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ORIGINAL RESEARCH ARTICLE

Mechanical properties of pyrolysis carbon black in rubber compound application

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ABSTRACT

Waste tire pyrolysis is a thermal decomposition process that converts waste tires into liquid fuel which also produce by product material such as producer gas, pyrolysis carbon black (CBp), and steel wire. Nowadays, carbon black produced by pyrolysis is being employed as a low-grade carbon base fuel. The technical feasibility of using CBp as a substitute for commercial carbon black N330 in styrene-butadiene rubber (SBR) was investigated in the study. The researcher also looked at how the composition ratio of CBp and N330 affected the mechanical characteristics of rubber in comparison to the outcomes of pure carbon black N330. It was discovered that the low composition ratio of 20% CBp and 80% N330 (R-2) had comparable Mooney viscosity to that of N330 carbon black, as well as the highest torque (MH) and torque increment (ΔM) values, but increased CBp content led to increased rubber viscosity and decreased cure time due to sulfur residues CBp was inferior to N330 in its effect on reinforcement. With an increase in CBp content, the tensile strength, shear strength, and elongation at break of SBR vulcanizates decreased considerably, while the hardness increased. Consequently, the CBp value evaluated for hardness applications provides significant manufacturing cost savings.

Keywords: pyrolysis carbon black; waste tires; styrene-butadiene rubber; mechanical properties; N330

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1. Introduction

The BCG Economy is an economic model for sustainable development that focuses on systems that are planned and designed to use resources and energy efficiently. It has infiltrated the modern automotive industry and focuses on systems that are planned and designed to use resources and energy efficiently. It is in line with at least five of the United Nations Sustainable Development Goals (SDGs), such as sustainable production and consumption, climate change conservation, diversity cooperation for sustainable development, and reducing inequality. It is also in line with the philosophy of sufficiency economy, which is an important principle in Thai economic and social development.

Pyrolysis is the process of heating hydrocarbon material at a temperature of 450–700 degrees Celsius in an oxygen-free condition in order to reform hydrocarbon fuel substances. It has many advantages such as low cost, high efficiency, and little environmental pollution. Focusing on tyre pyrolysis process, the products consist of gas and liquid products such as hydrogen gas, hydrocarbon gas (methane, ethane, propane, butane, etc.), oil products with several important properties, solid products such as steel wire, and pyrolysis carbon black (CBp). Pyrolysis carbon black has a mass ratio of 30% or more depending on the temperature of the pyrolysis, and its purity cannot be compared to the ASTM standard, causing the current pyrolysis plant to utilize carbon black as fuel with low value[1].

Pyrolysis carbon black (CBp) is comparable to commercial carbon black, but it contains high ash and sulfur. It is ideal for rubber manufacture, but its high concentration of impurities and particle structure limits its utilization[2]. Unprocessed CBp is used as a low-grade reinforced filler in the manufacture of low-quality rubber and plastic materials and as a pigment for ink. Therefore, there must be studies to improve the quality to be acceptable in the industry and applied.

The demineralization of pyrolytic carbon black obtained from vacuum pyrolysis of used tires was investigated. The carbon black was contaminated with various additives from the original tire and by products of the pyrolysis process. The study explores the reduction of ash content in the carbon black through treatment with sulfuric acid and sodium hydroxide. The variables studied include the ratio of reactant to carbon black, the reactant concentration, the treatment temperature, and the reaction time. The properties of the commercial carbon black filler grade N539 were compared to those of the CBp recovered before and after the demineralization treatment[3]. In addition, the demineralization process with common reagents (HCl and NaOH) to recover the carbon black was conducted by using different parameters such as soaking time, temperature, reagent/CBp ratio, and reagent concentration. The demineralized CBp (dCBp) showed a carbon content of 92.9 wt%, while the ash content decreased from 15.0 wt% to 4.9 wt%. The BET surface area was 76.3 m^2/g, and textural characterizations (SEM/EDX and TEM) revealed that dCBp is composed of primary particles lower than 100 nm. Finally, dCBp was used in stirene butadiene rubber (SBR) compounding, probing its technical feasibility as a substitute for commercial CB N550[1].

However, the basic properties of pyrolysis carbon black of waste tires and its application in the transition layer rubber of all steel radial tires was discussed. The chemical composition of pyrolysis carbon black includes C, O, Cu, Zn, and other elements. The content of ash and fine powder in pyrolysis carbon black is high, and the 300% elongation stress is high. Pyrolysis carbon black is different from furnace black N326, which is commonly used in rubber, in terms of chemical properties. The paper presents experimental results that show that the use of pyrolysis carbon black in the transition layer of all steel radial tire rubber reduces compression heat generation and dynamic loss, and increases elongation at break and resilience, while decreasing tensile stress and tear strength. The paper also calculates that the use of 15 used tire pyrolysis carbon black instead of furnace carbon black N326 in all steel radial tire transition layer rubber application saves about $22.86 in production costs per ton of blended rubber[4] and the evaluation of a chemical process for upgrading the recovered carbon black derived from the pyrolysis of end-of-life tires in terms of ash content and presence of acidic functional groups. The statistical analysis showed that the acid concentration is the only significant crease with respect to those found in the raw CBp (9.63 mmol NH_3/g) and in the reference virgin carbon black (N550) (3.37 mmol NH_3/g)[5]. Therefore, the HNO_3 reduced the ash content and increased both external surface area and concentration of acidic functional groups, which is expected to offer better filler/polymer interaction and in-rubber performance, at least regarding the raw CBp.

The researcher was intended to investigate the quality enhancement of carbon from the pyrolysis of used tires. The research team anticipates the significance of particulate utilization based on the current evaluation of rCB with landfill disposal costs of roughly 3500 baht/ton.

This study utilized CBp as a substitute for commercial carbon black N330 in stirene-butadiene rubber (SBR). Commercial carbon black N330 was selected because CBp had a comparable surface area (approximately 78 m^2/g) in this experiment. In addition, the researcher investigated the effect of the size and ratio of CBp on the mechanical properties of rubber compared to the carbon black N330 results.

2. Materials and methods

2.1. Materials

SBR, N330, and pyrolysis carbon black (CBp) were major materials for this work. The pyrolysis carbon black (CBp) used in this research was collected from Pyro Energie Co., Ltd. SBR (SBR1502) was a product of Microseen Co., Ltd. Stearic acid (SA-1810) was purchased from Sarapatchemical. ZnO was purchased from Cernic International Co., Ltd. Both SA and ZnO were activators for curing recipes. Sulfur supplied by Sarapatchemical Co., Ltd. was a curing agent for SBR. TBBS as an accelerator for sulfur curing were both obtained from Microseen Co., Ltd.

2.2. Sample preparations

The SBR compound formulation was based on the ASTM D3191 standard. The formulations of the compounds are shown in **Table 1**. R-1, R-2, R-3, R-4, R-5, and R-6 are sample codes representing the weight ratio of N330 and CBp as 100/0, 80/20, 60/40, 40/60, 20/80, and 0/1000, respectively. Formulations of the rubber compounds are based on parts per hundred of rubber (phr). SBR was combined with SA, Zinc Oxide, and carbon black in a two-roll mill until a homogenous mixture was obtained at 95 ℃ and 15 RPM. The mixture was then mixed with sulfur and TBBS.

Table 1. Formulations of the rubber compounds.

Material (phr)	**Composition**					
	R-1	**R-2**	**R-3**	**R-4**	**R-5**	**R-6**
SBR 1502	100	100	100	100	100	100
Carbon black N330	50	40	30	20	10	0
Pyrolysis carbon black	0	10	20	30	40	50
Zinc oxide	3	3	3	3	3	3
Stearic acid	1	1	1	1	1	1
TBBS	50	50	50	50	50	50
Sulfur	1.75	1.75	1.75	1.75	1.75	1.75

2.3. Measurements

2.3.1. Sample preparations

The main objective of the characterization process has been to compare the physical, chemical, and thermal properties of carbon black waste to the carbon black standard. These measures are taken to assure the functionality of the carbon black filler to be used in rubber compounding.

2.3.2. Characterization of carbon black

The ash content of carbon black was determined using ASTM D1506. The total and external surface area by nitrogen adsorption (BET) of carbon black was by multi-point N2 adsorption at 300 ℃ in the Thermo Fisher Scientific model Prisma E. SEM/EDX analyses were conducted using Axia ChemiSEM, Thermoscientific, Germany instrument.

2.3.3. Characterization of rubber compound

Vulcanization curves are determined using an Ektron Tek model EKT-2000S. The testing is conducted at a temperature of 160 ℃ for durations of 45 and 60 min, according to the ASTM D5289 standard. Density was determined from electronic densimeter. The Mooney viscosity was determined from a Mooney Viscometer model EKT-2001M. Tensile and tear resistance properties were measured using the Testometric M500-25AT model. The ASTM D412 test utilizes tensile strength to cut specimens into dumbbell shapes, meeting Type C requirements. The method ASTM D624 measures the tear resistance of specimens prepared per Die C. Shore A durometer measures material hardness using ASTM D2240 standard for testing.

3. Results and discussion

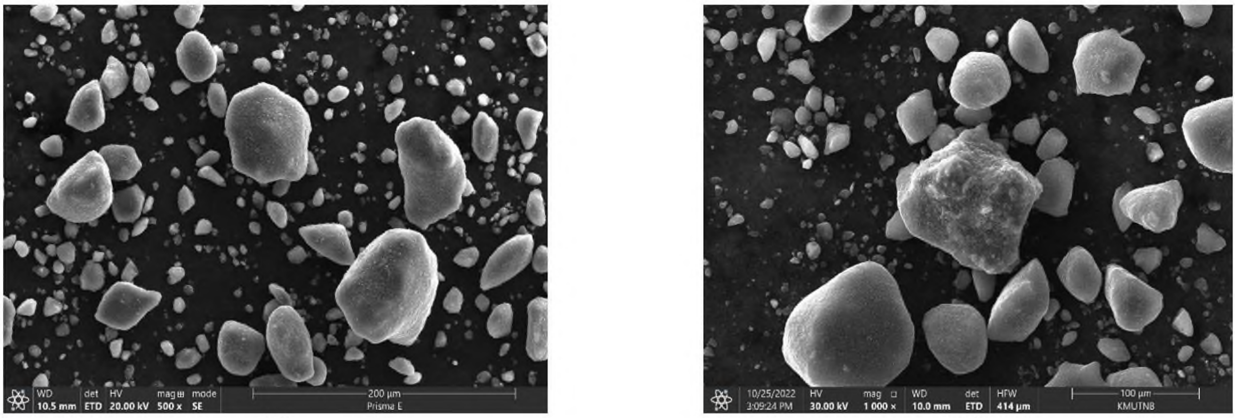
3.1. Characterization of carbon black

The characteristics of the CBp resulting from tire pyrolysis are detailed in **Table 2**. A significant distinction between N550 and CBp is the large inorganic component content of the ash contain. CBp contains 17.45%, which is considerably higher than N330. Inorganic components of CBp include ZnO and S, which are used as curing catalysts and agents, as well as mineral fillings or compounds such as SiO_2 and Al_2O_3[6]. In theory, increasing the surface area enhances reinforcement[7]. The surface area of N330 was 75.62 m^2/g, while that of CBp was 60.52 m^2/g.

Table 2. Characteristics of pyrolytic carbon black and commercial carbon black.

Sample	**Parameter**	
	Ash content (%)	**BET surface area (m^2/g)**
N330	0.25	75.62
CBp	17.45	60.56

As shown in **Figure 1**, SEM micrograph analysis revealed distinct morphological differences between carbon black N330 and CBp. **Figure 1b** depicted the morphological properties of pyrolysis carbon black, in contrast to **Figure 1a**. Examining the pyrolysis carbon black revealed that it possessed a physical surface area with particulates of varying sizes dispersed throughout the diagram. In addition, there are both mineral deposits and carbonaceous deposits.



(a) (b)

Figure 1. SEM micrographs **(a)** carbon black N330; **(b)** pyrolysis carbon black.

EDX characterization is shown in **Table 3**. On the pyrolysis carbon black showed high content of calcium (Ca), silica (Si), zinc (Zn), and aluminium (Al). The majority of passenger car tires contain silica as a polymer additive to improve road traction or reduce rolling resistance. The high calcium content is found to be a suitable substitute for calcium carbonate to partially replace carbon black as a filler in compounding in order to reduce costs[8]. In contrast, the N330 surfaces showed the predominant presence of C, S, and O.

Table 3. EDX characterization of N330 and CBp.

Element (wt%)	Sample	
	N330	CBp
C	93.8	61.3
O	5.5	25.8
Al	-	1.4
Si	-	5.3
S	0.6	1.6
K	-	0.2
Mg	-	0.1
Ca	-	1.3
Fe	-	0.7
Zn	-	2.3

3.2. Characterization of rubber compound

Table 4 contains the curing parameters for the specified compounds such as Mooney viscosity at 100 ℃, minimum torque (ML), highest torque (MH), scorch torque (MS), torque increment (ΔM), and scorch time (Ts). The Mooney viscosity experiments conducted on rubber samples filled with CBp using different formulas, in comparison to the standard grade N330 carbon black, revealed that the R-2 formula produced viscosity values comparable to those of the standard grade N330 carbon black. In addition, as the proportion of CBp was increased, a discernible trend of increasing rubber viscosity was observed. In addition, the experimental results revealed that the incorporation of CBp in various proportions as a substitute for standard grade N330 carbon black in synthetic rubber, specifically in the R-2 formula, had the most significant impact on reducing the cure time of the rubber. Additionally, the cure time of the rubber was shorter than that of the standard grade. This is due to the presence of some residual sulfur in CBp from the pyrolysis process, which accelerates the vulcanization of the rubber[9]. Moreover, the R-2 formula represents the highest MH and ΔM values. These parameters increase in composites containing CBp, indicating that the vulcanization network formed is denser[10].

Table 4. Cure characteristics of SBR compounds.

Parameter	Composition					
	R-1	R-2	R-3	R-4	R-5	R-6
Mooney viscosity (ML (1 + 4) 100 ℃)	93.55	94.9	109.6	150.30	124.75	154.95
ML (dN.m)	3.62	4.195	4.76	5.71	5.15	6.22
MH (dN.m)	25.08	28.08	27.66	27.76	25.84	26.27
ΔM = MH − ML (dN.m)	21.46	23.89	22.90	22.05	20.69	20.05
Ts2 (min)	5.26	3.44	4.25	3.33	3.81	3.15
Ts90 (min)	28.11	19.41	21.09	20.26	22.72	22.15

3.3. Comparison of physical properties of mixed rubber

3.3.1. Density test

The density test results of the rubber indicated that within the substitution ranges specified by the R-2, R-3, and R-4 formulas, the density values were close to that of the standard grade N330 carbon black. However, when

CBp was added in higher quantities according to different mixing ratios, it resulted in a decrease in density. This is attributed to the varying amounts of antioxidants present in CBp from the pyrolysis process, which affects the density accordingly[10]. This relationship is depicted in **Figure 2**.

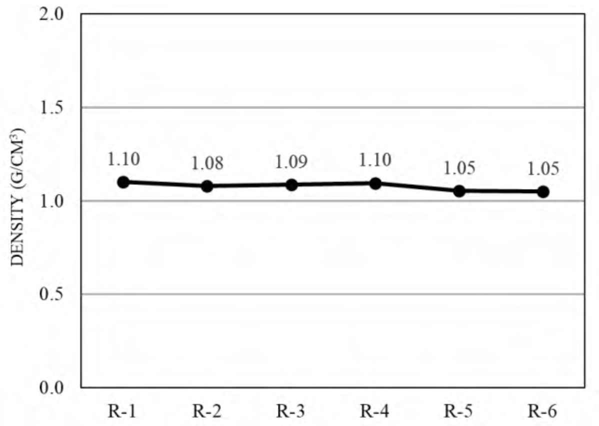


Figure 2. Comparison of density of rubber with different conditions.

3.3.2. Hardness test

Figure 3 depicts the outcome of this hardness test. The results obtained from testing the hardness of the composite rubber revealed that the incorporation of CBp had the ability to enhance the strength of the composite rubber. This can be attributed to the remaining sulfur present in CBp[9].

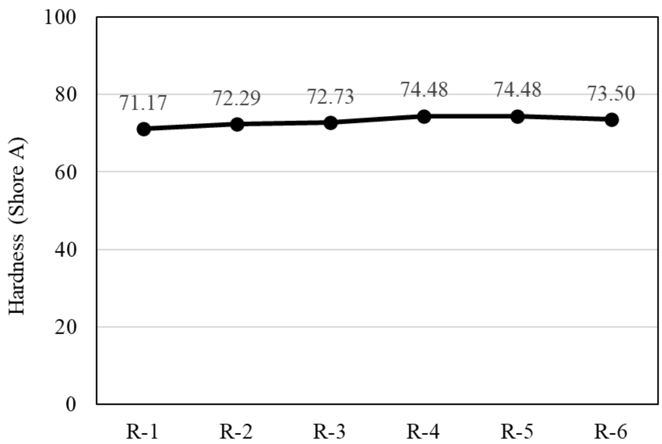


Figure 3. Comparison of Hardness of rubber with different conditions.

3.3.3. Tensile test

Figure 4a shows the tensile strength of SBR compounds at various ratios. Without any CBp, the tensile strength of the SBR compound was at 15.11 N/mm^2. At higher CBp content of N330/CBp 100/0 (R-1) and 80/20 (R-2), a significant decrease of over 29.04% was observed. Moreover, without N330, tensile strength decreased by 55.39%. Similarly, **Figure 4b** demonstrates that the elongation at break significantly decreased when a high content of CBp was applied. This decrease at a higher CBp content was primarily attributable to an increase in Si and Zn impurities, which posed the potential for defects, particularly under large deformation states during tensile deformation[11].

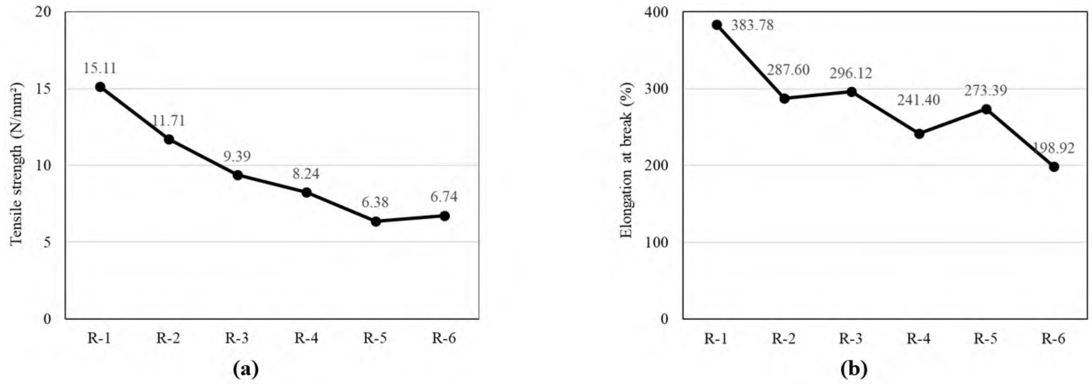


Figure 4. Comparison of tensile properties of rubber with different conditions. **(a)** tensile strength; **(b)** elongation at break.

3.3.4. Tear strength test

The tear strength test results, as illustrated in **Figure 5**, reveal that the incorporation of CBp demonstrates a tear resistance property similar to the standard grade N330 carbon black in the R-2 and R-3 ratios. At higher CBp contents of N330/CBp 80/20 (R-2) and 60/20 (R-3), the decline was 0.84% and 5.76%, respectively. However, in the R-4, R-5, and R-6 lower values are observed. In particular, the ratio of R-4 to R-5 decreased by approximately 37%. This can be attributed to the lower reinforcing capacity and higher dispersion characteristics of CBp compared to the standard grade N330[9].

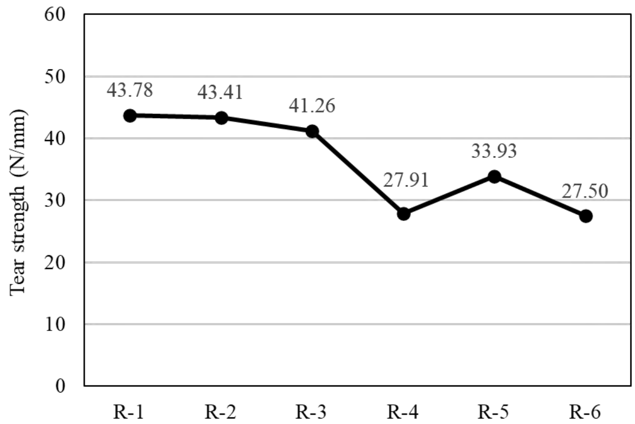


Figure 5. Comparison of tear strength of rubber with different conditions.

4. Conclusion

This study investigates the feasibility of substituting refuse tire pyrolysis carbon black (CBp) for N330 carbon black in SBR rubber compounds. Following the ASTM D3191 standard, six sample codes (R-1 to R-6) were formulated by varying the weight ratios of CBp and N330.

The characterization of curing parameters revealed that the R-2 formula containing CBp had a comparable Mooney viscosity to N330 carbon black, whereas a higher CBp content led to an increase in rubber viscosity and a decrease in cure time due to the presence of residual sulfur from pyrolysis. In addition, the R-2 formula exhibited the greatest MH and ΔM values, indicating the construction of a denser vulcanization network in the presence of CBp.

The hardness test revealed that the incorporation of CBp enhanced the strength of the composite rubber, attributed to the presence of residual sulfur in CBp.

Nonetheless, the tensile test revealed that a higher CBp content resulted in a significant decrease in tensile strength and elongation at break, as a consequence of the detrimental effects of increased Si and Zn impurities.

In the tear strength test, CBp demonstrated tear resistance comparable to N330 carbon black at ratios of 80/20 (R-2) and 60/40 (R-3). However, tear strength decreased considerably at higher CBp ratios (R-4, R-5, and R-6) due to CBp's lower reinforcing capacity and higher dispersion characteristics compared to standard N330.

Overall, the study demonstrates that CBp can be used as a partial replacement for N330 carbon black in rubber formulations. To accomplish the desired physical properties in the final rubber products, careful consideration of the mixing ratios is essential. These findings provide vital insights for the development of more environmentally responsible and cost-effective rubber manufacturing processes.

Author contributions

Conceptualization, TA, CW, and NN; methodology, TA and CW; validation, TA, NK, BS, and TN; formal analysis, TA, NK, BS, and TN; investigation, CW and NN; resources, TA; data curation, TA; writing—original draft preparation, TA; writing—review and editing, TA and CW; supervision, CW and NN. All authors have read and agreed to the published version of the manuscript.

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Conflict of interest

The authors declare no conflict of interest.

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