

Curing Characteristics, Morphology, Thermal Stability, Mechanical Properties, and Irradiation Resistance of Methyl ethylsilicone/Methylphenylsilicone Rubber Blends

Depeng Ma,¹ Jinglin Tan,¹ Yuling Li,¹ Chao Bian,¹ Guogang Wang,² Shengyu Feng¹

¹Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Ji'nan 250100, People's Republic of China

²Beijing Guodian Futong Science and Technology Development Company, Limited, Beijing 100070, People's Republic of China
Correspondence to: S. Feng (E-mail: fsy@sdu.edu.cn)

ABSTRACT: Methyl ethylsilicone rubber (MESR)/methylphenylsilicone rubber (MPSR) blends were cured with 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane. The curing characteristics, morphology, thermal behaviors, mechanical properties at different temperatures, radiation resistance, and thermal aging resistance of the MESR/MPSR blends were investigated. The results show that a high MPSR content could decrease the optimum curing time and improve the scorch safety. Dynamic mechanical analysis revealed that the glass-transition temperature of the blends increased slightly with the addition of MPSR. Scanning electron microscopy showed that MESR and MPSR had good compatibility in the blends. Thermogravimetric analysis indicated that the thermal stability of the blends increased with increasing quantity of MPSR. The blends had excellent mechanical properties at low temperatures. However, these properties were significantly reduced when the temperature was increased. Moreover, changes in the mechanical properties decreased with increasing MPSR content at high temperatures, especially at temperatures higher than 100°C. In addition, the radiation resistance and thermal aging resistance of the blends increased with increasing MPSR content. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40529.

KEYWORDS: blends; properties and characterization; rubber; thermal properties

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INTRODUCTION

Silicone rubbers have been widely used in various fields because of their unique properties, such as weather resistance, high- and low-temperature resistance, good electrical insulation properties, and chemical resistance.^{1–6} Methyl ethylsilicone rubber (MESR) has been widely applied in aircraft, space transport, and other similar industries, especially those involved in low-temperature environments, because there was no crystallization and a glass-transition temperature (T_g) as low as -120°C .^{7,8} The demand for materials with desirable comprehensive performances has recently increased. However, the application of MESR in some fields, such as electronics and machinery, especially in high-temperature regions, is limited because of the poor thermal stability of its ethyl groups. Hence, the development of high-performance MESR-base materials is essential.

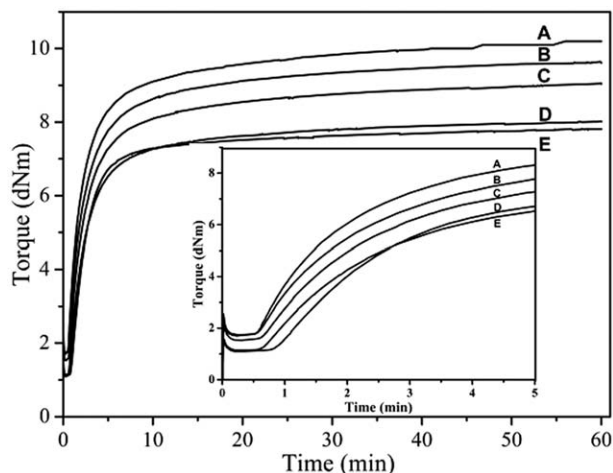
Two approaches are currently being used in the preparation of high-performance MESRs. The first approach is the synthesis of MESR-based copolymers. Liu et al.⁹ synthesized and investigated

a series of MESR-based polymers, including poly(dimethylsiloxane-*co*-diethylsiloxane-*co*-diphenylsiloxane) and poly(dimethylsiloxane-*co*-diethylsiloxane-*co*-methylphenylsiloxane). However, random copolymers with high molecular weights are difficult to obtain because comonomers have different reactivities. The second approach is the blending of MESR with other materials to achieve the desired properties.¹⁰ Compared with copolymerization, blending is an easier and more economical method for obtaining high-performance MESR products.^{11–14} To date, several materials have already been blended with MESRs. Metal oxides¹⁵ and antioxidants¹⁶ can improve the thermal stability. However, poor compatibility usually significantly reduces the mechanical properties of materials. Silicon resins¹⁷ can improve the heat resistance of MESR but increase the T_g of MESR.

Methylphenylsilicone rubber (MPSR) exhibits superior thermal stability and irradiation resistance.^{18–20} Some polymers have been blended with MPSR to produce high-performance materials. Zulfiqar and Ahmad²¹ prepared and studied blends of poly(vinyl acetate) (PVAC)/MPSR and found that the

Table I. Formulations of the MESR/MPSR Blends

	Sample				
	A	B	C	D	E
MESR (phr)	100	70	50	30	0
MPSR (phr)	0	30	50	70	100
TS-530 (phr)	50	50	50	50	50
DMPH (phr)	0.8	0.8	0.8	0.8	0.8

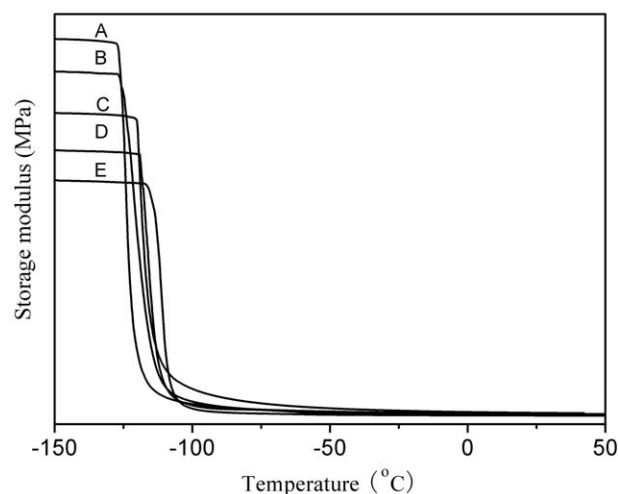
**Figure 1.** Rheograph curves of the MESR/MPSR blends at 160°C: (A) 0-, (B) 30-, (C) 50-, (D) 70-, and (E) 100-phr MPSR.

degradation temperature of these blends increased with increasing MPSR concentration. Chou and Yang²² prepared methylsilicone rubber/MPSR blends and found that the thermal stability of these blends dramatically improved with increasing MPSR content. Chien et al.²³ studied the irradiation resistance of methylsilicone rubber/MPSR and obtained satisfactory results.

MESR/MPSR blends have excellent potential because of the outstanding capacity of MPSR to overcome the drawbacks of MESR. In addition, MESR and MPSR were expected to have good compatibility because both exhibit the same main-chain structure. However, investigations that have focused on the blends of MESR and MPSR have been rare. In this article, the MESR/MPSR blends were prepared by the combination of

Table II. Curing Characteristics of the MESR/MPSR Blends at 160°C

Blend sample	M_H (dNm)	ts_2 (min)	Optimum t_{90} (min)
A	10.20	1.01	13.83
B	9.64	1.14	13.10
C	9.05	1.28	13.18
D	8.02	1.39	11.15
E	7.82	1.58	7.73

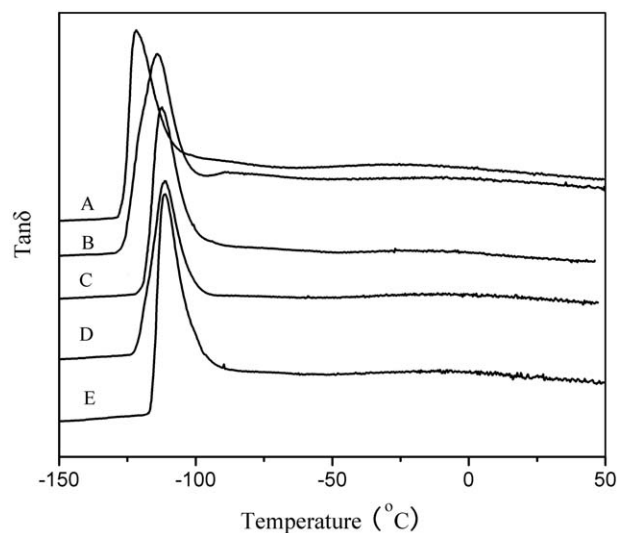
**Figure 2.** E' curves of the MESR/MPSR blends: (A) 0-, (B) 30-, (C) 50-, (D) 70-, and (E) 100-phr MPSR.

MESR and MPSR with 2,5-dimethyl-2,5-di(*tert*-butylperoxy)-hexane (DMPH) as a vulcanizing agent. The effects of MPSR on the curing characteristics, morphology, thermal performance, mechanical properties at different temperatures, and irradiation and thermal aging resistance of the blends were investigated. The results of this study proved the MESR/MPSR blends to be high-performance materials.

EXPERIMENTAL

Materials

MESR was prepared via the anionic equilibrium polymerization of hexaethylcyclotrisiloxane and octamethylcyclotetrasiloxane.²⁴ MPSR was purchased from Shanghai Resin Factory Co., Ltd. (China). DMPH was obtained from Akzo Nobel Peroxide (Tianjin, China). Fumed silica (TS-530) was supplied by Cabot and had a surface area of 220m²/g.

**Figure 3.** $\tan \delta$ curves of the MESR/MPSR blends: (A) 0-, (B) 30-, (C) 50-, (D) 70-, and (E) 100-phr MPSR.

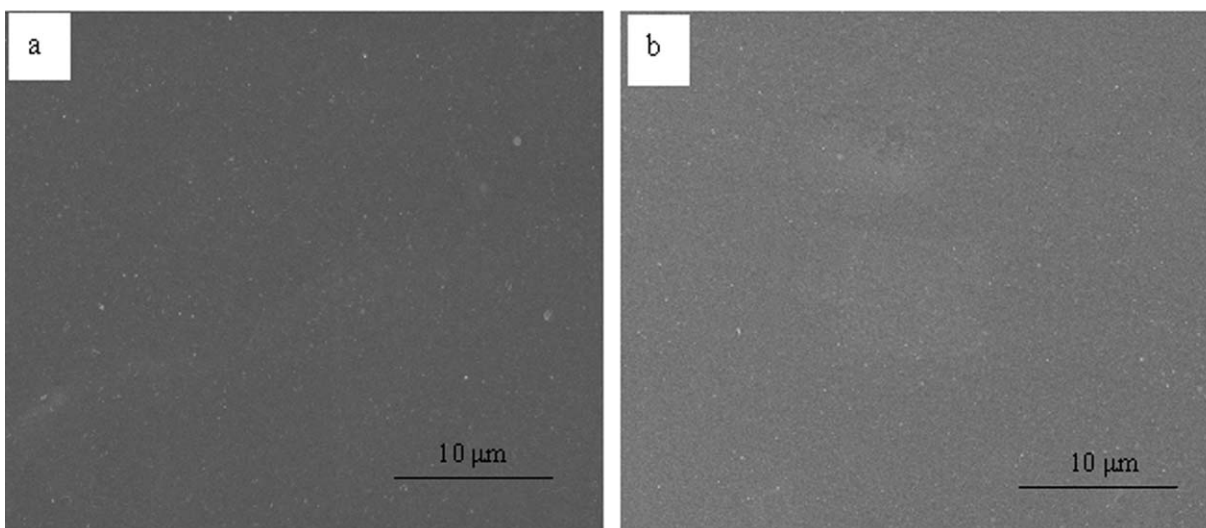


Figure 4. SEM micrographs of the MESR/MPSR blends: (a) 30- and (b) 50-phr MPSR.

Preparation of the MESR/MPSR Blends

The MESR/MPSR blends with five different combinations were prepared on a two-roll mixing mill. The formulations of the blends are listed in Table I. The curing characteristics were determined with an MDR-2000 Monsanto moving-disk rheometer (Alpha Technologies). The blends were compression-molded at 160°C at a pressure of 30 tons on the basis of the respective curing times (t_{90}); this was determined with an MDR 2000. Postcuring was conducted at 170°C for 2 h in an air oven.

Thermal Analysis

The low-temperature performances of the blends were evaluated with an SDTA 861e dynamic mechanical analyzer (DMA; Mettler) in shearing mode. The specimens were analyzed at a frequency of 1 Hz in a temperature range from -150 to 50°C at a heating rate of 3°C/min.

Thermogravimetric analysis (TGA) was performed on a TGA/DSC 1 thermal analyzer (Mettler). Specimens weighing 5 mg were heated in an Al₂O₃ crucible in a nitrogen atmosphere from 50 to 750°C at a heating rate of 10°C/min.

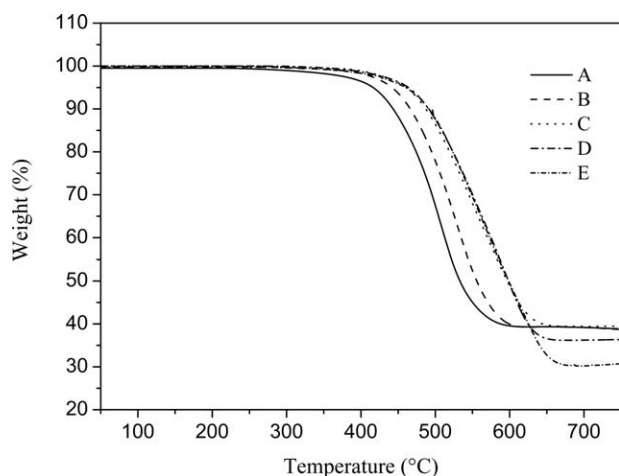


Figure 5. TGA curves of the MESR/MPSR blends in a nitrogen atmosphere: (A) 0-, (B) 30-, (C) 50-, (D) 70-, and (E) 100-phr MPSR.

Morphological Analysis

The morphology of the blends was examined with an S-4800 scanning electron microscope (Hitachi). The fracture surfaces of the specimens were used for morphological observation after they were coated with a thin layer of gold.

Mechanical Properties

The tensile strength and elongation at break of the blends were measured with an XLD-A universal testing machine (Second Experimental Machine Factory) based on ASTM D 412 at $25 \pm 2^\circ\text{C}$. The tear strength was conducted according to ASTM D 624 in the same instrument. The hardness of the blends was measured with a Shore A meter following ASTM D 2240.

Radiation Resistance

The specimens were exposed to γ radiation of a Co-60 source at a dose rate of 3 kGy/h. The total radiation dose was 500 kGy. All radiations were done at room temperature. Changes in the mechanical properties of the specimens before and after radiation were used to determine the radiation resistance.

Thermal Aging Resistance

The thermal aging resistance of the MESR/MPSR blends were tested based on ASTM D 573-04. The specimens were placed in an oven with an air-circulating system at a temperature of 150°C for 72 h and at 200°C for 24 h. The aged specimens

Table III. TGA Results of the MESR/MPSR Blends in a Nitrogen Atmosphere

Sample	T_{onset} (°C) ^a	T_{max} (°C)	Residual yield (%)
A	420	508	38.8
B	439	521	38.7
C	458	548	39.1
D	464	575	36.1
E	460	554	30.9

^aTemperature for 5% weight loss.

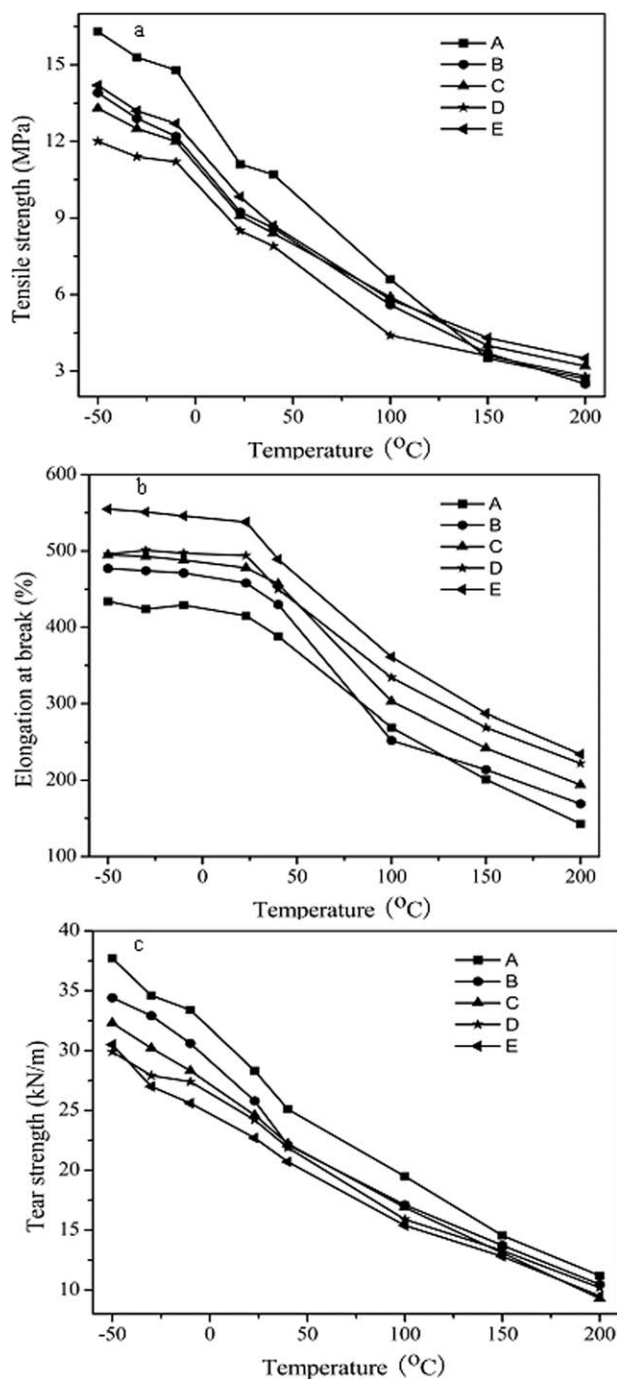


Figure 6. Mechanical properties of the MESR/MPSR blends at different temperatures: (A) 0-, (B) 30-, (C) 50-, (D) 70-, and (E) 100-phr MPSR.

were then evaluated for changes in the mechanical properties. Similar to the measurement of radiation resistance, the changes in the mechanical properties of the specimens before and after thermal aging were used to determine the aging resistance.

RESULTS AND DISCUSSION

Figure 1 shows the rheographs of the MESR/MPSR blends at 160°C. The rheographs of all of the blends initially decreased but subsequently increased. The initial decrease in the torque was

due to the softening of the matrix. The torque then increased because of crosslink formation. Table II lists the rheometric characteristics of the blends under investigation. The maximum torque (M_H) was related to the crosslinking density. M_H of the blends decreased with increasing MPSR content because the

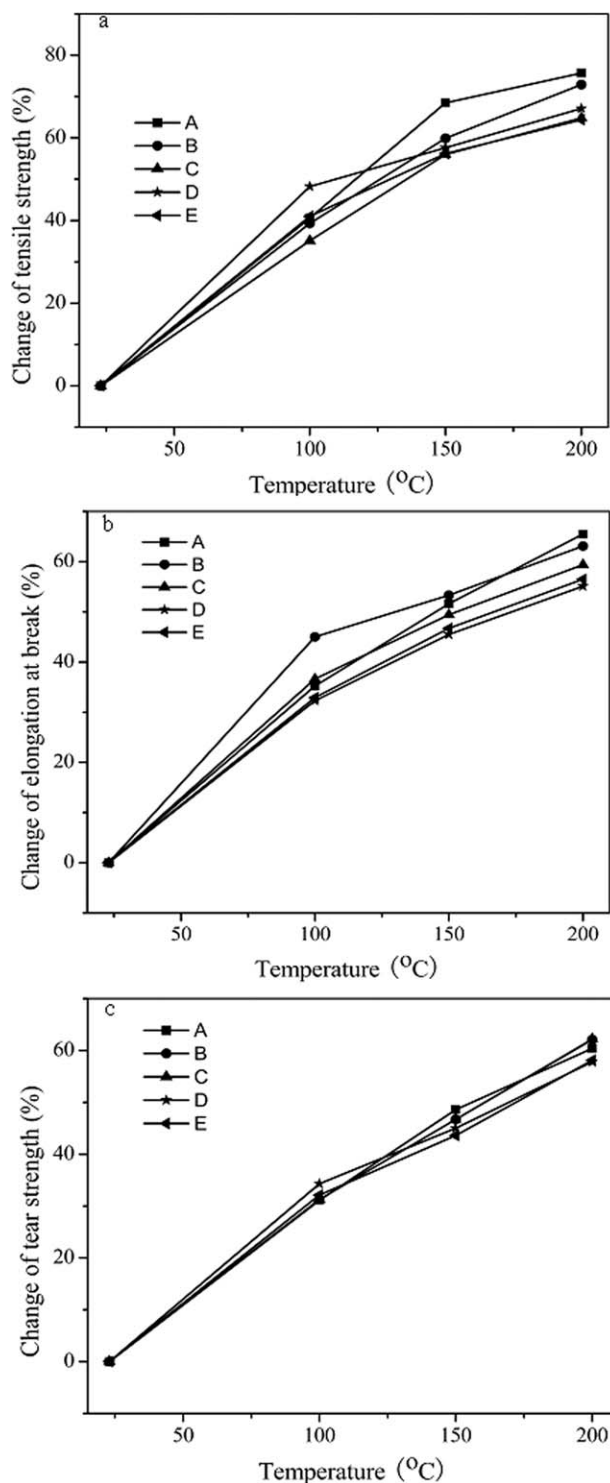


Figure 7. Changes in the mechanical properties of the MESR/MPSR blends at more than 100°C: (A) 0-, (B) 30-, (C) 50-, (D) 70-, and (E) 100-phr MPSR.

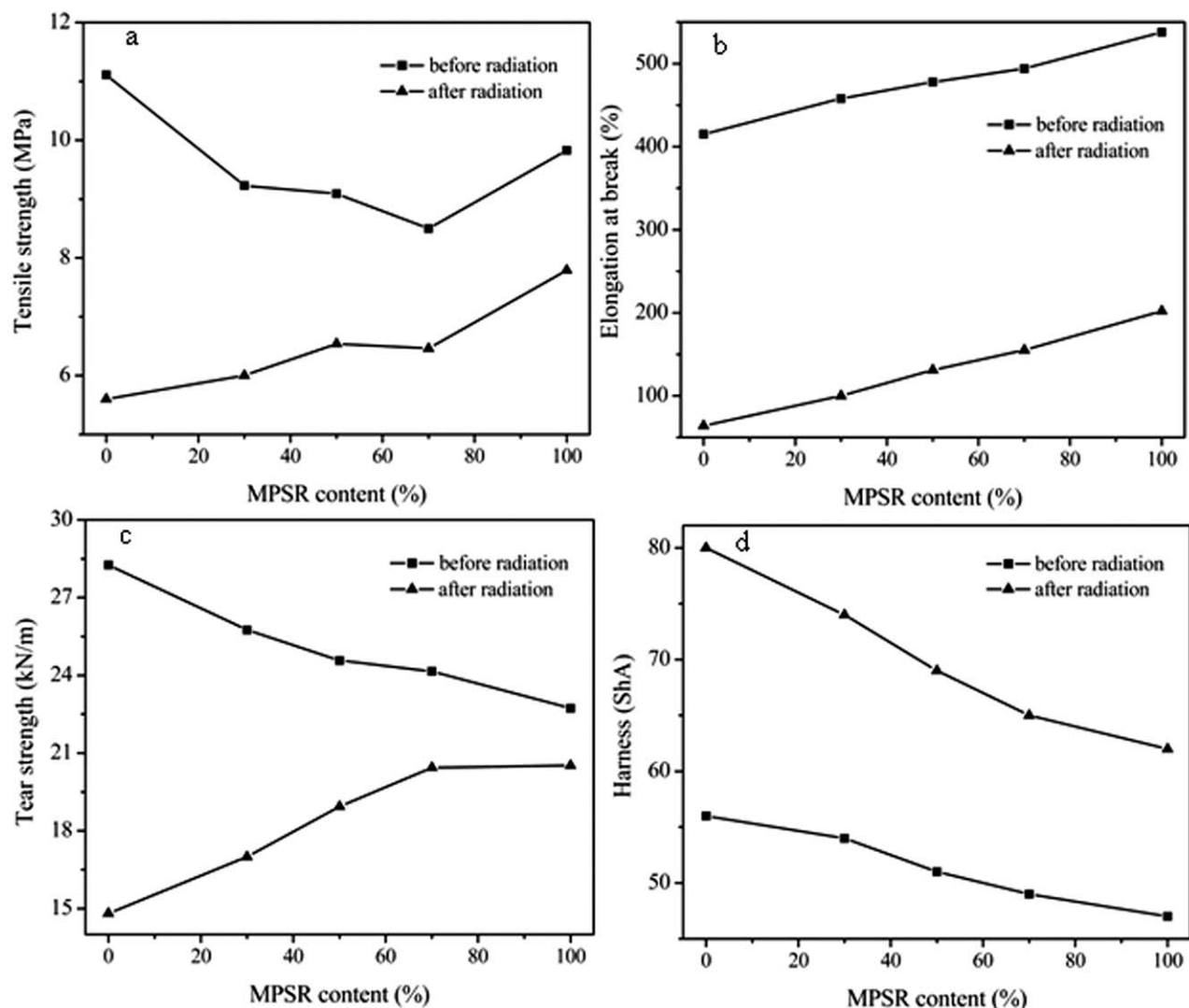


Figure 8. Mechanical properties of the MESR/MPSR blends before and after irradiation.

phenyl substituent could apparently stabilize the adjacent free radicals.^{25,26} t_{90} decreased with increasing MPSR percentage in the blends. The scorch time (t_{s2}) was defined as the time elapsed for the minimum torque value to increase by two units, and this value reflected the premature vulcanization of the materials.²⁷ Thus, t_{s2} increased with increasing MPSR content; this indicated that the scorch safety of blends also increased.

DMA measurements were used to study the low-temperature performance of the MESR/MPSR blends. The storage modulus (E') of the blends is shown in Figure 2. The E' curve of the blends had only one thermal transition. This result indicated that all of the blends were not crystalline. Moreover, E' of the pure MESR sharply decreased at approximately -125°C because of the glass transition. The temperature at which E' dropped sharply shifted to a higher temperature with the addition of MPSR. This result suggested that the incorporation of MPSR increased the T_g of MESR in the blend.

The loss factor ($\tan \delta$) of the blends is shown in Figure 3. All of the blends exhibited only one peak (glass transition); this

showed the significant compatibility and miscibility of MESR and MPSR. In addition, the T_g values of the blends decreased with increasing MESR content. This result was attributed to the high low-temperature flexibility of MESR and the crosslinking between the MESR and MPSR phases.

Scanning electron microscopy (SEM) micrographs of the fracture surface of blends B and C are shown in Figure 4. As shown in Figure 4(a), the dispersion of MESR and MPSR was uniform, and the rubbers had microcosmic compatibility. Similar results are depicted in Figure 4(b). These results proved the good compatibility of MESR and MPSR in blends. The homogeneous structure of the blends agreed with the results obtained from the DMA measurements.

The TGA results of the MESR/MPSR blends in nitrogen are shown in Figure 5. The important characteristic data are listed in Table III. The temperatures at 5% mass loss (T_{onset}) and the peak decomposition temperature (T_{max}) of the blends shifted to higher temperatures with increasing MPSR content. This result indicates that the thermal stability of MESR was improved.

Table IV. Mechanical Properties of the MESR/MPSR Blends Before and After Thermal Aging

	Sample				
	A	B	C	D	E
Tensile strength (MPa)	11.11	9.23	9.09	8.5	9.83
Tear strength (kN/m)	28.26	25.75	24.57	24.15	22.73
Elongation at break (%)	415	458	478	494	538
Hardness (Shore A)	56	54	51	49	47
150°C for 72 h					
Tensile strength (MPa)	10.79	8.99	8.93	8.39	9.73
Tear strength (kN/m)	27.24	24.97	23.95	23.67	22.43
Elongation at break (%)	353	402	431	463	517
Hardness (Shore A)	62	59	54	52	50
200°C for 24 h					
Tensile strength (MPa)		3.11	7.52	7.57	9.04
Tear strength (kN/m)		4.52	21.35	21.98	21.33
Elongation at break (%)		23	301	377	416
Hardness (Shore A)		82	64	58	55

Moreover, the decomposition residual weights of the blends were considerably different. The residual weights of samples A, B, C, and D were considerably higher than the mass fraction of their silica content (33.3%) in the sample. However, the residual ratio of MPSR (30.9%) was lower than the mass fraction of silica (33.3%) in the sample. These results could be explained by the crosslinking induced by the presence of ethyl groups in MESR. During the curing of blends containing MESR, the ethyl groups could have been attached to the vinyl double groups through the inducing effect of the free-radical produced in the peroxide and improved the crosslinking density of the blends.^{28,29} In this case, the cyclic depolymerization of blends was very difficult. However, this crosslinking would not be induced in MPSR because of the absence of ethyl groups in the chains.²¹

The mechanical properties of the blends at different temperatures are presented in Figure 6. The tensile strength of the blends decreased with increasing temperature. The tensile strength of the blends was principally affected by the volume contraction effect under low temperatures. At high temperatures, polymer chain segment motion was accelerated because of thermal effects and volumetric expansion. Thus, the weak interaction between silica and polysiloxane decreased the tensile strength of the blends. Similar changes in the tear strength and the elongation at break were observed.

The mechanical properties change values of the blends at 100°C or greater are shown in Figure 7. Less change in the mechanical properties of the blends were observed when the MPSR content was higher and when the temperature exceeded 100°C. This effect was attributed to the fact that the conjugate structure of phenyl side groups in MPSR could absorb thermal energy to improve the heat resistance of the blends.²²

The mechanical properties of the MESR/MPSR blends before and after irradiation are presented in Figure 8, and the results

show that the hardness of the blends increased after radiation relative to that before radiation. However, the tensile strength, tear strength, and elongation at break of the blends decreased after radiation. The increased hardness indicated that crosslinking occurred during γ -ray radiation.³⁰ The reduction in the tensile strength, tear strength, and elongation at break indicated that overcrosslinking and degradation occurred. This effect could have been due to the molecular structure of the polymer being damaged by energetic γ rays.³¹ The results show that the crosslinking reaction occurred with the degradation reaction during γ -ray radiation.³²

Another phenomenon observed was the increase in the irradiation resistance of the blends with increasing MPSR content. This increased stability was due to the delocalized π -electron structure of the phenyl side groups, which could absorb large amounts of energy before the bond could be broken during radiation.³³ Thus, MPSR had excellent radiation resistance, and the blends exhibited improved radiation resistance because of the addition of MPSR. When the MPSR content was increased, this resulted in improved radiation resistance in the blends.

During thermal aging, main-chain scission, additional crosslink formation, and crosslink breakage of the polymer are known to take place.³⁴ The thermal aging properties of the MESR/MPSR blends are tabulated in Table IV. The increase in the MPSR content resulted in an increase in the mechanical properties of the blends. Regardless of the aging conditions for the specimens, a high MPSR content in the blend resulted in the improved mechanical properties of the blends. This result indicated that MPSR had a better thermal aging resistance, whereas that of MESR was worse. In addition, all of the mechanical properties of the blends, including the tensile strength, tear strength, elongation at break, and hardness, had no considerable variation at 150°C for 72 h. This result showed that the blends had a good

thermal resistance at 150°C. However, a change in the mechanical properties at 200°C for 24 h was higher than that at 150°C for 72 h. This result was attributed to the degradation or cracking of the blend chains and indicated that the degradation or cracking of the blend at 200°C for 24 h was severe.

CONCLUSIONS

In this study, high-performance MESR/MPSR blends were prepared. The curing characteristics, morphology, thermal behavior, mechanical properties at different temperatures, radiation resistance, and thermal aging resistance of the blends were studied. The results show that the optimum t_{90} decreased with increasing MPSR content. However, a high MPSR content increased t_{52} and thereby improved the scorch safety of the blends. The DMA results indicate that the blends had only one glass transition and that T_g slightly increased with the addition of MPSR. The TGA results show that the thermal stability of the blends improved with the addition of MPSR. The SEM micrographs showed that MESR had good compatibility with MPSR. The blends showed excellent mechanical properties at low temperatures because of a volume contraction effect. However, these mechanical properties decreased significantly with increasing temperature. In addition, high MPSR contents lessened the changes in the properties of the blends at temperatures greater than 100°C. The radiation study showed that the hardness of the blends increased after γ -ray radiation compared with that before radiation. However, the tensile strength, tear strength, and elongation at break all decreased. The changes in the blend properties after radiation were due to the occurrence of cross-linking and degradation reactions. However, a high MPSR content resulted in less drastic changes in the blend properties. The result of thermal aging experiments showed that the thermal resistance of the blends increased with increasing MPSR content.

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