

# Direct Bonding between Poly(oxy-2,6-dimethyl-1,4-phenylene) and Rubber with Radicals

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**ABSTRACT:** The solubility parameter value (SP value,  $\delta$ ) is one of the most important factors in bonding technology. It was found that various kinds of rubber, such as VMQ ( $\delta \approx 7.3 \text{ cal}^{1/2}/\text{cm}^{3/2}$ ) compounds, EPDM ( $\delta \approx 7.9 \text{ cal}^{1/2}/\text{cm}^{3/2}$ ) compounds, and X-NBR ( $\delta \approx 9.3 \text{ cal}^{1/2}/\text{cm}^{3/2}$ ), can bond to poly(oxy-2,6-dimethyl-1,4-phenylene) in their vulcanization process. This means that this bonding mechanism depends less on SP values. In this study, the bonding mechanism is

hypothesized as an interfacial radical reaction, and the hypothesis is validated by molecular orbital (MO) calculations and experiments. All experimental results and MO calculation results are consistent with each other. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 53–59, 2005

**Keywords:** adhesion; interfaces; poly(phenylene oxide); rubber; vulcanization

## INTRODUCTION

Technologies for combining different materials are of great interest to academic researchers and commercial developers, because required properties often cannot be obtained using one material alone. The combination of a hard material and a soft material is a typical case. Adhesive-free plastics–rubber composites are well known using systems based on chemically similar materials, i.e., miscible combinations. For example, the combination of poly(propylene) and poly(ethylene-co-propylene) rubber, polyamides, and poly(ether-block-amide)s, etc., can be overmolded and bonded together.

To determine such combinations, the Hildebrand<sup>1</sup> solubility parameter concept provides a lot of information. The idea is that two materials that have matched solubility parameters (SP) will have balanced forces and therefore will be miscible. Techniques for estimating SP by calculations have been reported by Small,<sup>2</sup> Hoy,<sup>3</sup> Fedors,<sup>4</sup> von Krevelen,<sup>5</sup> and Okitsu.<sup>6,7</sup> A general relationship is

$$F = \sum n_i F_i, \quad (1)$$

where  $F$  is a molar property,  $n_i$  is the number of contributing components of type  $i$ , and  $F_i$  is the numerical contribution. In the case of solubility parameter determination of a compound, the following relationship is defined:

$$\delta = \frac{\sum F_i}{V}, \quad (2)$$

where  $\delta$  is the SP value,  $F_i$  is the molar attraction constant, and  $V$  is the molar volume. Small<sup>2</sup> showed  $F_i$  values of some chemical groups, and after that, many works were done to get accurate SP values. Okitsu<sup>6,7</sup> focused on the effects of hydrogen bonding and suggested amending Small's parameters and the equation with the experimental results. As a result, Okitsu's parameters and the equation could obtain more accurate SP values of 113 solvents and 30 polymers.

The polymer–polymer interaction parameter  $\chi$  can be calculated by the equation<sup>8,9</sup>

$$\chi = \frac{V_r}{RT}(\delta_A - \delta_B)^2, \quad (3)$$

where  $V_r$  is the molar volume of the rubbery phase of the repeat unit,  $R$  is the gas constant, i.e., about 1.985 cal/mol · K,  $T$  is the absolute temperature, and  $\delta_A$  and  $\delta_B$  are the solubility parameter values of the two polymers. Molecular mixing of two high-molecular-weight polymers can occur only when  $\chi$  is very close to zero, i.e.,  $\delta_A$  and  $\delta_B$  are very close each other. The critical value of  $\chi$  which sets the upper limit on miscibility is<sup>8</sup>

$$\chi_{\text{crit}} = \frac{1}{2} \left( \frac{1}{\sqrt{N_A}} + \frac{1}{\sqrt{N_B}} \right)^2, \quad (4)$$

where  $N_A$  and  $N_B$  are the degrees of polymerization.  $N_A$  and  $N_B$  are normally assumed to be about 1000 and  $V_r$  to be 100 cm<sup>3</sup>. Therefore,  $\chi_{\text{crit}} \approx 0.002$ , and in this case, the difference of SP values  $|\delta_A - \delta_B|$  was

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TABLE I  
Polymer Materials

Sample	Chemical species	$M_n \times 10^{-4}$	$M_w/M_n$	$T_g$ (°C)	$T_m$ (°C)
PPE-0	Poly(oxy-2,6-dimethyl-1,4-phenylene)	2.64	2.49	213	—
HIPS-0	High-impact polystyrene <sup>a</sup>	8.57	2.13	72	—
PPE-1	Blend PPE-0 and HIPS-0, 90:10 by weight	—	—	193	—
PBT-1	Poly(oxytetramethyleneoxyterephthaloyl)	2.26	2.06	61	223

<sup>a</sup> Weight fraction of butadiene is 0.056.

obtained as about  $0.11 \text{ cal}^{1/2}\text{cm}^{3/2}$  at  $T = 298 \text{ K}$  and about  $0.13 \text{ cal}^{1/2}\text{cm}^{3/2}$  at  $T = 443 \text{ K}$ .

In 1987 Huels A.G (from 2001, Degussa A.G.) started development of the technology that is a direct bonding between plastics and rubber. In 1998, Daicel-Huels, Ltd. (from 2001, Daicel-Degussa Ltd.), joined in the development, and they determined that the poly(oxy-2,6-dimethyl-1,4-phenylene) compound (m-PPE) can adhere directly to rubbers of SP values that are different from that of m-PPE. This study attempts to investigate and propose the mechanism of the adhesion phenomenon.

## EXPERIMENTAL

### Materials

Table 1 shows the grades of thermoplastics materials that we used in this investigation. We synthesized PPE-0, HIPS-0, and PBT-1 by conventional methods. PPE-1 was obtained by mixing 90 wt% of PPE-0 and 10 wt% of HIPS-0 with an extruder at 300°C.

The number average molecular weight ( $M_n$ ) and the weight average molecular weight ( $M_w$ ) in Table I were measured by gel permeation chromatography with a polystyrene standard.

The glass transition temperature ( $T_g$ ) and the melting point ( $T_m$ ) in Table I were measured by differential scattering calorimetry (DSC). The heating ratio of the DSC measurement was 20°C/min at the first heat process. The specimens for the DSC measurements were 10,000 mm<sup>2</sup> square, the 3 mm of the thickness plates were molded by an injection molding, i.e., made by the same process as the specimens for adhesion tests.

All rubbers were compounded by an internal mixer and an open roller. Their compound recipes are given under Results and Discussion.

### Experimental methods

PPE-1 and PBT-1 were molded into a square plate, 10,000 mm<sup>2</sup> in size and 3 mm thick, by injection molding. Aluminum tape (30 mm wide) was fixed on the upside of the plate of PPE-1 or PBT-1 masked with an adhesive tape (40 mm thick) for a peeling test, and the plate was put into metal square frame of 6-mm thickness. After that a rubber compound was put on the plastics' plate and heated at 170°C for 10 min under a pressure of  $4.0 \times 10^7 \text{ N/m}^2$ . Then a composite consisting of the plastic plate, 3 mm thick, and the vulcanized

TABLE II  
The Results of the Peeling Tests at 23°C for PPE-01, PBT-01, and E-01 to E-05

Component	E-01	E-02	E-03	E-04	E-05	
EPDM	DSM Keltan 509 $\times 100^a$	200	200	200	200	200
Zinc oxide	—	5	5	5	5	5
Stearic acid	—	1	1	1	1	1
Carbon black	N550	0.5	0.5	0.5	0.5	0.5
Magnesium silicate		50	50	50	50	50
1,1,1-Trimethylolpropane trimethacrylate		1	1	1	1	1
Polyoctenylene <sup>b</sup>		0	1	5	10	25
1,3-bis( <i>t</i> -Butylperoxy isopropyl)benzene		3	3	3	3	3
SP value <sup>c</sup>	( $\text{cal}^{1/2}/\text{cm}^{3/2}$ )	7.79–8.51	7.79–8.50	7.80–8.50	7.80–8.49	7.82–8.46
Peeling test <sup>d</sup> strength(N)/mode	PPE-1 ( $\delta = 9.36^\circ$ ) PBT-1 ( $\delta = 10.30^\circ$ )	22/B-C 0/C	35/B 0/C	65/A 0/C	67/A 0/C	21/C 0/C

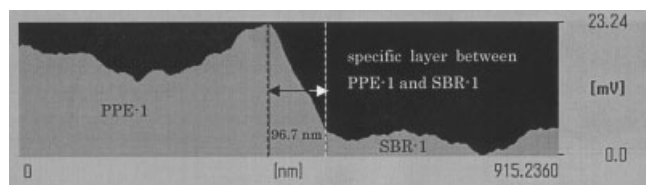
<sup>a</sup> Keltan 509  $\times 100$  consists of about 65 wt% ethylene base segment, 27 wt% propylene base segment, 8 wt% 2-ethylidene 2-norbornene base segment, and 100 parts paraffinic oil.

<sup>b</sup> Vestenamer 8012 by Degussa A.G.,  $M_w = 75,000$ ,  $T_g = -65^\circ\text{C}$ ,  $T_m = 54^\circ\text{C}$ , *cis/trans* ratio of double bonds = 20/80.

<sup>c</sup> Used following SP values: EPDM as 7.84–8.58<sup>15</sup>, paraffinic oil as 7.74–8.43<sup>15</sup>, polyoctenylene as 8.10 (by calculation).

<sup>d</sup> 90° peeling test at 23°C; A, cohesive; B, adhesive; C, no adhesion.

<sup>e</sup> By calculation.



**Figure 1** The AFM observation of the interface between PPE-1 and SBR-1. The thickness of the layer is about 10 nm.

rubber, 3 mm thick, was obtained. The composite plate was cut to a rectangular plate of size  $15 \times 70$  mm for the peeling test.

To evaluate the adhesion,  $90^\circ$  peeling tests were carried out at a set temperature with a tensile machine, RTA-1T, produced by A&D. The tensile speed was 50 mm/min. The peeling strength was defined as the maximum tensile strength, and we judged a peeling mode, i.e., (A) cohesive or (B) Interface, by observation of the peeling surface.

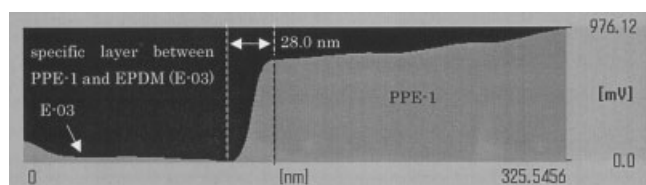
For analysis of the interface between plastics and rubber, a Seiko Instruments Industries SPI3800 was used for atomic force microscopy (AFM) analysis of VE-AFM mode.

Most SP values were quoted from published books such as the *Polymer Handbook*.<sup>10</sup> Others were obtained by a calculation with Okitsu's parameters and equation.<sup>6,7</sup>

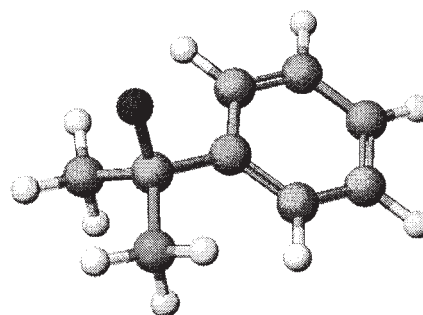
The MOPAC PM3 program was used for molecular orbital (MO) calculations. CAChe 5.0 for Windows was used as the computer software. I focused on the possibilities of hydrogen abstraction reactions be-

**TABLE III**  
The Recipe of SBR-1

	Component	phr
SBR	JSR #0202	100.0
Zinc oxide	—	5.0
Stearic acid	—	1.0
Carbon black	N550	50.0
Naphthenic oil		10.0
Poly(2,2,4-trimethyl-1,2-dihydroquinoline)		1.0
N-(Cyclohexylthio)phthalimide		0.2
N-Cyclohexyl-2-benzothiazolyl		1.0
Sulfenamides		
Tetramethyl thiuram monosulfide		0.3
Sulfur		1.8



**Figure 2** The AFM observation of the interface between PPE-1 and EPDM (E-03). The thickness of the layer is about 30 nm.

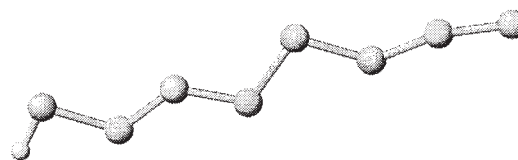


**Figure 3** The model structure of cumyl oxy radical.

tween radicals from vulcanization agents and thermoplastics polymers. To estimate the possibilities of hydrogen abstraction reactions, we defined the reactivity,  $S$ , as following the equation based on the frontier molecular orbital concept<sup>11</sup> and the Superdelocalizability concept.<sup>12-14</sup>

$$S = \frac{C_{\text{SOMO}}^2 \times C_{\text{HOMO}}^2}{|E_{\text{SOMO}} - E_{\text{HOMO}}|} + \frac{C_{\text{SOMO}}^2 \times C_{\text{LUMO}}^2}{|E_{\text{SOMO}} - E_{\text{LUMO}}|}, \quad (5)$$

where  $C_{\text{SOMO}}$  is a MO coefficient of a singly occupied MO (SOMO) of a radical from a vulcanization agent,  $C_{\text{HOMO}}$  is a MO coefficient of the highest occupied MO (HOMO) of a hydrogen atom of a thermoplastics polymer,  $C_{\text{LUMO}}$  is a MO coefficient of the lowest occupied MO (LUMO) of a hydrogen atom of a thermoplastics polymer,  $E_{\text{SOMO}}$  is the energy level of SOMO of a radical from a vulcanization agent,  $E_{\text{HOMO}}$  is the energy level of HOMO of a thermoplastics polymer, and  $E_{\text{LUMO}}$  is the energy level of LUMO of a thermoplastics polymer. All  $C_{\text{SOMO}}$ ,  $C_{\text{HOMO}}$ ,  $C_{\text{LUMO}}$ ,  $E_{\text{SOMO}}$ , and  $E_{\text{LUMO}}$  are obtained by MO calculations. The trimer



**Figure 4** The model structure of H-S8 radical.

**TABLE IV**  
SOMO of Cumyl Oxy Radical and H-S8 Radical by MO Calculation

	Cumyl oxy radical	H-S8 radical
Energy level of SOMO	-6.677 eV	-6.142 eV
MO coefficient		
$s$	0.0013	-0.0445
$p_x$	-0.2535	0.6531
$p_y$	-0.6764	-0.0731
$p_z$	-0.5359	0.0000
$p_x^2 + p_y^2 + p_z^2$	0.8090	0.4319

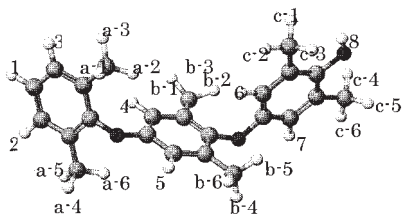


Figure 5 The model compound of PPE for MO calculation.

was used as a model chemical compound of PPE and the dimer was used as a model chemical compound of PBT for the calculations.

## RESULTS AND DISCUSSION

### EPDM and polyoctenylene

Table II shows the recipe of E-01 to E-05 and the results of peeling tests of PPE-1, PBT-1, and E-01 to E-05. From the results, polyoctenylene— $(\text{CH}_2\text{—CH}_2\text{—CH}_2\text{—CH=CH—CH}_2\text{—CH}_2\text{—CH}_2)_n$ —could improve adhesion to PPE-1, and adding 25 phr of polyoctenylene diminished the effect. From our calculation of SP values, polyoctenylene did not have much influence on the SP values of E-01 to E-05 (see Table II). If the effect of polyoctenylene was only the enhancement of the affinities between PPE-1 and EPDM, the effect should not be diminished by increasing polyoctenylene. Therefore, these results suggest that polyoctenylene has another effect on adhesion besides increasing affinity. On the other hand, there was no adhesion between PBT-1 and E-01 to E-05.

In 1990, Machate et al. investigated a combination of PXE and polystyrene.<sup>16, 17</sup> According to their results, polystyrene would diffuse into PXE above 180°C. Figure 1 shows the interface between the styrene-butadiene rubber (SBR) compound (SBR-1) and PPE-1 with AFM observation. The recipe for the SBR-1 is shown in Table III. According to AFM, a specific layer in which viscoelasticity is between that of PPE-1 and that of rubber was observed. In the case of PPE-1 and SBR-1, the AFM observation shows an ~96-nm-thick layer (i.e., the diffusion layer) between PPE-1 and SBR-1, because PPE-1 and SBR-1 can interdiffuse each other.<sup>16,17</sup> Figure 2 shows the interface between PPE-1 and E-03 using AFM observation. In this case, only a

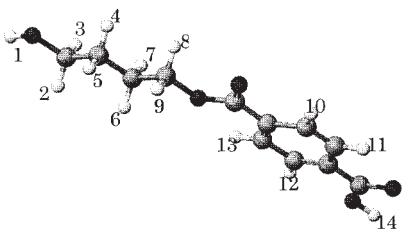


Figure 6 The model compound of PBT for MO calculation.

TABLE V  
The Result of MO Calculation of PPE<sup>a</sup>

Atom No.	MO coefficient		S	
	HOMO −8.603eV	LUMO 0.046eV	Cumyl oxy radical	H-S <sub>8</sub> · radical
1	0.0000	0.0009	0.0000	0.0000
2	0.0003	−0.0017	0.0000	0.0000
3	0.0000	−0.0010	0.0000	0.0000
a-1	0.0005	0.0642	0.0006	0.0003
a-2	0.0001	−0.0107	0.0000	0.0000
a-3	−0.0005	−0.0502	0.0003	0.0002
a-4	0.0002	0.0647	0.0006	0.0003
a-5	−0.0001	−0.0537	0.0004	0.0002
a-6	−0.0002	−0.0072	0.0000	0.0000
4	−0.0119	−0.0170	0.0001	0.0000
5	0.0111	−0.0150	0.0001	0.0000
b-1	−0.0047	−0.0046	0.0000	0.0000
b-2	−0.0096	−0.0007	0.0000	0.0000
b-3	0.0090	0.0094	0.0000	0.0000
b-4	0.0072	−0.0012	0.0000	0.0000
b-5	−0.0103	0.0078	0.0001	0.0000
b-6	0.0089	−0.0027	0.0000	0.0000
6	−0.0008	0.0015	0.0000	0.0000
7	0.0004	0.0013	0.0000	0.0000
c-1	−0.0680	0.0000	0.0022	0.0008
c-2	0.0639	0.0001	0.0019	0.0007
c-3	0.0038	−0.0005	0.0000	0.0000
c-4	−0.0680	−0.0004	0.0022	0.0008
c-5	0.0675	−0.0002	0.0021	0.0008
c-6	0.0005	0.0003	0.0000	0.0000
8	0.0025	0.0001	0.0000	0.0000

<sup>a</sup> Optimized final heat of formation was −76.1880 kcal.

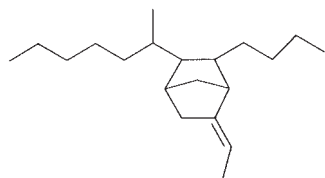
28-nm-thick layer could be observed. The differences in the thickness of these two layers suggest that the bonding mechanism of PPE-1 and EPDM is different from that of PPE-1 and SBR, i.e., diffusion phenomenon.

It can be estimated that the bonding was caused by a radical reaction and focused on possibilities of hydrogen

TABLE VI  
The Result of MO Calculation of PBT<sup>a</sup>

Atom No.	MO coefficient		S	
	HOMO −10.389eV	LUMO −1.149eV	Cumyl oxide radical	H-S <sub>8</sub> · radical
1	0.0000	0.0000	0.0000	0.0000
2	0.0003	0.0002	0.0000	0.0000
3	−0.0003	−0.0002	0.0000	0.0000
4	0.0000	0.0004	0.0000	0.0000
5	0.0000	−0.0004	0.0000	0.0000
6	−0.0010	−0.0013	0.0000	0.0000
7	0.0010	0.0012	0.0000	0.0000
8	−0.0028	−0.0169	0.0000	0.0000
9	0.0028	0.0167	0.0000	0.0000
10	−0.0007	−0.0002	0.0000	0.0000
11	0.0007	0.0004	0.0000	0.0000
12	−0.0001	0.0003	0.0000	0.0000
13	0.0000	0.0002	0.0000	0.0000
14	0.0000	0.0001	0.0000	0.0000

<sup>a</sup> Optimized final heat of formation was −199.0334 kcal.



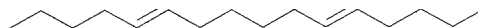
**Figure 7** The model compound of EPDM for MO calculation.

abstraction reactions<sup>18, 19</sup> between radicals from vulcanization agents and thermoplastics polymers.

Cumyl oxy radical (Figure 3) was used as a model radical from organic peroxides and  $\text{H-S}_8 \cdot$  radical (Figure 4) as a model chemical compound of sulfur radicals. The optimized final heat of formation of cumyl oxy radical was 20.1395 kcal, and that of  $\text{H-S}_8 \cdot$  radical was 29.9792 kcal. Table IV shows the MO calculation results of each SOMO's energy level and MO coefficients. In these case,  $P_x^2 + P_y^2 + P_z^2$  can be used as  $C_{\text{SOMO}}^2$  in Eq. (4).

Oxy-2,6-dimethyl-1,4-phenylene trimer (Figure 5) was used as a model chemical compound of PPE and a condensation product of 1,4-buthylenediol and terephthalic acid, i.e., PBT dimer (Figure 6), was used as a model chemical compound of PBT for MO calculations. Each number in Figures 5 and 6 shows the attribute number of each hydrogen atom. Tables V and VI show the results of the MO calculation.

In Table V, a-1, a-3, a-4, a-5, c-1, c-2, c-4, and c-5 hydrogen atoms had high  $S$  values with a cumyl oxy radical and the  $S$  values were higher than with the  $\text{H-S}_8 \cdot$  radical. Therefore, it is reasonable to suppose that there is the possibility of hydrogen abstraction reaction between a cumyl oxy radical and the methyl groups of PPE, especially those located at the end of the polymer chain. In Table VI, neither the cumyl oxy radical nor the  $\text{H-S}_8 \cdot$  radical had any reactivity with any hydrogen atom of PBT. These results can explain the differences in the bonding phenomena between PPE-1 and PBT-1 as the difference in reactivity to radicals. It may then be



**Figure 8** The model compound of polyoctenylyene for MO calculation.

presumed that the bonding is caused by a kind of radical reaction, such as hydrogen abstraction reactions.

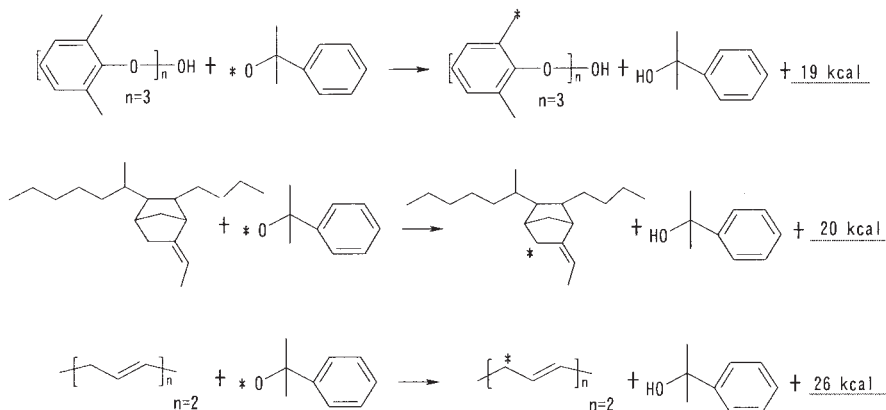
From the standpoint of the hypothesis of the bonding mechanism, the effect of polyoctenylyene in E-01 to E-04 may be explained as a radical stabilizing effect because of its order structure.<sup>20</sup>

The enthalpy of reactions can be estimated by the final heat of formation. The model chemical compounds' structures of EPDM and polyoctenylyene are shown in Figures 7 and 8. Regarding the reactions with a cumyl oxy radical, the differences of enthalpy are as follows: PPE is about 19 kcal, EPDM is about 20 kcal, and polyoctenylyene is about 26 kcal (see Figure 9). From this result, it is estimated that the radical reactivities of PPE and EPDM are almost same, and they are a little lower than that of polyoctenylyene.

Table VII shows the estimation of the reactivity of radical-radical recombination among PPE, EPDM, and polyoctenylyene radicals. Their reactivities are almost same.

The hypothesis of the mechanism of the reactions is shown in Figure 10. From the result shown in Figure 9, a cumyl oxy radical reacts with polyoctenylyene more easily than PPE and EPDM. But Table VII shows that the reactivity of radical-radical recombination is not difference. Therefore, it can be hypothesized that some amount of polyoctenylyene would promote a cross linking among PPE, EPDM, and polyoctenylyene; however, too much polyoctenylyene would consume the radicals from the peroxide and disturb the radical reactions between the radicals and PPE or EPDM.

Table VIII shows a comparison of a peroxide vulcanization system and a sulfur vulcanization system in EPDM. In a peroxide vulcanization system, almost the same results were obtained as for E-01 to E-04; on the other hand, bonding could not be achieved in a sulfur



**Figure 9** The estimation of the heat of reaction by the final heat of formation.



**TABLE VII**  
The Estimation of Radical–Radical Recombination Reactivity

Species of radicals	S
EPDM* + polyoctenylene*	4.7
PPE* + polyoctenylene*	1.4 <sup>1</sup> 0.5 <sup>2</sup> 3.6 <sup>3</sup>
EPDM* + PPE*	1.6 <sup>1</sup> 0.06 <sup>2</sup> 6.8 <sup>3</sup>

<sup>a</sup> With a PPE radical at a-1–a-6;; 2, b-1–b-6; 3, c-1–c-6 in Figure 5 and Table 5.

vulcanization system. PBT-1 also could not get good bonding these combinations. Regarding the peeling tests, there are no differences in the broken mode between RT and 90°C. These results are consistent with the results of the MO calculation, i.e., the reactivity of the cumyl oxy radical is more than two times higher than that of the sulfur radical (Table V). Addi-

tionally, this is one of the reasons why sulfur has many side reactions.

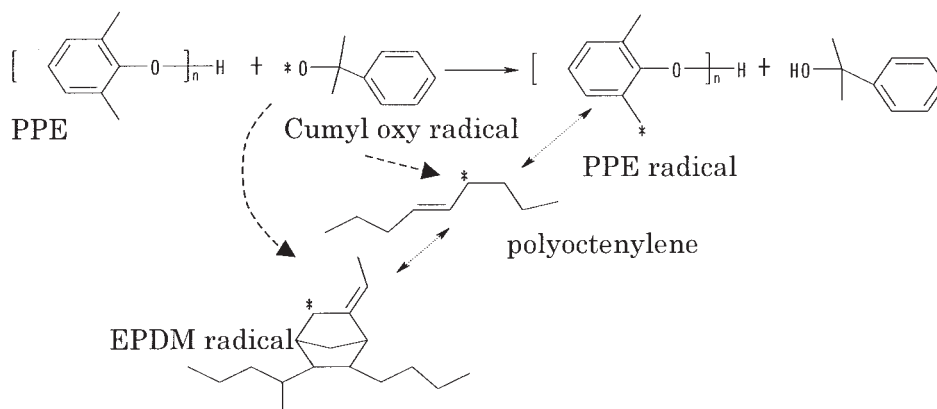
### SP values and bonding

For more discussion of the independence of SP values in this study, I investigated combinations with a poly-(dimethylsiloxane) rubber (VMQ), an acid-modified acrylonitrile–butadiene rubber (X-NBR).

Table IX shows the result of the combinations with VMQ. From the results, we can see that the bonding between PPE-1 and VMQ depends on the amount of a peroxide agent.

Table X shows the recipe of the X-NBR. PPE-1 was able to bond with X-NBR.

These two examples suggest that bonding is not a special case in the combination between PPE and EPDM and also that bonding is less dependent on SP values.



**Figure 10** The hypothesis of the reactions among PPE, polyoctenylene, and EPDM with radicals.

**TABLE VIII**  
Comparison of a Peroxide Vulcanization System and a Sulfur Vulcanization System in EPDM

Component	E-06	E-07	E-08	E-09	E-10	
EPDM	Bayer AP341 <sup>a</sup>	100	100	100	100	100
Zinc oxide	—	5	5	5	5	5
Stearic acid	—	1	1	1	1	1
Carbon black	N550	50	50	50	50	50
Paraffinic oil	Idemitsu PW-90	25	25	25	25	25
Butanediol dimethacrylate	—	—	1	1	1	1
Polyoctenylene <sup>b</sup>	—	5	0	5	25	25
1,3-bis( <i>t</i> -Butylperoxy isopropyl)benzene	—	—	1.4	1.4	1.4	1.4
Dibenzothiazyl disulfide	1.0	1.0	—	—	—	—
Tetrabutylthiuram disulfide	1.0	1.0	—	—	—	—
Sulfur	1.5	1.5	—	—	—	—
SP value <sup>c</sup>	[cal <sup>1/2</sup> /cm <sup>3/2</sup> ]	-7.86–8.55	7.83–8.53	7.86–8.55	7.83–8.53	7.87–8.48
Peeling test <sup>d</sup>	PPE-1 ( $\delta = 9.36^e$ )	0/C	0/C	55/B	118/A	42/B
Strength (N)/mode	PBT-1 ( $\delta = 10.30^e$ )	0/C	0/C	0/C	0/C	0/C

<sup>a</sup> Bayer AP341 consists of about 58 wt% ethylene base segment, 38 wt% propylene base segment, and 4 wt% 2-ethylidene 2-norbornene base segment. ML(1+4) at 125°C is 46.

<sup>b</sup> Vestenamer 8012 by Degussa A.G.,  $M_w = 75,000$ ,  $T_g = -65^\circ\text{C}$ ,  $T_m = 54^\circ\text{C}$ , *cis/trans* ratio of double bonds = 20/80.

<sup>c</sup> Used following SP values: EPDM as 7.84–8.58<sup>15</sup>, paraffinic oil as 7.74–8.43<sup>15</sup>, polyoctenylene as 8.10 (by calculation).

<sup>d</sup> 90° peeling test at 23°C; A, cohesive; B, adhesive; C, no adhesion.

<sup>e</sup> By calculation.

## CONCLUSION

It was found that some combinations of PPE and rubbers could bond to each other directly during the vulcanization process of rubber. The bonding is less dependent on SP values and our experimental results suggest that the bonding mechanism is concerned with some radical reactions such as hydrogen abstraction reaction. These experimental results could be estimated by the results of the MO calculation. It could be estimated that (i) each polymer became closer, (ii) radicals from the peroxide compound attacked these polymers, and polymers' radicals would be generated by a hydrogen abstraction reaction, and (iii) some chemical bonding would be generated by a recombination of polymer radicals.

This hypothesis does not deny other bonding mechanisms such as hydrogen bonding and van der Waals effects. Plural kinds of interaction forces must exist at the interface; however, it is reasonable to suppose that the chemical bonding caused by this hypothesis will disturb phase separation and will enhance the other interaction forces at the heterogeneous interface.

In this study, all phenomena have not been thoroughly explained yet, but the most important point is that there are some possibilities of a chemical reaction at the heterogeneous interface. The chemical reactions at the heterogeneous interface make the possibilities of composite technology wide open.

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TABLE IX  
The Combination with VMQ

	Component	Q-01	Q-02	Q-03
VMQ Tray-Dow 4104U peroxide agent <sup>a</sup>		100	100	100
		0.4	0.8	1.6
SP value [cal <sup>1/2</sup> /cm <sup>3/2</sup> ]		7.30–7.60 <sup>15</sup>		
Peeling test <sup>b</sup>	PPE-1	29	56	84
Strength (N) mode	$\delta = 9.36^c$	C	B	A
	PBT-1	0	0	0
	$\delta = 10.30^c$	C	C	C

<sup>a</sup> 2,5-Dimethyl-2,5-di(*t*-butylperoxy)hexane.

<sup>b</sup> 90° peeling test at 23°C.

<sup>c</sup> By calculation.

TABLE X  
The Combination with X-NBR

	Component	Amount
X-NBR	Zeon, Nipol 1472 <sup>a</sup>	100
Ammonium silicate <sup>b</sup>		80
Carbon black	N660	3
Plasticizer <sup>c</sup>		10
Stearic acid		1
1,1,1-Trimethylpropanetrimethacrylate		2
1,3-bis( <i>t</i> -Butylperoxy isopropyl)benzene		2.5
SP value <sup>d</sup>	[cal <sup>1/2</sup> /cm <sup>3/2</sup> ]	9.60
Peeling test Strength (N)/mode	PPE-1 $\delta = 9.36^d$	81/A
	PBT-1 $\delta = 10.30^d$	0/C

<sup>a</sup> Nitrile content is 27 wt%.

<sup>b</sup> Hoffmann Mineral, Sillitin Z-86.

<sup>c</sup> Dibutylmethylene bis-thiogluconate.

<sup>d</sup> By calculation.

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