

# Formulation and Curing Characteristics of EPDM/NR and EPDM/SBR Polyblends Used in Metallic Surfaces Rubber Lining

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**ABSTRACT:** In this work, a new elastomeric liner was introduced to protect the metal surfaces of storage tanks against corroding materials in petrochemical industries. This new liner was prepared on the basis of EPDM/NR and EPDM/SBR compounds. The elastomeric compounds were cured by using super-heated water vapor at atmospheric pressure. To increase the rate of curing in these rubber samples, the optimum curing system contained 15 phr sulfur and 1.5 phr mercaptobenzothiazole, 1.5 phr zinc diethyl dithiocarbamate, and 1.8 phr tetramethylthiuram disulfide accelerators. Mechanical tests showed that ultimate tensile strength, elongation at break, and hardness of both polyblend samples were comparable to the SBR/NR blend, which is widely used in the rubber lining of metallic surfaces. In the next step, the chemical resistance of the

samples was measured by placing them in a 30 wt % HCl solution. The tensile strength, elongation at break, and weight loss of the samples were measured before and after immersion in HCl. Also, the chemical resistances for EPDM/NR, EPDM/SBR, and SBR/NR samples were qualitatively measured in caustic solution. The cracking, blistering, permeability, and adhesion of the rubber samples to steel surface were observed. Finally, the results showed that EPDM/SBR (70/30) polyblend can be a suitable substitute for conventionally used SBR/NR (50/50) for a successful rubber used to line metallic surfaces. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 849–854, 2009

**Key words:** rubber lining; adhesion; elastomers; mechanical properties; super-heated water vapor

## INTRODUCTION

Nowadays metal equipment is widely used in chemical industries such as gas scrubbers, valves, and chemical reservoir tanks. Considering environmental concerns, chemical leakages as a result of chemical attacks to the metallic surfaces is the main problem.<sup>1</sup> One of the most effective methods for the protection of metals against corrosion is to coat a thin layer of rubber onto the surface of the metallic equipment.<sup>2</sup> The chemical nature and mechanical properties of the rubber layer and the choice of a suitable adhesive are decisive factors for their useful lifetime.<sup>3–5</sup> Many researchers have studied the effect of the type and functionalization of rubbers to improve the interfacial adhesion between the rubber layer and the metallic surfaces, the evaluation of the process cost, and the application of different methods of rubber lining such as butt, lap, and skive joints.<sup>6–10</sup> However, in the rubber lining of metallic surfaces, usually the choice of a suitable curing system has gained little attention.

Metallic rubber lining based on SBR/NR polyblend formulations known as ebonite has attracted the interest of petrochemical industries because of its superior chemical and mechanical properties, ease of handling, and low cost. On the other hand, SBR/NR can not be cured by water vapor because of the formation of degraded and porous surfaces.<sup>11,12</sup> Also, hydrogen sulfide gas produced as a result of the vulcanization process promotes the degradation of rubber lining.<sup>13</sup>

The advantages of using a super-heated water vapor at atmospheric pressure curing system for rubber lining are minimum equipment requirements, in addition to open space working conditions, and minimum cure time requirements, compared with a curing system using an autoclave at high pressure and temperature.<sup>10</sup>

EPDM has high thermal resistance, suitable lifetime, and good atmospheric resistance. The main advantage in using EPDM in a rubber compound is its resistance against many chemicals. By controlling the extent of unsaturation in EPDM, it can be cured by a sulfur-curing system.<sup>14,15</sup>

In this work, NR and SBR were separately compounded with EPDM containing a high degree of unsaturated bonds. The main purpose of this work

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**TABLE I**  
Accelerators Used for the Curing System of the Samples

Accelerator	Density (g/cm <sup>3</sup> )	Melting point ( $T_m$ ) (°C)	Trade name
Zinc diethyl dithiocarbamate (ZDEC)	1.49	175	Vulkacit LDA
Mercaptobenzothiazole (MBT)	1.5	174	Vulkacit Mercapto
Tetramethylthiuram disulfide (TMTD)	1.4	146	Vulkacit Thiuram

was to obtain a rubber compound that can be cured with super-heated water vapor to achieve mechanical and chemical properties comparable to SBR/NR. By designing compound formulations based on EPDM/NR and EPDM/SBR, the best weight percentage compositions for desirable physical and mechanical properties were selected. Also, the possibility of using a curing system for these samples in open space and in situ assemblies was investigated to increase the rate of the rubber-lining process.

## MATERIALS AND METHODS

### Materials

EPDM (Esperene E-505) was obtained from Sumitomo [10 wt % of ethylidene norbornene,  $M_L$  (1 + 4) of 59 at 125°C]. SBR (grade 1502) was received from Arak Petrochemical (Iran) ( $M_L$  (1 + 4) of 52 at 100°C with styrene content of 23.5 wt %). NR (grade SMR20) was provided by Syarikat Chuan Lee Rubber SDN BHD (Malaysia). Carbon black (N 550) was purchased from Carbon (Iran) (average diameter of 47 nm, dibutyl phthalate adsorption number of 116–124 cm<sup>3</sup>/100 g). Sulfur as the curing agent was purchased from Taban Powder (Iran). The characteristics of the accelerators used are presented in Table I (Bayer, Germany). Chemosile (grade X6025) was used as a heat activated binding adhesive supplied by Henkel (Germany). The other rubber ingredients used were technical grade (Iran and Malaysia).

### Samples preparation

EPDM/NR, EPDM/SBR samples with weight ratios of 30/70, 40/60, 60/40, 70/30, and 80/20 (w/w) and a sample of SBR/NR (50/50) (w/w) were prepared. According to Table II, the mixing time for these samples was 20 min at 60°C on a two-roll mill with a nip gap of 2 mm and speed of the rolls of 1 : 1.4.

The cure time of the samples was selected according to ASTM D 2084 by using a rheometer 100 (Hyundai). The cure curves were obtained at 140°C for these samples.

The cure time of these samples with super-heated water vapor at 140°C was obtained from cure curves. Because SBR/NR samples cannot be cured by water vapor, a compression-molding process was used at 140°C and 40 bar.

### Properties measurements of the samples

Tensile properties of the samples were measured on an Instron model 4505 according to the ASTM D 412 method, with a cross-head speed of 100 mm/min. Standard dumbbell-shaped specimens were cut directly from molded sheets. An average of five specimens was tested for each determination. The shore A hardness was measured according to ASTM D 2240 by using a Zwick durometer hardness (Germany). For tensile and hardness test results, the average of at least five measurements with standard deviation less than 5% was reported.

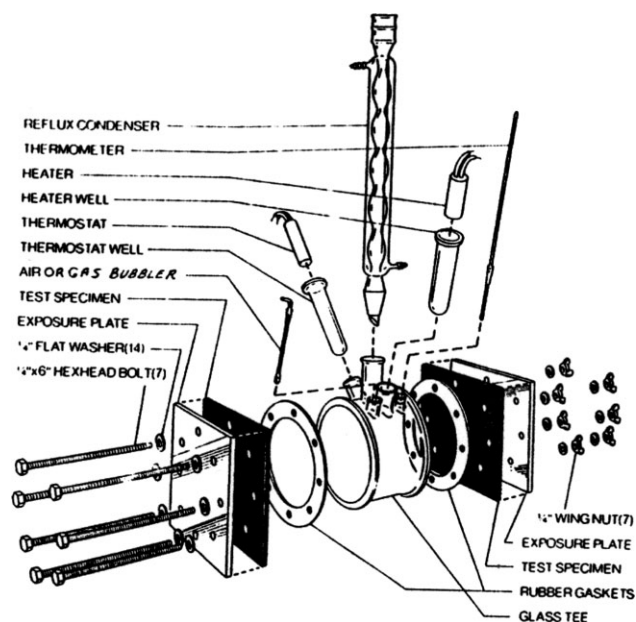
The effects of aggressive chemical environments on the characteristics of the samples were evaluated according to ASTM D 471. The aggressive chemical medium was hydrochloric acid (HCl) with a concentration of 30 wt % at 85°C for 166 h. The mechanical properties of these samples were then measured. The weight variations were measured for five specimens weighed with 1 mg accuracy and then left in the HCl solution. The samples were dried after submersion in acetone at room temperature. The weight variations of the samples were calculated as follows:

$$\text{Weight loss} = \Delta M = \frac{M_2 - M_1}{M_1} \times 100, \quad (1)$$

where  $M_1$  is the initial weight of the sample and  $M_2$  is the weight of the sample after being submerged in HCl. The variations of other properties such as ultimate tensile strength ( $\Delta$ UTS), elongation at break

**TABLE II**  
Recipes for SBR/NR, EPDM/NR, and EPDM/SBR Polyblends

Ingredient	Carbon black (N-550)	ZnO	Stearic acid	Sulfur	ZDEC	MBT
phr	70	5	2	20	1.5	4



**Figure 1** Typical disassembled test cell for chemical resistance testing of rubber tank lining.

( $\Delta E_b$ ), and hardness variations ( $\Delta$ shore A) were also calculated similar to eq. (1).

Qualitative evaluations of the chemical resistance of the rubber-lined metallic surfaces were investigated according to ASTM D 3491. Cured rubber samples with a dimension of  $203 \times 203 \times 3$  mm were placed on stainless steel surfaces using Chemosil X6025.<sup>16</sup> These samples were placed in the test cell for measurement of chemical resistance of rubber lining (Fig. 1). Two-thirds of the test cell space was filled with caustic solution. These samples were left in caustic solution for 2 months at 85°C. At the end of this period, the last samples were taken out and washed with water and dried. Finally, the samples were visually inspected for evidence of cracking and blistering. The adhesion of the rubber lining to the metallic surface and liquid or vapor permeation in the rubber lining were determined by cutting the test panel through the contact areas with the liquid, vapor, or liquid/vapor interface test media and the depth of penetration was measured by the use of a scale or a magnifying glass. Also, observations of the final inspection include an assessment of adhesion of the lining to the substrate and notation of any signs of substrate corrosive effects, such as metal rusting, metal darkening, or the present of oxides.

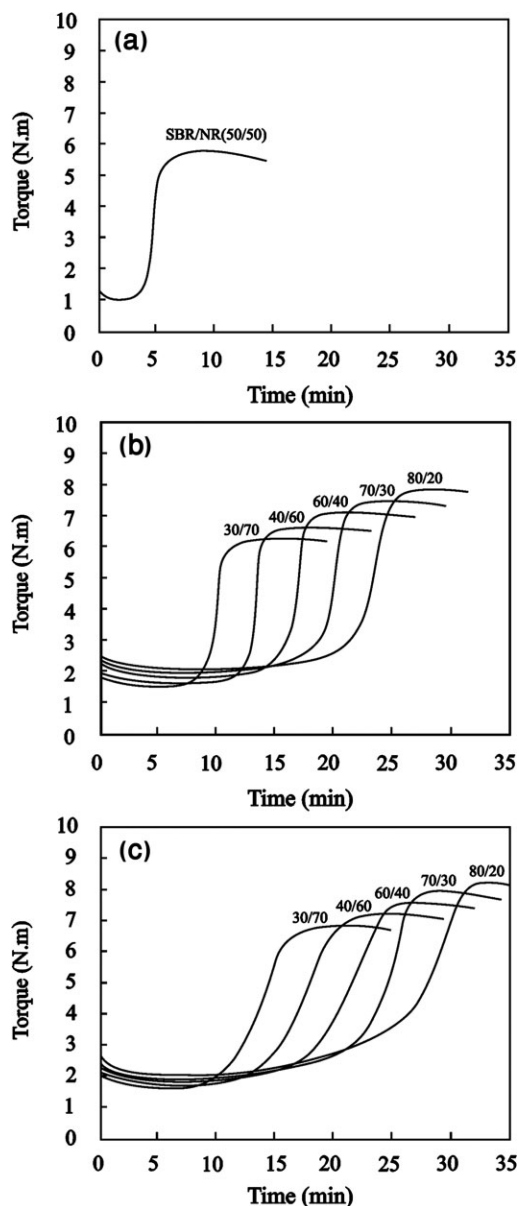
## RESULTS AND DISCUSSION

### Cure trend

Figure 2(a–c) shows cure curves at 140°C for polyblend samples SBR/NR (50/50), EPDM/NR, and

EPDM/SBR with ratios of 30/70, 40/60, 60/40, 70/30, and 80/20 (w/w). The selected cure system for these rubber compounds is given in Table II.

As can be seen in Figure 2(a), the optimum cure time ( $t_{90}$ ) for sample SBR/NR (50/50) was about 6 min. This value at  $t_{90}$  for SBR/NR was less than  $t_{90}$  EPDM/NR [Fig. 2(b)] and EPDM/SBR [Fig. 2(c)]. The reason for this difference is due to fewer numbers of unsaturated bonds in EPDM compared with SBR. Consequently, a higher rate of network formation between the double bonds and sulfur in SBR is observed. On the other hand, because the degree of unsaturation in SBR is less than NR, the values of  $t_{90}$  and scorch time ( $t_{s2}$ ) for EPDM/NR relative to



**Figure 2** Cure curves for (a) SBR/NR, (b) EPDM/NR, and (c) EPDM/SBR before modification in the curing system.

**TABLE III**  
**Mechanical Properties of the Samples Before and After Immersion in HCl Solution**

Sample	Hardness (shore A)	Ultimate tensile strength (UTS) (MPa)	Elongation at break ( $E_b$ ) (%)	Weight loss ( $\Delta M$ ) (%)	$\Delta UTS$ (%) <sup>a</sup>	$\Delta E_b$ (%)	$\Delta$ shore A (%) <sup>a</sup>
EPDM/NR (30/70)	93.5	8.7	125	27.4	-52.5	30	-3
EPDM/NR (40/60)	95	9.1	115	24	-45.3	12	-2
EPDM/NR (60/40)	97	9.4	84	21.8	-38.4	5	-2
EPDM/NR (70/30)	97.2	11.8	71	19.2	-25	8	-2
EPDM/NR (80/20)	98	10.9	55	18.5	-20.1	4	-1
EPDM/SBR (30/70)	95.5	8.8	98	25.5	-55.7	22	-5
EPDM/SBR (40/60)	97	10.1	65	23	-48.4	18	-4
EPDM/SBR (60/40)	97.5	11.3	68	21.5	-39.5	14	-4
EPDM/SBR (70/30)	98	12.7	55	17.5	-23	11	-2
EPDM/SBR (80/20)	98.3	11.6	40	16.9	-19.8	9	-2
SBR/NR (50/50)	98.1	13.1	40.5	17	-22	11	-2

<sup>a</sup> Minus sign is due to properties decrement after HCl immersion compared to the properties before HCl immersion.

EPDM/SBR for similar percentages in the polyblend samples are reduced. For instance,  $t_{90}$  values for EPDM/NR (30/70) and EPDM/SBR (30/70) samples were about 11 and 15 min in Figure 2(b) and (c), respectively. Because the cure temperature of these samples in the actual curing system is taken, 140°C equals the cure temperature in the rheometer; therefore, the technical cure can be taken equal to  $t_{90}$  in the cure curve obtained from the rheometer. In this case, vulcanization thermal index ( $T_f$ ) is equal to 1, which is defined as measuring for every 10°C temperature increase, the rate of vulcanization increases linearly and at each moment is equal to  $t_{90}$  of the cured samples.<sup>17</sup>

### Mechanical properties of the samples

Table III shows mechanical properties including hardness, ultimate tensile strength (UTS), and elongation at break ( $E_b$ ). Also, in Table III, changes of these mechanical properties are calculated for polyblend samples before and after immersion in HCl solution.

From the point of view of sample hardness, the higher values of  $t_{90}$  correspond to a higher cross-link density of the cured rubber compound and consequently the hardness of the sample is increased. Therefore, moving from SBR/NR toward EPDM/NR and then EPDM/SBR, respectively, the hardness of the samples is increased because of an increase in the cure time, which increases because of a reduction in the amount of unsaturated bonds. On the other hand, comparing EPDM/NR and EPDM/SBR polyblend samples for similar component percentages, the hardness of EPDM/SBR is higher than EPDM/NR. The reason for this difference is due to fewer unsaturated bonds in SBR relative to NR.

In mechanical properties, by increasing cross-link density, first an increase and then a reduction in UTS values are observed. The reason for this

unusual behavior can be contributed to unusual cross-links leading to stress concentration and failure in these sections of the samples. Also, cross-link density increases usually lead to a reduction in elongation at break, which is attributed to increases of the elasticity behaviors in the samples.

After the immersion of the samples in HCl solution, they swelled. Weight changes of the samples depend on the extent of the cross-linking. For samples with lower cross-link density, HCl can easily penetrate and break the double bonds and ultimately tensile strength decreases. Reduction in UTS values is followed by an increase in elongation at break results. Samples with greater swelling by HCl have softer surface and lower hardness.

Mechanical tests carried out on these samples showed that EPDM/NR and especially EPDM/SBR containing 70 phr EPDM showed better results compared with other samples and these results are comparable for the value obtained in the case of SBR/NR (50/50).

### Optimization of the curing system

To increase the rate of cure for samples containing 70 wt % EPDM in EPDM/SBR and EPDM/NR and also to reach  $t_{90}$  at optimum cure and to obtain similar properties to SBR/NR, some changes were made on the choice of the type and amount of the accelerators used in the curing system of polyblend samples under investigation.

The use of mercaptobenzothiazole (MBT) from the thiozole family of accelerators usually provides a relatively longer scorch time and a moderate cure rate. The use of zinc diethyl dithiocarbamate (ZDEC) accelerator from the dithiocarbamate family of accelerators in a rubber compound gives short scorch time and high cure rate. To modify the cure system, a three-part accelerator system was used. In this modified cure system, in addition to using MBT and



**TABLE IV**  
The Mechanical Properties of the Samples After Modifications in the Curing System

Sample	Sulfur (phr)	Hardness (shore A)	UTS (MPa)	$E_b$ (%)	$\Delta M$ (%)	$\Delta UTS$ (%)	$\Delta E_b$ (%)	Ashore A (%)
EPDM/NR (70/30)	15	95	10.9	118	20.5	-38	-15	-2
EPDM/SBR (70/30)		96.5	12.2	66	19.8	-33	14	-3
EPDM/NR (70/30)	10	89	9.8	124	27.5	-41	-25	-3
EPDM/SBR (70/30)		91	11.4	71	25.7	-40	19	-2

ZDEC, a third accelerator, tetramethylthiuram disulfide (TMTD), which is from the thiuram group, was used. The reason for using three different types of accelerators was to get a synergism effect for increasing the cure rate.<sup>18,19</sup> In the optimum formulation, 1.5 phr MBT, 1.5 phr ZDEC, and 1.8 phr TMTD were used. One of the objectives of this work was to increase the efficiency of the curing system and reduce the  $t_{90}$  for EPDM/NR and EPDM/SBR polyblend samples. Normally, TMTD gives a higher rate of curing and reinforcing effect on cross-links.<sup>20</sup>

To find out the optimum amount of sulfur in the vulcanization system of these samples, three samples containing 10, 15, and 20 phr sulfur were prepared. These samples were then cured with the optimized curing system. No significant change in initial hardness was observed for the samples containing 15 and 20 phr sulfur. However, the hardness of a similarly cured sample with 10 phr sulfur decreased significantly. Table IV shows mechanical properties of EPDM/NR (70/30) and EPDM/SBR (70/30). The results show that the variations of hardness for the samples containing 15 and 20 phr sulfur are very small. The ultimate tensile strength for the modified cure system is reduced and this is due to the reduction of sulfur percentage in the samples.

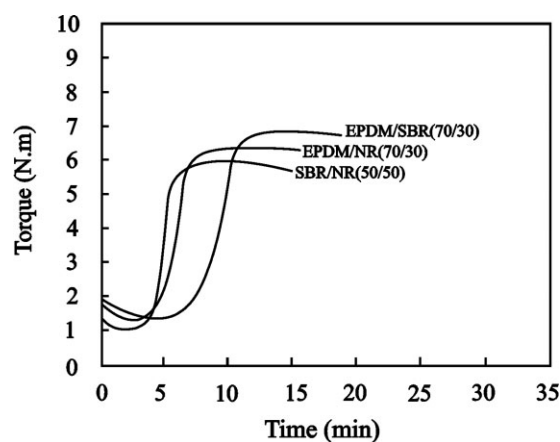
The variations of UTS ( $\Delta UTS$ ) and hardness (Ashore A) of the samples after immersion in HCl are negligible. The variations in  $E_b$  ( $\Delta E_b$ ) for EPDM/NR (70/30) are negative. The reason for this result is because the sulfur reduction in the formulation and, therefore, in all the double bonds in NR, is unable to form cross-links with sulfur. In the formulation of the samples, therefore, EPDM/NR is more susceptible to HCl penetration. Because in both cure systems, the ratio of sulfur/accelerator (S/A ratio) is between 3 and 4, the cure system is conventional (CV) in this system, due to polysulfide cross-links, and their rigidity and hardness is high, elasticity is low, and fatigue is high.<sup>21,22</sup>

Figure 3 shows cure curves for the samples EPDM/SBR (70/30), EPDM/NR (70/30), and SBR/NR (50/50). As can be seen, the value of  $t_{90}$  for the samples containing EPDM/NR is about 7 and for EPDM/SBR is about 11 and is reduced relative to the system before modification. This can help to increase the rate of cure in the curing process of the

samples. Comparing the mechanical properties of the samples under investigation, we can conclude that EPDM/SBR (70/30) samples have similar and acceptable properties to SBR/NR (50/50).

### Chemical resistance for the optimized composition

Table V shows qualitative test results for cracking, blistering, permeability, and adhesion strength of the rubber liner to metallic surface. Cracking and blistering test observations for EPDM/NR (70/30), EPDM/SBR (70/30), and SBR/NR (50/50) were negative and there was a smooth surface with out any cracking and blistering effects. As was explained in penetration tests of liquid and vapors of caustic solution, only EPDM/NR samples are affected by penetration due to a more flexible structure and a softer surface because of more double bonds and free movements of elastomeric chains, which are not bonded by sulfur cross-links. Evaluation tests related to the strength of the rubber layer bonded to metallic surface by using heat activated binding adhesive, Chemosil X6025, show that for all three samples, the adhesive forms suitable bonds between the surfaces of rubber layer with the metal surface. The activation of these bonds for the cure system at 140°C is resistant to caustic liquids and vapors and there is no penetration between the rubber layer-metallic surface and no corrosion was observed at the metallic surface.



**Figure 3** Cure curves for SBR/NR (50/50), EPDM/NR (70/30), and EPDM/SBR (70/30) after modification in the curing system.

**TABLE V**  
**The Qualitative Observation After Immersing the Samples in Caustic Solution**

Sample	Cracking	Blistering	Permeation	Rubber-metal adhesion
EPDM/NR (70/30)	–	–	+	+
EPDM/SBR (70/30)	–	–	–	+
SBR/NR (50/50)	–	–	–	+

+: observed; –: not observed.

### CONCLUSION

In this study, elastomeric polyblends EPDM/NR, EPDM/SBR with different weight percentage compositions, and also a SBR/NR sample, which is usually used in industry for rubber lining metallic surfaces known as ebonite, were prepared. Mechanical and chemical tests were carried out for these samples before and after improvements in the cure system. All the samples except SBR/NR were cured with super-heated water vapor. The SBR/NR samples were cured in an autoclave. Mechanical properties of the samples such as hardness, ultimate tensile strength, and elongation at break for 15 and 20 phr sulfur in the rubber compound formulations before and after composition modification showed no major differences. However, when 10 phr sulfur was used in the formulations, a considerable loss in the mechanical properties of the samples was observed. The other important factor in the correction of the cure system was the use of three different accelerators, MBT, ZDEC, and TMTD in the formulation. A synergic effect of the accelerators and a remarkable increase in the cure rate of the samples occurred. As a result,  $t_{90}$  for EPDM/NR and EPDM/SBR samples was comparable to SBR/NR. Quantitative chemical property observations of the samples after the immersion in HCl gave very good results for the samples EPDM/SBR (70/30). Qualitative observations of chemical resistance of the samples in caustic solution showed that EPDM/SBR (70/30) had a better performance than EPDM/NR (70/30) and can be replaced by SBR/NR (50/50). On the other hand, using a heat activated binding adhesive such as Chemosil X6025 for a suitable interaction between the metal and rubber layer was confirmed. Finally, EPDM/SBR (70/30) samples, which can be cured easily by water vapor at atmospheric pressure, has

the ability to be assembled on the surface of the metal; the result will be a reduction in the rubber-lining costs and a comparable rate of process relative to conventional SBR/NR.

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