Organic co-agents for maintaining mechanical properties of rubber elastomers at high processing temperatures

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Abstract−Heat easily degrades a common organic co-agent with a ring structure based on C-N and C-C bonds that is frequently used in conjunction with peroxide-based initiators to cross-link polymer main chains, leading to the shattering of cross-linking points and deterioration of the physical properties of rubbers. In our study, we used co-agents based on phenyl rings that had better bond strengths to improve the heat resistance of co-agents in an effort to maintain the mechanical qualities of rubber at high temperatures. Our results show that the mechanical properties of cross-linked rubbers were considerably maintained after heat treatment at a high temperature. Through extensive investigation, it was discovered that utilizing co-agents with stronger bond strengths caused to reduce the disintegration of the crosslinking sites, which was the basis for retaining mechanical qualities.

Keywords: Rubber, Co-agent, Mechanical Properties, Thermal Degradation

INTRODUCTION

Materials for parts in semiconductor fabrication processes must be able to endure a severe environment of high temperature, high pressure, and high plasma in the processing sector. A manufacturing method free of contaminants is necessary to meet the requirement for decreasing the defect rate and semiconductor line width [1-3]. By enhancing the adhesion between process parts and avoiding gas and liquid leaks, sealing parts provide a significant contribution to the process' safety and the completeness of the final product. A sealing part is a consumable item, so it is crucial to choose a sealing material that can withstand the harsh process environment, because early sealing part degradation necessitates replacement, which raises process costs and results in defects in semiconductor products by releasing contaminants.

Rubbers have historically incorporated inorganic nanoparticles including alumina (Al_2O_3), silica (SiO_2), zirconia (ZrO_2), and yttria (Y_2O_3) to increase the heat and plasma resistance of sealing components used in the semiconductor industry, such as O-rings and gaskets [4,5]. This is because organic co-agents used to crosslink rubbers frequently exhibit low heat and plasma resistance. Triallyl isocyanurate (TAIC), for instance, is a good example of a co-gent since it possesses a thermally fragile ring structure based on C-N and C-C bonds along with vinyl moieties for radical cross-linking initiated by peroxides. The co-agent applied to rubbers creates cross-links between the primary polymer chains to create elastomers with a three-dimensional network structure [6,7]. When peroxide is used to crosslink rubber, it is simple to combine with rubber, has a quick crosslinking time, and produces elastomers with good insulating and mechanical qualities ideal for sealing components [8-16]. To this end, the most common co-cross-linking agent used with peroxide cross-linking agent is TAIC with the isocyanurate ring [17-22]. However, the rubber matrix cross-linked with TAIC is easily decomposed under harsh processing conditions during multiple process cycles, and this can result in serious damage to semiconductor devices during fabrication because the inorganic additives can be ejected from the rubber nanocomposites (Scheme 1(a)). Therefore, the development of a cross-linking method that is free of inorganic components but nevertheless possess strong mechanical qualities is crucial for elastomers.

Because phenyl rings have higher binding strength (602 kJ/mol for C=C) than TAIC (346 kJ/mol for C-C and 305 kJ/mol for C-N) (Scheme 1(b) and 1(c)), we hypothesize in this study that using co-agents with them can increase the thermal stability of elastomers. To test the viability of our idea, we employed ethylene-propylene-diene monomer (EPDM) as a model rubber, and 1,3,5-trivinyl benzene (TVB) and 1,3,5-tri-2-propen-1-yl benzene (TPB) as co-agents (Scheme 1(d)). We examined whether the cross-linking points of phenyl rings have more heat resistance than the isocyanurate ring of TAIC and the degradation of mechanical properties of the resultant elastomers before and after heat treatment at high temperatures. The objective was to develop a novel technique to improve the physical properties of elastic bodies without the use of inorganic chemicals. It is because the best way to lessen contamination caused by sealing materials is to only employ organic cross-linking and co-cross-linking agents without inorganic additives.
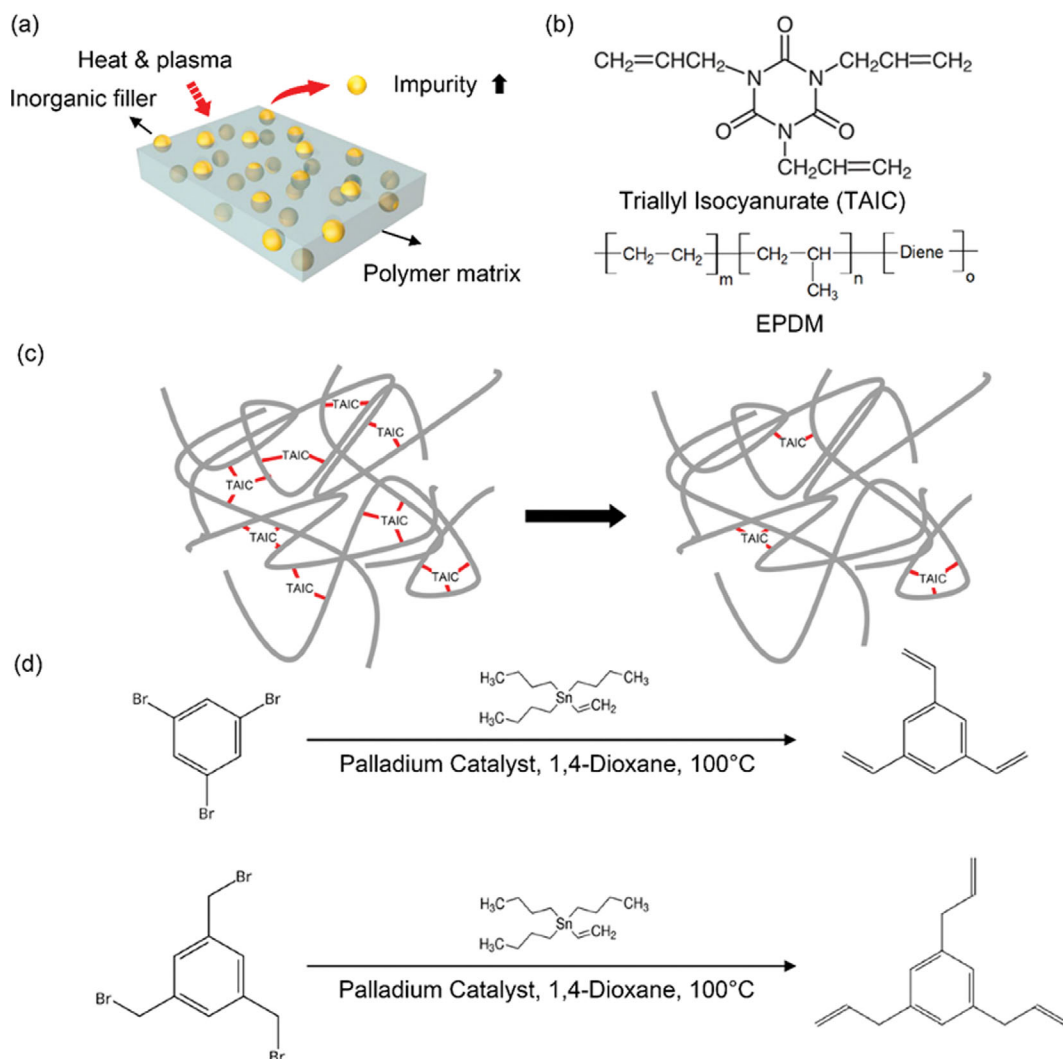
MATERIALS AND METHODS

1. Materials

1,3,5-Tribromo benzene ($C_6H_3Br_3$), N-bromosuccinimide ($C_4H_4BrNO_2$), and dicumyl peroxide ($[C_6H_5C(CH_3)_2]_2O_2$) were purchased

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Scheme 1. (a) A schematic illustration of an elastomer with inorganic filler nanoparticles, (b) chemical structures of TAIC and EPDM, and schemes of (c) degradation of crosslink points by heat or plasma and (d) synthesis of TVB and TPB.

from Alfa Aesar (Heysham, UK). Tetrakis(triphenylphosphine)palladium(0), tributyl(vinyl)tin (CH₂=CHSn[CH₃(CH₂)₃]₃), and TAIC were purchased from Acros Organics (Geel, Belgium). Benzoyl peroxide and ZnO powder (nanopowder <100 nm) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Mesitylene (C₆H₃(CH₃)₃) were purchased from ThermoFisher Scientific (Waltham, Massachusetts, USA). EPDM (KEP240) was produced from KUMHO POLYCHEM (Seoul, Republic of Korea). All the reagents were used as received.

2. Synthesis
2-1. TVB

Following a literature procedure [23], a solution of 1,3,5-tribromo benzene (315 mg, 1 mmol), LiCl (25 mg, 0.6 mmol), tetrakistriphenyl phos-phanpalladium(0) (69 mg, 6 mol%), and vinyltributylstannane (0.96 ml, 3.3 mmol) in 10 ml of anhydrous dioxane was heated at 100 °C for 15 h. After the reaction mixture was cooled to room temp, dichloromethane (75 ml) was added and the organic layer was extracted with water (4,350 ml), dried (Na₂SO₄), filtered, and evaporated under reduced pressure. The crude product was puri-

fied by chromatography on silica gel with petroleum ether as eluent. The product was obtained as a colorless liquid. The yield was 60%. ¹H NMR (300 MHz, CDCl₃) δ 7.36 (s, 3H), 6.73 (dd, J=17.6, 10.9 Hz, 3H), 5.80 (d, J=17.6 Hz, 3H), 5.29 (d, J=10.8 Hz, 3H).

2-2. 1,3,5-Tris(bromomethyl)benzene

1,3,5-Triethyl benzene (0.3 g, 1.8 mmol), N-bromosuccinimide (1.2 g, 6.7 mmol), 20 ml of dichloromethane and 0.02 g of benzoyl peroxide were placed in 50 ml round bottom flask. The mixture was refluxed for 12 hours at 70 °C, followed by neutralizing using a saturated NaHCO₃ aqueous solution. Dichlromethane was used to extract the product after washing the reaction mixture with water. The combined organic layer was concentrated, dried over sodium sulfate, and then washed with brine. The final mixture was purified by column chromatography using n-hexane as the eluent. The product was obtained as a brown color powder. The yield was 72%. ¹H NMR (300 MHz, CDCl₃) δ 7.35 (s, 3H), 4.45 (s, 6H);

2-3. TPB

1,3,5-Tris(bromomethyl)benzene (356 mg, 1 mmol), LiCl (25 mg, 0.6 mmol), tetrakistriphenyl phosphanpalladium(0) (69 mg, 0.06

Table 1. Compositions of samples

Sample	EPDM (g)	Co-agent (μmol)	ZnO (g)	Dicumyl peroxide (g)
No_agent	1	-	0.03	0.005
TAIC_1%	1	40.1	0.03	0.005
TAIC_3%	1	120.4	0.03	0.005
TAIC_5%	1	200.6	0.03	0.005
TVB_1%	1	40.1	0.03	0.005
TVB_3%	1	120.4	0.03	0.005
TVB_5%	1	200.6	0.03	0.005
TPB_1%	1	40.1	0.03	0.005
TPB_3%	1	120.4	0.03	0.005
TPB_5%	1	200.6	0.03	0.005

mmol) and vinyltributylstannane (0.96 ml, 3.3 mmol) were dissolved in 10 ml of anhydrous dioxane in round bottom flask and heated at 100 °C for 15 h under a nitrogen atmosphere. After the reaction mixture was cooled to room temperature, dichloromethane (75 ml) was added and the organic layer was separated and subjected to four water washes. The white precipitates were then filtered off after the addition of a saturated KF solution. Hexane was used as the eluent in column chromatography on silica gel to purify the filtrate. The product was acquired as a colorless liquid. There was a 60% yield. ^{1}H NMR (500.13 MHz, CDCl$_3$) δ 3.35 (d, J=6.5 Hz, 6H, 3CH$_2$ sp3), 5.08 (m, 6H, 3CH$_2$CH]CH$_2$), 5.96 (m, 3H, 3CH$_2$CH]CH$_2$), 6.87 (s, 3H, PhH);

3. Preparation of Sample

In a 50 ml beaker, 10 ml of toluene was used to dissolve EPDM, co-agent, dicumyl peroxide, and zinc oxide. The mixture was then stirred at 150 rpm for three hours at room temperature. Toluene was evaporated at reduced pressure after the resulting solution was poured into a frame to create film. For 40 minutes at 155 °C, the film sample was crosslinked in the furnace. Reaction mixture details are compiled in Table 1.

4. Swelling Test

The sample size for the swelling test was between 4 and 5 mm^2. The samples were placed inside the beaker and submerged in toluene. Each sample was submerged in enough solvent to make it entirely disappear. Cover glasses and periodic solvent refills were employed to stop the solvent from evaporating. The samples were weighed while being removed excess solvent and dried on paper until no rise was seen. Each sample's crosslinking density was determined using the Flory-Rehner equation [24], Eq (1).

$$\rho_c = \frac{-[\ln(1-\phi_2) + \phi_2 + \chi\phi_2^2]}{V_s\left(\phi_2^{1/3} - \frac{\phi_2}{2}\right)} \quad (1)$$

$$\text{Swell ratio } (v_r) = \frac{(w_s + w_d)}{w_d} \quad (2)$$

$$\chi = 0.34 + \frac{V_s(\delta_s - \delta_r)^2}{RT} \quad (3)$$

$$\phi_2 = 1/v_r \quad (4)$$

where $w_s + w_d$, w_d, V_s, δ_s, and δ_r are the total weight of swollen rubber, the initial weight of rubber, the molar volume of solvent, the solubility of parameter of solvent, and the solubility of parameter of polymer, respectively. In this experiment, V_s and δ_s values of toluene were 106.5 cm^3/mol and 18.2 (MPa)$^{1/2}$, whereas EPDM's δ_r value was 16.3 (MPa)$^{1/2}$ [25]. R was set to 8.3144598 J/mol·K, while T was set to 300 K.

5. Thermal Stability

Thermogravimetric analysis (TGA, N-1000, Scinco, Republic of Korea) was carried out on the prepared samples. From room temperature to 600 °C in an environment of air, the samples were heated at a rate of 10 °C/min. Sample masses ranged from 5 to 7 mg. With a predetermined heating rate, the change in mass was measured as a function of temperature.

6. Tensile Strength and Elongation

To investigate the mechanical properties of the composites, tensile strength and strain were measured by using a Universal Testing Machine (UTM, NA-ST250K, NANOTECH, Republic of Korea). Samples with dimensions of 10 mm×5 mm×0.3 mm were clamped and dragged till cut-off in the tensile mode. The results from five samples were averaged.

RESULTS AND DISCUSSION

1. Optimization of Crosslinking Temperature

To identify the optimal crosslinking temperature, TAIC 1% samples were crosslinked for 40 minutes at 145 °C, 155 °C, and 170 °C. The crosslinking density was then calculated using the Flory-Rehner equation after performing a swelling test (Table 2). The samples that were crosslinked at 140 °C and 170 °C had crosslinking densities of 1.03 and 1.15, respectively, while the sample that was crosslinked at 155 °C had a crosslinking density of 4.33, which was around four-times higher. It is thought that TAIC, which serves as a crosslinking point, broke down at 170 °C because the temperature was too high. In the case of 140 °C, it seems that the temperature is too low for the complete cross-linking reaction, resulting in insufficient crosslinking. To prepare samples, cross-linking in this study was done at the optimal conditions of 155 °C for 40 min.

2. Thermal Stability Depending on Co-agents

The thermal stability of EPDM elastomers dependent on types of co-agents was investigated by assessing thermal breakdown of the elastomers made using 1% of TAIC, TVB, and TPB at a 10 °C/min ramping speed in ambient atmosphere (Fig. 1(a)). It is shown that residual solvent effects influence thermograms up to 200 °C (Fig. 1(a)), and differential thermogravimetric analysis (DTG) in Fig. 1(b) makes it evident that co-agent effects can be seen on the thermal stability of EPDM elastomers above 200 °C. Above 200 °C,

Table 2. Different crosslinking density and swell ratio according to crosslinking temperatures at 145 °C/ 155 °C/ 170 °C

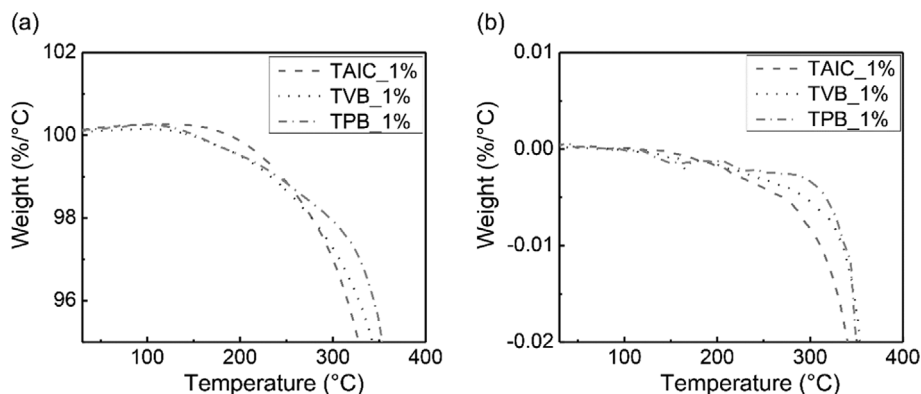| Crosslinking temperature (°C)	Swell ratio (v_r)	Crosslinking density (ρ_c; 10^{-6} mol/cm^3)
145	23.86	1.03
155	13.52	4.33
170	22.83	1.15

Fig. 1. (a) Effect of co-agents on initial thermal degradation of TAIC_1%, TVB_1%, and TPB_1%. and (b) their differential thermogravimetric analysis.
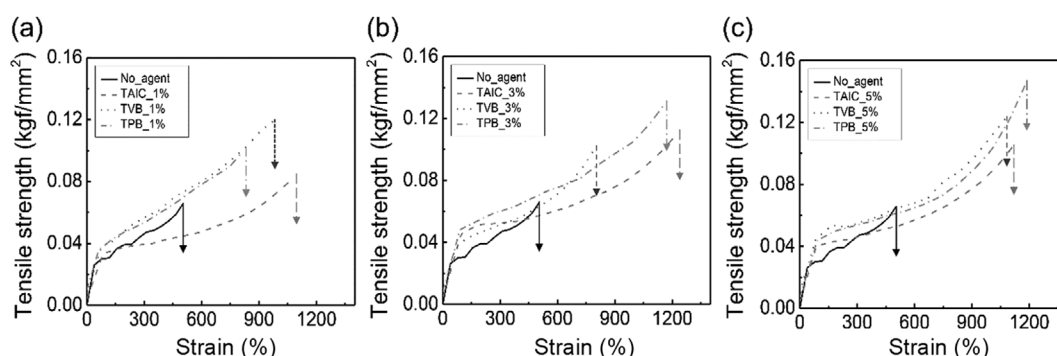

Fig. 2. Tensile strength-strain curves of EPDM elastomers crosslinked with (a) 1%, (b) 3%, and (c) 5% of TAIC, TVB and TPB.
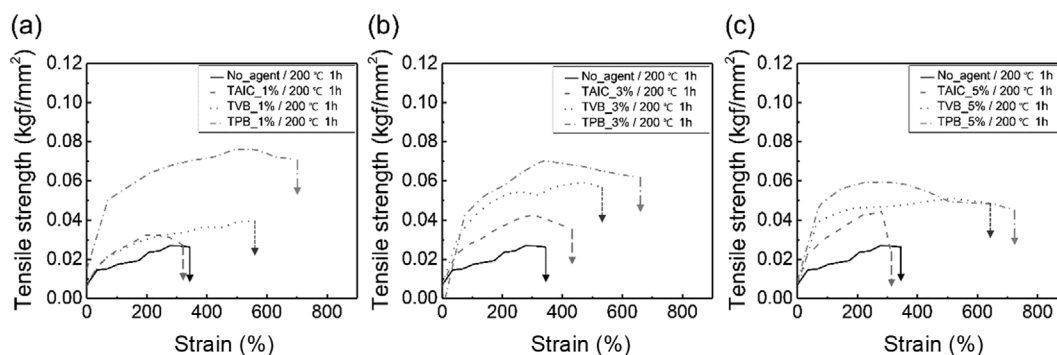

Fig. 3. Tensile strength and strain rate of the sample after heat treatment (200 °C, 1 h) comparable to the group average in (a) TAIC_1%/ TVB_1%/ TPB_1%, (b) TAIC_3%/ TVB_3%/ TPB_3%, (c) TAIC_5%/ TVB_5%/ TPB_5%.

TAIC_1% starts to drastically degrade thermally, while TVB_1% and TPB_1% start to lose weight at roughly 210 and 290 °C, respectively. These findings unequivocally show that aromatic ring co-agents produce more thermally stable elastomers than TAIC that has thermally fragile isocyanurate ring structure.

3. Mechanical Properties

Tensile strength and elongation at the break point were measured at a rate of 50 mm/min for the samples produced at each co-agent mixing ratio to compare the mechanical properties of elastomers before and after heat treatment. The average values of tensile strength and elongation percentage were derived from the results of five measurements, and each sample was cut into a standard size of 15 mm by 6 mm. Tensile strength and elongation curves of the samples with values that are most similar to averages are shown in Figs. 2 and 3. The sample without co-agents had an initial tensile strength and elongation value of 0.0748 kg/mm^2 and 656.6%, respectively. The average tensile strength for TAIC_1%, TVB_1%, and TPB_1% was 0.0868, 0.0858, and 0.119 kg/mm^2, while the average elongation was 1011.9, 1152.9, and 1281.5%, respectively. These findings unequivocally demonstrate that TVB and TPB serve as a co-agent and a site of crosslinking for the polymer main chains [26,27], resulting in EPDM treated with co-agents exhib-
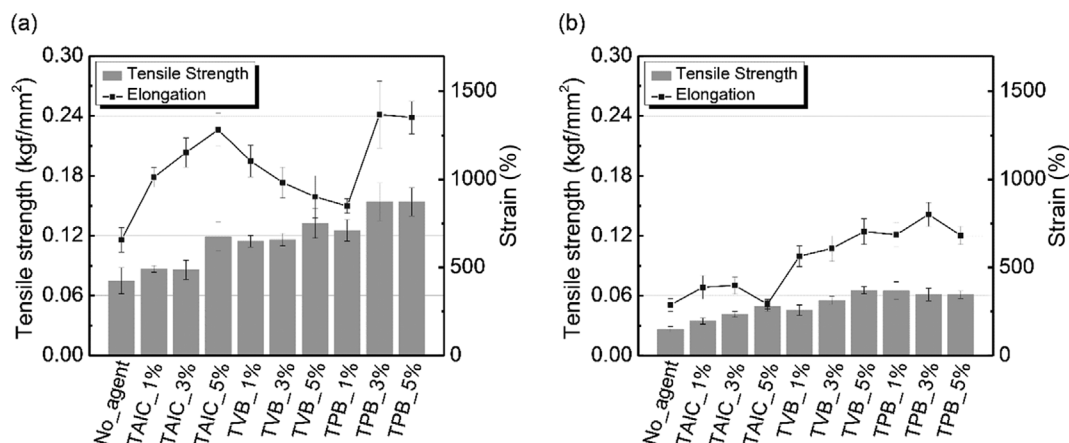
Fig. 4. Maximum tensile strength and strain rate of samples (a) before and (b) after heat treatment.

Table 3. Average tensile strengths and elongations of samples before and after heat treatment

Co-agent	Tensile strength (kg/mm^2)		Elongation (%)	
	Before	After	Before	After
No_agent	0.0748	0.0264	656.6	287.5
TAIC_1%	0.0868	0.0346	1,011.9	387.5
TAIC_3%	0.114	0.0456	1,004.1	398.0
TAIC_5%	0.125	0.0650	849.2	291.7
TVB_1%	0.0858	0.0414	1,152.9	564.5
TVB_3%	0.120	0.0552	982.2	607.9
TVB_5%	0.154	0.0612	1,368.5	704.4
TPB_1%	0.119	0.0496	1,281.5	686.5
TPB_3%	0.143	0.0656	900.9	801.8
TPB_5%	0.154	0.0610	1,350.6	681.9

iting greater tensile strength and elongation. Note that the shape of the tensile strength-strain curves before and after heat treatment clearly changes, demonstrating that for the samples before heat treatment the ultimate strength was at the fracture point but not after. We assume that the discrepancy in our sample films for model study is due to the varying thickness of the film samples after heat treatment. Because weakened parts are first fractured and stretched under tensile strength, the film becomes stretchy like cheese after heat treatment.

Elastomers synthesized with TVB and TPB behave differently from those prepared with TAIC when co-agent concentrations rise. Tensile strength of elastomers prepared with 1, 3, and 5% of TAIC increases from 0.0868 to 0.114 and 0.125 kg/mm^2, respectively, before heat treatment, whereas elongation percentages decrease from 1,011.9 to 1,004.1 and 849.2%, respectively. This finding suggests that increased crosslinking points increase tensile strength but decrease tensile elongation. Tensile strength for elastomers made with TVB and TPB increased up to 0.154 kg/mm^2 with an increase in co-agent concentrations (Table 3 and Fig. 3(b) and 3(c), Fig. 4(a)). Their elongation rates, however, exhibited erratic behavior. The elongation rates considerably fell to 982.2 and 900.9%, respectively,

with a 3% concentration of TVB and TPB, and then increased to 1,368.5 and 1,350.6%, respectively, with a 5% concentration of co-agent. We believe that the unequal distribution of TVB and TPB in the EPDM matrix is the cause of this erratic behavior. The stiff phenyl ring in TVB and TPB would prefer to self-aggregate via π-π interactions at certain concentrations rather than combining with the alkyl chains of EPDM via hydrophobic interactions, in contrast to TAIC based on C-C and C-N single bonds.

Despite this erratic behavior in tensile elongation, the advantage of the stiff phenyl ring in TVB and TPB was evident when tensile strength and elongation were evaluated after treating these elastomers at a high temperature. To assess the loss of mechanical qualities brought on by the breakdown of crosslinking sites, the sample was heated at 200 °C for 1 hour in air. Then, using UTM in the same manner, the average values of tensile strength and elongation were determined. Tensile strengths of elastomers made with TVB and TPB declined below 50% from their initial values, as shown by the tensile strength and elongation curves after heat treatment in Fig. 3. For instance, the tensile strength of TPB_5% dropped by 60.3% from 0.154 to 0.061 kg/mm^2 (Table 3). The elastomers' tensile elongation was also reduced by 10-80% from its initial values (Table 3). Nevertheless, Fig. 4 makes it evident that elastomers prepared with TVB and TPB have superior thermal stability than those prepared with TAIC. Tensile elongation of elastomers prepared with TVB and TPB is still evident beyond 560%, whereas elongation percentage for those prepared with TAIC is less than 400%. It is clear that the central isocyanurate ring, which has C-N and C-C single bonds, decomposes at high temperatures, which clearly breaks the cross-linking point [28,29], and that co-agents TVB and TPB, which use phenyl rings as their core structures, contribute to their improved heat resistance. It should be noticed that the tensile elongation has the lowest value at 3% TPB, reaching 900.9%, and rises to 1,281.5 and 1,350.6% at 1 and 5% TPB. Moreover, after heat treatment, the variance of tensile elongation is lowest at 3% TPB (801.8%) and significantly lower at 1 and 5% TPB (686.5 and 681.9%, respectively). The rubber elastomer that was cured with 3% TPB is clearly the most thermally stable according to these data, most likely as a result of the uniform distribution of cross-linking points.

Table 4. The swell ratio and crosslinking density of samples before and after heat treatment

Co-agent	Swell ratio (v_r)		Crosslinking density (ρ_c; 10^{-6} mol/cm^3)		
	Before	After	Before	After	Change%
TAIC_1%	13.44	26.90	4.39	0.77	−82.5
TAIC_3%	12.02	18.86	5.87	1.85	−68.5
TAIC_5%	11.28	14.23	6.93	3.78	−45.5
TVB_1%	13.89	17.91	4.03	2.10	−47.9
TVB_3%	13.54	15.56	4.07	3.00	−26.3
TVB_5%	12.99	13.65	4.29	4.21	−1.9
TPB_1%	13.79	16.30	4.10	2.67	−34.9
TPB_3%	12.86	13.59	4.91	4.26	−13.2
TPB_5%	12.54	15.55	5.26	3.01	−42.8

4. Swelling Index

A swelling test was carried out to look into the relationship between the crosslinking density and the mechanical characteristics of the manufactured samples. All elastomers have crosslinking densities that are greater than 4.0×10^{-6} mol/cm^3 and their crosslinking densities increased with co-agent concentrations (Table 4). For elastomers made with TAIC, the increase in crosslinking densities was greatest, rising from 4.39×10^{-6} to 6.93×10^{-6} mol/cm^3, whereas for elastomers made with TVB, the increase was only slight, rising from 4.03×10^{-6} to 4.29×10^{-6} mol/cm^3. The crosslinking densities of the elastomers made with TPB increased at a moderate rate, from 4.10×10^{-6} to 5.26×10^{-6} mol/cm^3. It appears that TVB without alkyl groups may be less miscible with EPDM than TAIC, resulting in an increase in crosslinking densities in a narrow range. TAIC appears to be the most miscible with EPDM, exhibiting a monotonic increase in the crosslinking densities with its added concentrations [30,31]. These findings seem to indicate that the crosslinking densities of the resultant elastomers are directly influenced by the co-agents' dispersibility in the EPDM matrix. Following heat treatment, the crosslinking densities of the TAIC_1%, _3%, and _5% were decreased by 82.5%, 68.5%, and 45.5%, respectively. TVB_1%, _3%, and _5% elastomers, on the other hand, showed declines of 47.9%, 26.3%, and 1.9%, respectively, and for TPB_1%, _3, and _5%, the decrease in the crosslinking densities were 34.9%, 13.2%, and 42.8%, respectively. These findings show that crosslinking sites of elastomers made with TVB and TPB are largely maintained in the presence of extreme thermal conditions, whereas TAIC decomposes to a significant extent due to its low heat resistance. According to the smallest variation of the swelling ratio (13.59%) after heat treatment in comparison to that before heat treatment (12.86%), the rubber crosslinked with 3% of TPB has the most evenly distributed cross-linking points in the rubber matrix, resulting in the most thermally stable rubber during the heat treatment. On the other hand, there is a noticeable difference between the samples at 1 and 5% TPB before and after heat treatment. The swelling ratio increased from 13.79 to 16.30 for 1% TPB and from 12.54 to 15.55% for 5% TPB, and the crosslinking density decreased from 4.10 to 2.67 μmol/cm^3 for 1% TPB and from 5.26 to 3.01 μmol/cm^3 for 5% TPB, indicating that rubber elastomers cured with 1 and 5% TPB are less thermally stable than that cured with 3% TPB. Our findings should be understood in light of TPB's ability to disperse in the rubber matrix. To equally distribute and crosslink TPB in the rubber matrix, we think 3% TPB is the optimal amount. It appears that there may be some unevenness in the distribution of crosslinking points at 1 and 5% TPB.

CONCLUSIONS

The disadvantage of rubber elastomers cured with TAIC, one of the most popular co-agents, is low thermal stability at high processing temperatures because of the rapidly decomposable isocyanurate ring core. The results showed that following heat treatment at a high temperature, the tensile strength and elongation of the EPDM elastomers produced by co-agents TVB and TPB with a phenyl ring as its core structure were significantly preserved. It was established that the greatly increased thermal stability of EPDM elastomers was caused by the phenyl ring's greater bond strength in TVB and TPB compared to C-C and C-N single bonds in TACI. The data, on the other hand, indicated that TVB and TPB had worse compatibility with EPDM than TAIC, most likely as a result of strong π-π interactions, and that additional integration of alkyls into the chemical structure of the phenyl-based co-agents would resolve this compatibility issue.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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