± 0.79	0.81	5.67
50% CSM	1.98 ± 0.85	0.70	4.57
B4: 20% CSM	1.55 ± 0.69	0.56	4.85
30% CSM	2.02 ± 1.07	0.52	5.17
40% CSM	1.94 ± 1.09	0.52	6.45

* Added 3 phr of Strucktol®60NS.
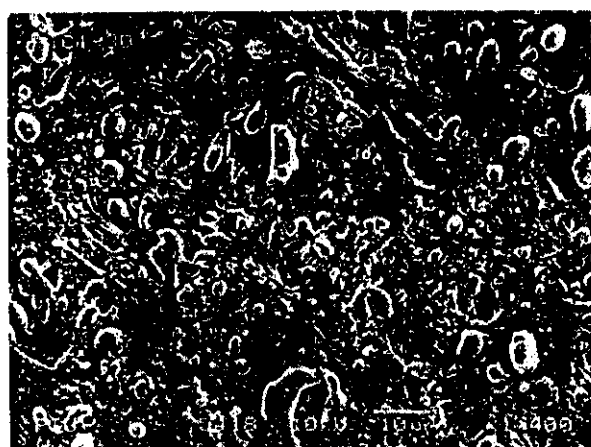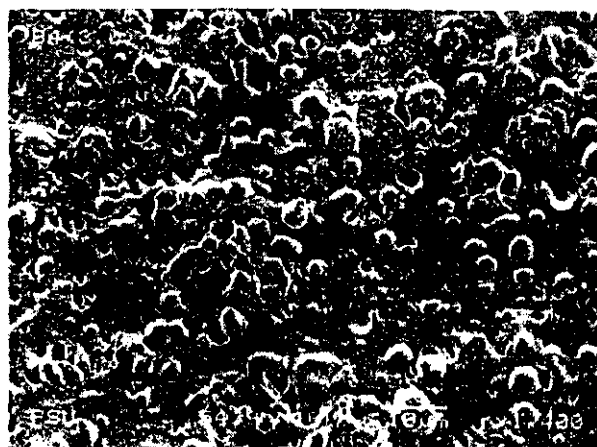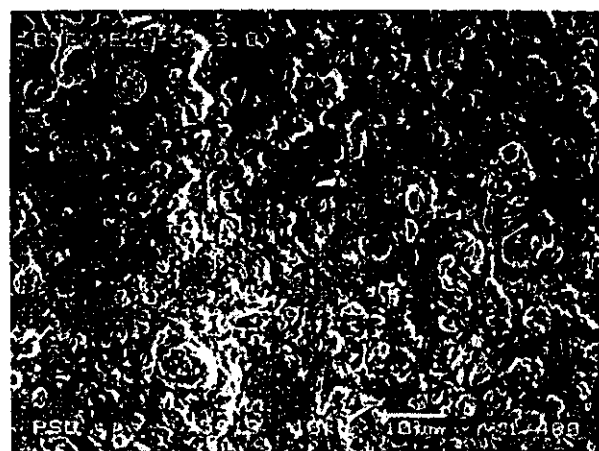

(a)
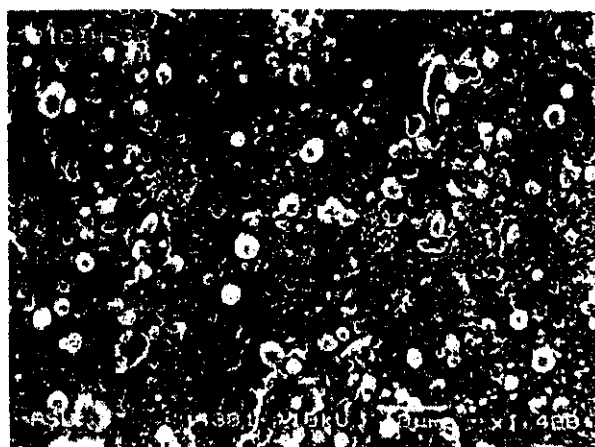
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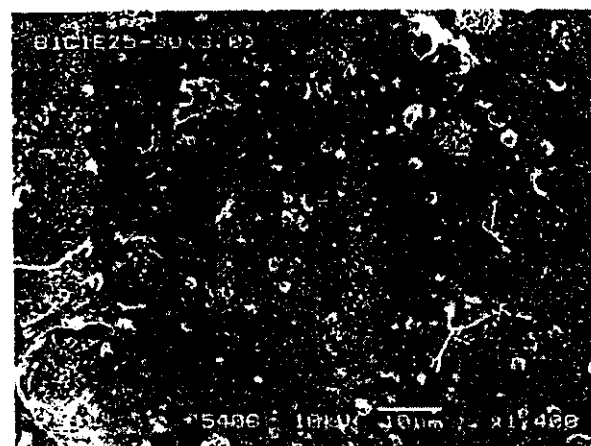
(c)
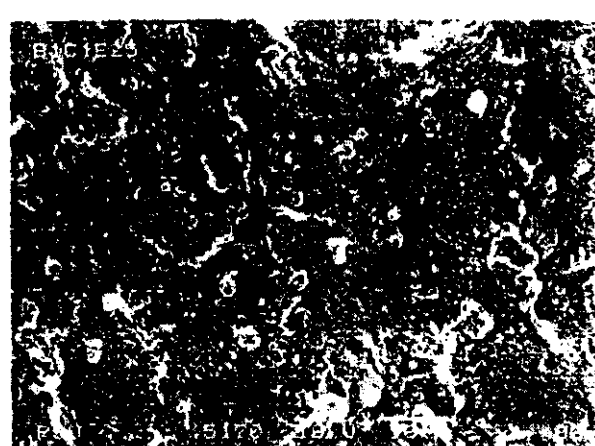
(d)

Figure 11   SEM micrographs of the blends (B5) containing 30% CSM, showing effect of ENR: (a) no homogenizer, (b) 3 phr Struktol (B1), (c) 3 phr ENR, (d) 5 phr ENR. Big particles of CSM showed only in (a) and (b). All photographs were recorded at the same magnification ($\times$ 1400). [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]
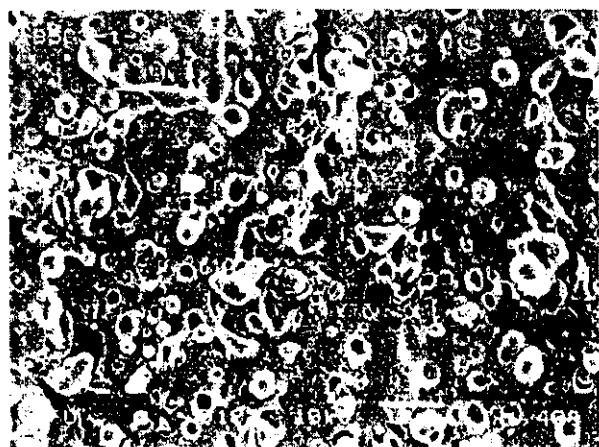
(a)

(b)

(c)

(d)

Figure 12   SEM micrographs of the blends (B4) containing 30% CSM, showing effect of ENR: (a) no homogenizer, (b) 3 phr Struktol, (c) 3 phr ENR. (d) Higher magnification of (c). Big particles of CSM disappeared with the presence of ENR. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

NR/CSM blend. Furthermore, Struktol® also does not affect the morphology of the blends, which will be explained later. As a result, we looked for another polymer to act as a compatibilizer in the NR/CSM blend.

Effect of ENR on blend compatibility

As Stuktol®60NS is not suitable for the present system, we then utilized epoxidized natural rubber (ENR) as a compatibilizer. It is established that *in situ* grafting reaction (crosslinking) between ENR and CSM has taken place in the ENR/CSM blend.[43] Miscibility of this self-vulcanizable rubber blend was investigated by DMTA, FTIR, and NMR techniques, and a single T_g (α transition temperature) was observed from the

CSM/ENR blend. A crosslink reaction between CSM and ENR in the blend was proposed and confirmed by the absence of SO_2 symmetric stretching at 1160 cm^{-1} and the presence of new bands at 1196 and 1142 cm^{-1}, which were due to the SO_2 symmetric stretching vibration in sulfonates [$R(RO)SO_2$]. The proposed mechanism of reaction between ENR and CSM by De et al.[43] is seen in Scheme 1.

In fact, the miscibility of CSM/ENR blends depended on the epoxy content and the blend ratio. For example, 50/50 and 75/25 blends of CSM and ENR with 50% epoxidation were immiscible, whereas the 25/75 blend was miscible.

Based on the above hypothesis, ENR with 25 and 50 mol % of epoxidation was added in the present blends. Based on the preliminary test, ENR with 50
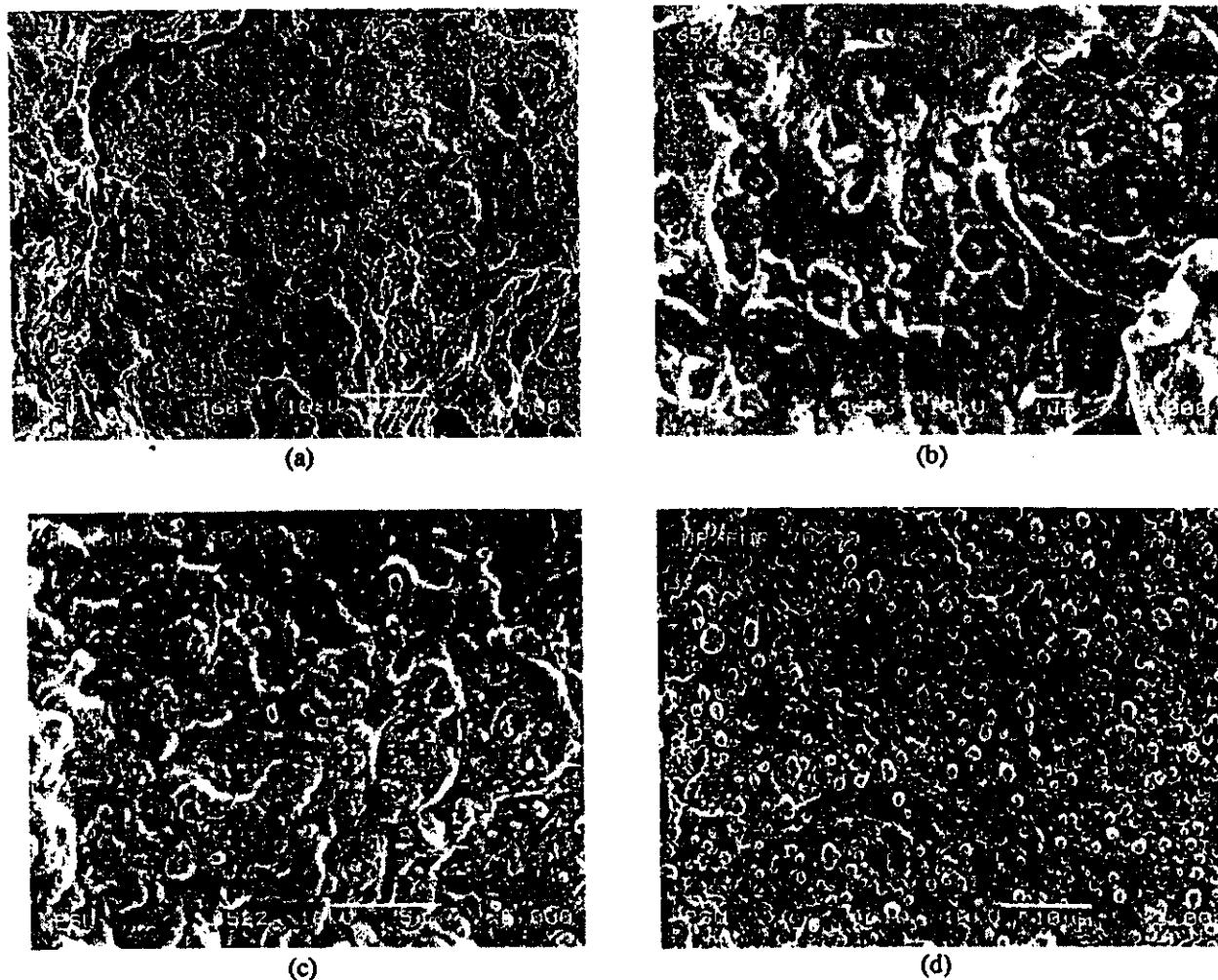
Figure 13 SEM micrographs of the NR/ENR/CSM blends (B4): (a) and (b) the 65/5/30 blend at low and high magnification (× 2000 and × 10,000, respectively); (c) the 60/10/30 blend (× 5000); (d) NR/ENR (70/30) blend (× 2000). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

mol % of epoxidation (5 phr) did not improve tensile properties of the blends; as a result, ENR with 25 mol % of epoxidation was chosen. The 70/30 blend of B4 was selected to investigate the effect of ENR. Tensile properties of the ternary blends are tabulated in Table V. A small amount of ENR (5–10 phr) increases tensile strength and slightly decreases elongation at break of the NR/CSM blends, while higher ENR content decreases tensile properties. The presence of ENR in the blends also increases thermal aging resistance of the blends, as shown in Table VI. In contrast, the addition of ENR does not improve tear strength of the blends, as shown in Table VII.

In general, the addition of a compatibilizer should add less as we get the optimal property. Based on the above results, 5 phr of ENR shows more efficiency in tensile properties than 10 phr. For that reason, we compared tensile properties of the 70/30 blends of all

formulations by adding a slight amount (1, 3, and 5 phr) of Stuktol® and ENR. Figures 9(a–d) represent tensile strength and elongation at break of the 70/30 blends of B2, B3, B4, and B5, respectively. Each Figure displays the value of tensile strength of virgin NR and CSM as well. In Figure 9(d), B5 with 3 phr Stuktol® was B1. Stuktol® slightly increases tensile strength in B3 and B4 for 3%, and decreases tensile strength of B5 and B2 for 12 and 5%, respectively. In contrast, ENR increases tensile strength of all the blends in the range of 22–52%. Noticeably, only 1–3 phr of ENR is sufficient to increase compatibility of the NR/CSM blends. ENR not only increases tensile strength but also increases ozone resistance of the blends, as shown in Figure 10 and described in Table III.

Compatibility of the NR/CSM blends is successfully improved by adding a small amount of ENR. The compatible NR/CSM blends show increases in tensile
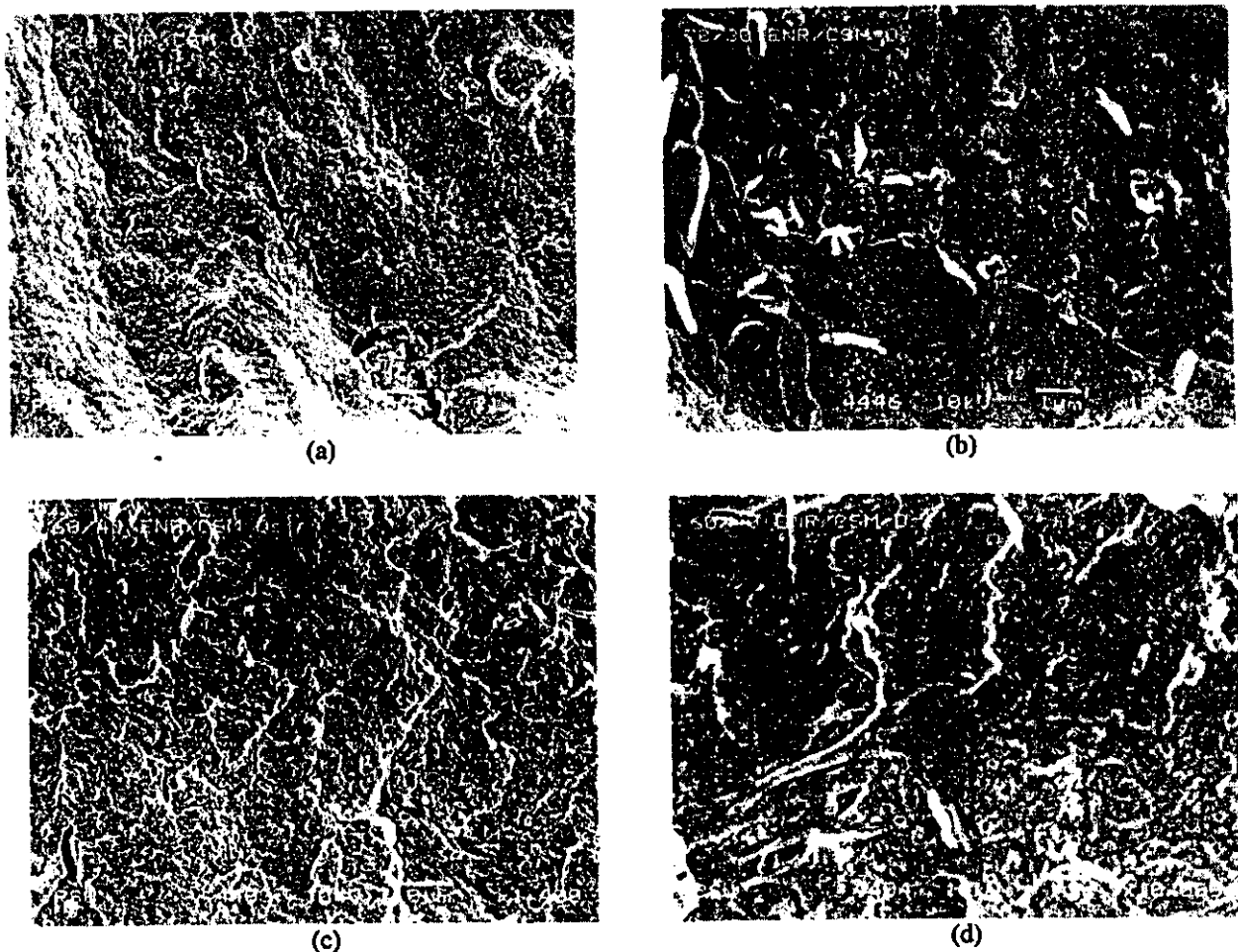
Figure 14 SEM micrographs of ENR/CSM blends showing partial miscibility: (a) and (b) the 70/30 blend at low and high magnification (× 1400 and × 10,000, respectively); (c) and (d) the 60/40 blend at low and high magnification (× 1400 and × 10,000, respectively). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

strength, aging, and ozone resistance. We believe that this is due to the miscibility between ENR and CSM causing an *in situ* grafting reaction between ENR and CSM on the surface of CSM particles. The graft copolymer reduces interfacial tension between CSM particles and the NR matrix, and ENR acts as the load transferring between NR and CSM. Investigation of ENR-CSM miscibility is beyond the scope of this study since it is well established by De et al.[43]

Blend characterization

Morphological aspects

The NR-rich blends show spherical particles of CSM dispersed phase. Average particle diameters of the CSM phase in the blends are listed in Table VIII, and SEM micrographs of the blends are shown in Figures 11–14. The average particle size of all blends falls in the range of 1.55–2.45 μm. There is no significant

change in particle size as CSM content increases for all formulations, and no significant difference in particle size among all formulations is observed. SEM micrographs of the 70/30 blends of B5 and B4 are displayed in Figures 11(a) and 12(a), respectively. The addition of Struktol® has no influence on blend morphology, as shown in Figures 11(b) and 12(b) for blends B5 and B4, respectively. On the other hand, ENR considerably changes blend morphology by decreasing CSM diameter dramatically. Figures 11(c,d) and 12(c,d) represent blends B5 and B4 containing ENR. There are no big CSM particles (> 1 μm) showing in these Figures. The enlarged surface of Figure 12(c) is shown in Figure 12(d) (× 10,000). The NR/ENR/CSM blends show submicron size of CSM. Figure 13(a,b) represent the 65/5/30 blend. At low magnification (× 2000), we could not see CSM particles as we observe in Figures 11(a,b) and 12(a,b). Increasing the magnification up to × 10,000, particle size of CSM less than 1 μm is ob-
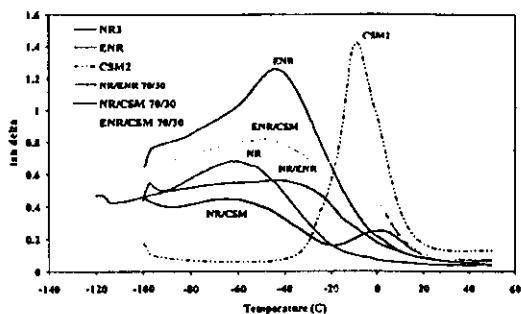
Figure 15 DMTA spectra of rubbers and rubber blends (B4).

served, as shown in Figure 13(b). The submicron size of CSM also is revealed in the 60/10/30 blends, as shown in Figure 13(c). To verify the miscibility of the NR/ENR and ENR/CSM blends, we investigated the morphology of these blends. Figure 13(d) shows ENR particles with average diameter of 1 μm in the NR/ENR blend, indicating immiscibility. As predicted, the ENR/CSM blend shows partial miscibility. CSM particles become smaller than 0.1 μm and no distinct surface boundary of CSM particles is observed, represented in Figures 14(a–d). SEM micrographs substantiate the assumption that ENR acts as the compatibilizer of the NR/CSM blends.

Transition temperature

The tan δ peak of NR, ENR, CSM, and their blends are shown in Figure 15 and tabulated in Table IX. CSM shows a shoulder at 0.13°C. The 70/30 blend of B4 in Figure 15 exhibits two tan δ peaks, which belong to NR and CSM. Although the NR/ENR blend shows multiphase morphology by using the SEM technique, shown in Figure 13(d), the DMTA spectrum of this
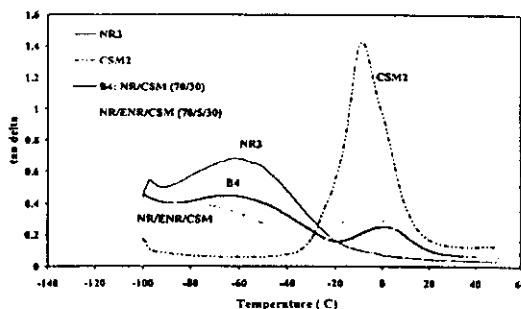

Figure 16 DMTA spectra of rubbers and rubber blends (B4) showing effect of ENR by reducing α transition temperature of CSM in the blends.

blend becomes a very broad, single peak. A strong shift in tan δ peak of CSM in the ENR/CSM blend is obtained. Incorporation of ENR into the NR/CSM blends lowers the tan δ peak of CSM in the blends, shown in Figures 16–18 and Table IX. DMTA results also confirm that compatibility of the NR/CSM blends increases by the addition of ENR.

CONCLUSIONS

1. Compatible blends of NR/CSM blends without the compatibilizer could be obtained by opti-
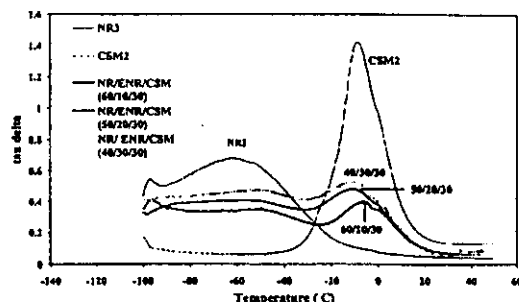

Figure 17 DMTA spectra of ternary blends (B4). More ENR content resulted in more temperature shift in the α transition temperature of CSM in the blends.

TABLE IX
α Transition Temperature (T$_g$) of the Blends

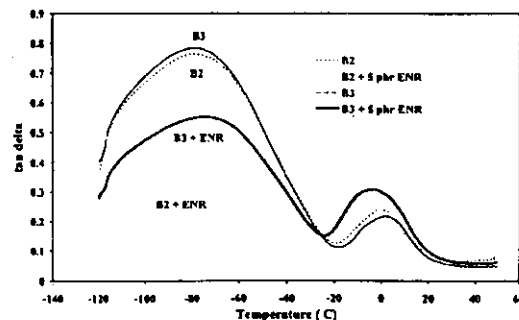| Rubber	Blend composition	T$_g$ of NR (°C)	T$_g$ of CSM (°C)
NR3	—	−62.8	—
CSM2	—	—	−8.5
ENR25	—	−44.3	—
B2: NR/CSM	70/30	80.1	0.2
B2: NR/ENR/CSM	70/5/30	−89.0	−7.6
B3: NR/CSM	70/30	−79.5	2.83
B3: NR/ENR/CSM	70/5/30	−74.1	−4.1
B4: NR/CSM	70/30	−63.0	1.9
B4: NR/ENR/CSM	70/5/30	−80.0	−9.1
	65/5/30	77.8	−7.5
	60/10/30	−49.6	−7.2
	50/20/30	−56.8	−11.0
	40/30/30	−51.2	−11.3
ENR/CSM	70/30	−49.1	−15.6

Figure 18 DMTA spectra of B2 and B3 blends (70/30 NR/CSM). Addition of 5 phr ENR decreased the α transition temperature of CSM in the blends.

mizing blend, formulation and blend ratio, regarding the selected properties. In the present study, synergistic properties of NR-rich blends depend on blend formulation. Oil and ozone resistance of the blends increase with increasing CSM content.

2. ENR with 25 mol % of epoxidation acts as a compatibilizer of the NR/CSM blends by increasing tensile properties, aging, and ozone resistance.

3. SEM and DMTA techniques verify that ENR interacts with CSM in the blends, which may cause a reduction in interfacial tension between NR and CSM, resulting in an increase in compatibility of the NR/CSM blends.

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