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Effect of Filler and Curing Agent on Mechanical, Damping Properties and Heat Resistance of Ethylene Propylene Diene Rubbers†

HAE YOUN PARK[1], TAE KYEONG NO[1], DONG GUK KANG[2], JAE SIK SEO[3], KYUNG MO YANG[3] and KWAN HO SEO[1,*]

[1]Department of Polymer Science & Engineering, Kyungpook National University, Daegu 702-701, Republic of Korea
[2]R&D Center, Pyunghwa Oilseal Industry Co. Ltd., Daegu 711-855, Republic of Korea
[3]Polymeric Materials Research Team, Hyundai Motor Company, Hwaseong-si 445-706, Gyeonggi-do, Republic of Korea

*Corresponding author: Fax: +82 53 9506623; Tel: +82 53 9505628; E-mail: khseo@knu.ac.kr

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Ethylene propylene diene rubber has been used for damping applications owing to its high tan δ value. This study measured the mechanical and damping properties of tyre compounds containing ethylene propylene diene rubber. High abrasion furnace black, semi-reinforcing furnace black, acetylene black and black pearl were used as fillers. Sulfur and dicumyl peroxide were used as curing agents. The mechanical and damping properties of compounds with ethylene propylene diene rubber and carbon black were examined and the effects of the curing agent on these compounds were observed. The measurements were carried out using a durometer, universal testing machine and dynamic mechanical analysis. The tensile strength and hardness increased with decreasing ethylene concentration in ethylene propylene diene rubber. In addition, the effects of carbon black and the curing agent for ethylene propylene diene rubber were examined. The tensile strength increased and the compression set improved when black pearl was added as a filler to ethylene propylene diene rubber. The tan δ of ethylene propylene diene rubber was enhanced by curing with dicumyl peroxide.

Key Words: Ethylene propylene diene rubber, Carbon black, Curing agent, Mechanical property, Damping property.

INTRODUCTION

Polymer compounds have gained importance for many years because the compounding of two polymers gives rise to enhanced physical properties for specific applications[1,2]. Ethylene propylene diene rubber is one of the fastest growing synthetic rubber materials, both in general purpose and specialty applications, since its commercialization in the 1960s[3-6]. The outstanding versatility of ethylene propylene diene rubber has broadened its use in thermoplastic vulcanisates, electrical insulation, roofing membranes, hoses, plastic impact modifications, motor oil additives and automotive applications. Ethylene propylene diene rubber is a type of self-reinforced rubber, which limits its usage. Reinforcing ethylene propylene diene rubber with carbon black or resin is a possible solution. Reinforcing fillers for elastomers include carbon black, silica, clay, plastic and fibers[7-10].

The dynamic mechanical properties are important parameters for determining the processing and properties of polymeric materials. For polymer compounds or polymer composites filled with inorganic particles, the relationship between the structure and properties tends toward greater complexity due to the formation of an interface between the components and between the fillers and matrix. The dynamic mechanical parameters of polymer materials, such as the storage modulus, loss modulus and mechanical damping, might be measured by dynamic mechanical analysis. In addition, dynamic mechanical measurements over a range of temperatures provide valuable insights into the structure, morphology and properties of polymer compounds. Dynamic mechanical analysis has been performed on polymer compounds[11-14]. Ethylene propylene diene rubber is used as a damping material owing to its high tan δ value. Therefore, it is expected that the compounding of carbon black with ethylene propylene diene rubber can increase the damping peak zone and produce a compounded, multi-functional damping material with good mechanical properties[15,16].

This study examined the mechanical and damping properties of ethylene propylene diene rubber and carbon black compounds, as well as the effects of the curing agent on the compounds.

EXPERIMENTAL

Two types of ethylene propylene diene rubber (EPDM) were used. KEP220 [ML (1 + 4) at 125 ºC, 28.0; ENB content,

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TABLE-1
COMPOUND FORMULATION OF THE COMPOUNDS (phr)*

Sample	EHS2	EHD2	ESS2	ESD2	EAS2	EAD2	EHS9	EHD9	ESS9	ESD9	EAS9	EAD9
KEP220	100	100	100	100	100	100	-	-	-	-	-	-
KEP960	-	-	-	-	-	-	100	100	100	100	100	100
HAF	45	45	-	-	-	-	45	45	-	-	-	-
SRF	-	-	60	60	-	-	-	-	60	60	-	-
Acetylene black	-	-	-	-	50	50	-	-	-	-	50	50
ZnO	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1	1	1	1	1	1
TMQ	2	2	2	2	2	2	2	2	2	2	2	2
Naphthene oil	50	50	50	50	50	50	50	50	50	50	50	50
Sulfur	0.5	-	0.5	-	0.5	-	0.5	-	0.5	-	0.5	-
DCP	-	5	-	5	-	5	-	5	-	5	-	5

*part per hundred; DCP = Dicumyl peroxide; TMQ = 2,2,4-Trimethyl-1,2-dihydroquinoneline.

4.6 wt %; ethylene content, 57.0 wt %] and KEP960 [ML (1 + 8) at 125 ºC, 49.0; ENB content, 5.7 wt %; ethylene content, 50.0 wt %] were obtained from Kumhopolychem, (Korea). The fillers were HAF (grade, N330; surface area, 79 m^2/g; OAN, 102 $cm^3/100$ g), SRF (grade, N762; surface area, 28 m^2/g; OAN, 65 $cm^3/100$ g) carbon black, supplied by Korea Carbon Black Co., (Korea). Acetylene black (purity > 99.9 %) was purchased from Ningbo Shanshan Co., (China).

Sample preparation: Table-1 lists the compounds used. The preparation was performed in a dispersion kneader (DK20, MIRAE rubber and plastic machinery Co., Korea). Ethylene propylene diene rubber was cut short and masticated on a two-roll mill (TRX-2100, INTCE, Korea) for 10 min at 100 ºC. Carbon black was then added. Zinc oxide, stearic acid, 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) and naphthene oil were then added and mixed for a further 0.5 h. The mixture was then compounded with a curing agent sulfur or dicumyl peroxide for 5 min and then sheeted-off. The vulcanized specimens were exposed to air at 130 ºC for 240 h in a Geer oven (Toyoseiki, Japan). The aging properties of the specimens were examined by measuring their physical properties.

Measurements: The hardness measurements were taken using a durometer (DPX-1000, USA). The shore A type hardness of the samples was measured according to ASTM D2240. The heat resistance of the samples was characterized using the ASTM D573 method. The mechanical properties, such as tensile strength, modulus and elongation at break were determined according to the ASTM D 412 using a Universal Testing Machine (UTM, Model-M 4465, Instron Corp., USA) at a cross-head speed of 500 mm/min and 25 ± 2 ºC. Dumb bell-shaped specimens were punched out from a vulcanized sheet using ASTM Die C. Five specimens were measured for each compound at the same elongation rate. Compression set tests (ASTM D 395) were performed on standard test specimens that had been vulcanized by a compression mold method. The test specimens were placed between the plates of the compression device with the spacers on each side, allowing sufficient clearance for bulging of the rubber when compressed. The bolts were tightened to allow the plates to be drawn together uniformly until they were in contact with the spacers. The percentage compression used was 25 % of the original thickness. The sample was placed at 100 ºC for 22 h. After compression, the specimen was removed from the device and allowed to recover for 0.5 h. The compression set was calculated using eqn. (1).

$$\text{Compression set } (\%) = [(t_0-t_1)/(t_0-t_2)] \times 100 \quad (1)$$

where t_0 is the original thickness of the specimen, t_1 the final thickness of the specimen and t_2 the thickness of the spacer bar used.

Dynamic mechanical analysis (Model-N535, Perkin-Elmer, USA) was used to measure the dynamic mechanical properties (shear, tensile and flexile modulus) and mechanical damping as a function of temperature or as a function of the impressed frequency. The samples were heated from -70 to 100 ºC at a heating rate of 10 ºC/min at a frequency of 10 Hz.

RESULTS AND DISCUSSION

Mechanical properties and heat resistance: Figs. 1-3 show the mechanical properties of the samples. KEP220 had higher hardness, tensile strength and elongation at break than KEP960. The hardness and tensile strength of the ethylene propylene diene rubber compounds increased with increasing ethylene content. Acetylene black mostly showed good mechanical properties. Moreover, the addition of dicumyl peroxide increased the hardness and elongation significantly. On the other hand, the tensile strength varied with the hardness and elongation. Conventional reinforcing fillers in rubber, such as carbon black, cause an increase in modulus with a consequent decrease in the elongation at break[17]. In the case of ethylene propylene diene rubber compounds with acetylene black, the hardness and tensile strength increased in presence of the reinforcing filler.

After aging (aged 240 h at 130 ºC), the change in the hardness of all vulcanizates tended to increase after the high temperature treatment. In addition the tensile strength of the samples increased or decreased. The elongation at break of the samples decreased to some extent. This suggests that the EAD2 sample possesses good tensile strength, modulus and elongation among the samples. The thermal stability increased with increasing dicumyl peroxide content.

Compression set: A compression set test was carried out to determine the effects of the filler loading on the compression set of ethylene propylene diene rubber. Fig. 4 shows the changes in the compression set against ethylene propylene diene rubber at various carbon black and curing agent loadings. Carbon black functions as a physical crosslinking agent, which helps in improving the crosslink density and reduce the compression set. Some crosslinks were broken during this resistance.

Therefore, when the load is relieved, there are fewer crosslinks responsible for this strain recovery than the number of crosslinks responsible for resisting compression, meaning that the specimen does not recover to its original thickness. As a result, even if filled with HAF, the EHS2 sample has a high-compression set when compressed at 100°C for 22 h. On the other hand, the compression set value decreased when acetylene black was used in the sealants simultaneously. This shows that the ethylene propylene diene rubber prepared using a combination of acetylene black has better compression performance.

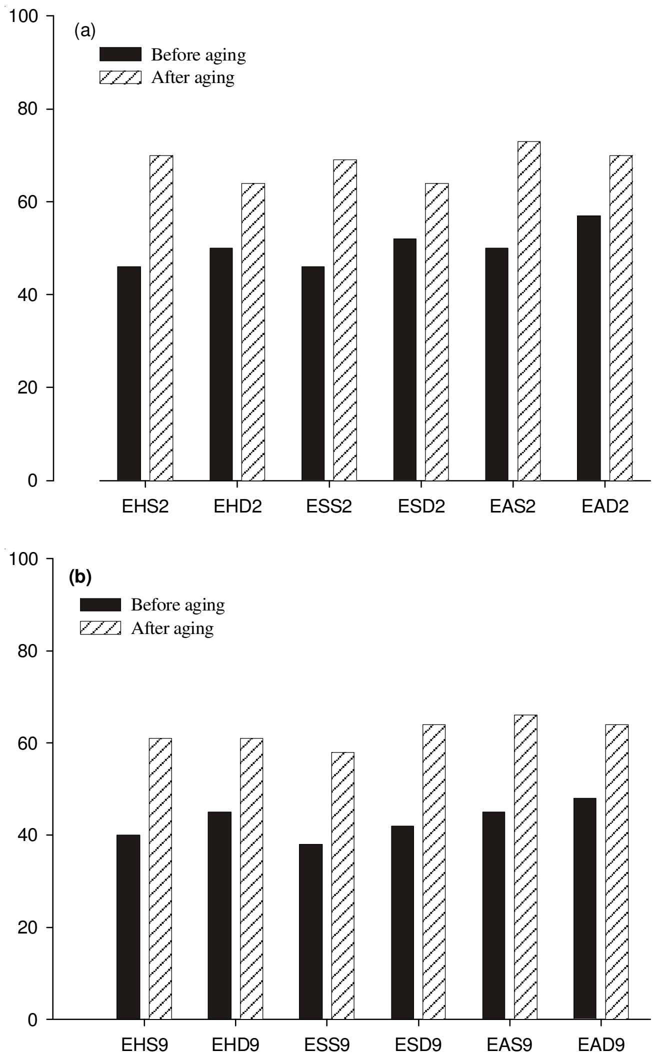


Fig. 1. Hardness of the prepared samples, before and after aging (a) KEP-220 and (b) KEP-960

Dynamic mechanical analysis: The damping properties of the samples were examined by dynamic mechanical analysis at room temperature. Fig. 5 shows the mechanical properties of the ethylene propylene diene rubber compounds. The technique provides information on the storage modulus and loss modulus, which are related to the storage and dissipation of energy, respectively. The loss modulus to storage modulus ratio is referred to as the internal damping or loss tangent (tan δ). The temperature ranged from -70 to 100 ºC, which is above the glass transition temperature (T_g) of ethylene propylene diene rubber, because the working temperature of the damping material is far above its T_g. KEP220 has a low crosslink density and the movement of molecules at higher temperatures results in higher viscosity. In the inspecting temperature range, samples ESD2 and EHS9 had the highest and lowest tan δ, respectively. This suggests that the tan δ of KEP220 with dicumyl peroxide increases.

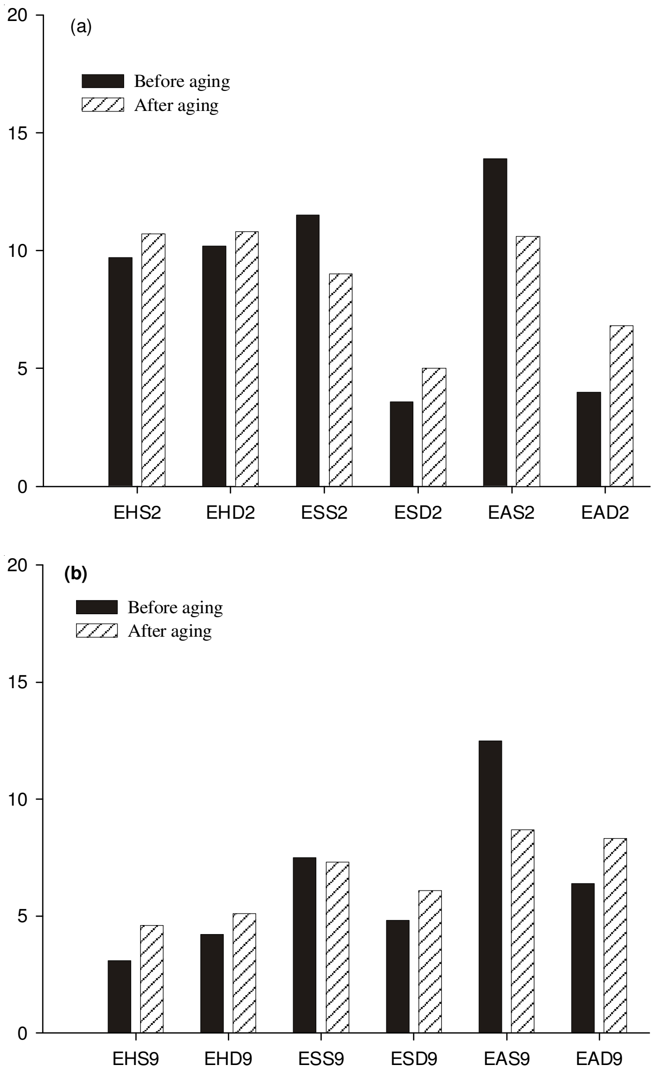
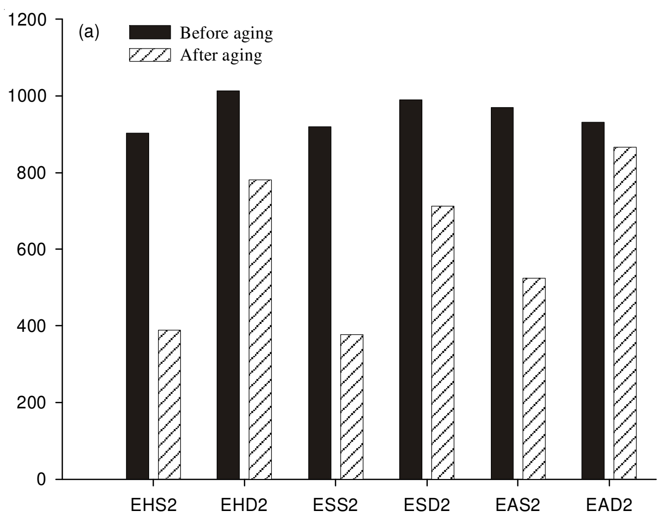


Fig. 2. Tensile strength of the prepared samples, before and after aging (a) KEP-220 and (b) KEP-960



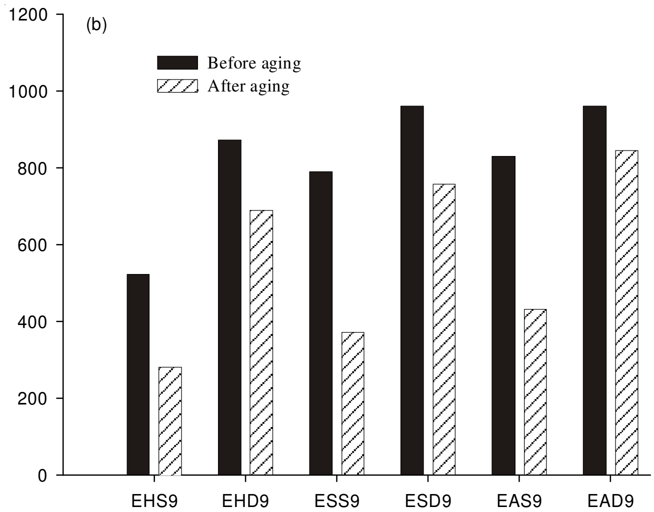


Fig. 3. Elongation at break of the prepared samples, before and after aging (a) KEP-220 and (b) KEP-960.

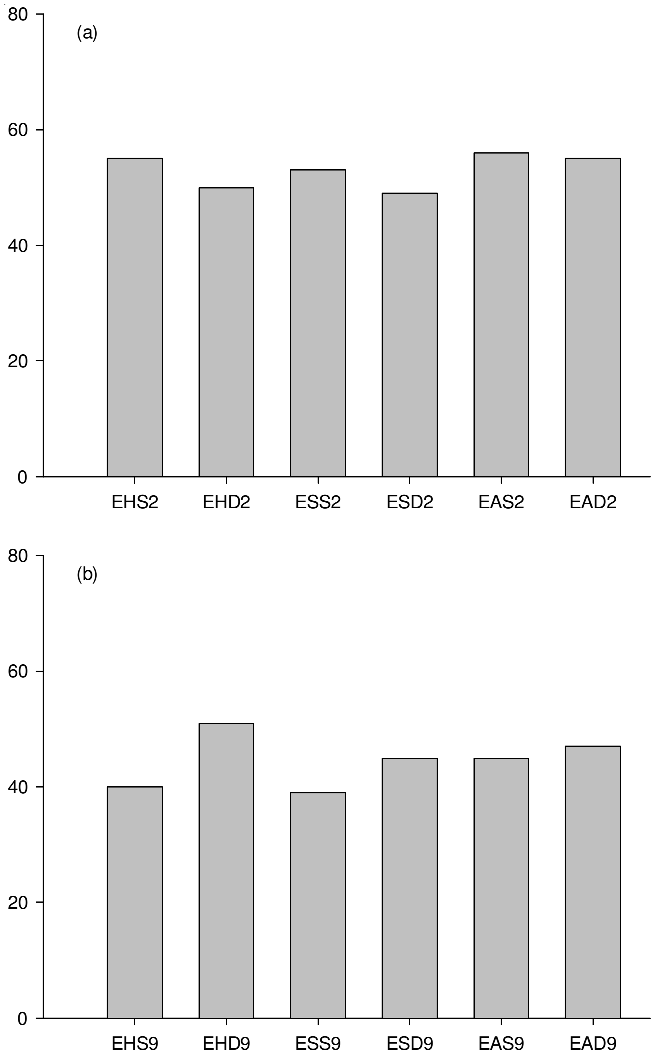


Fig. 4. Compression set of the prepared samples (a) KEP-220 and (b) KEP-960

Effect of dicumyl peroxide on the mechanical and damping properties of the ethylene propylene diene rubber compounds: Sulfur is used as a curing agent for all ratios of rubber compounds. In this part of the study, dicumyl peroxide was used instead as a curing agent and compared with sulfur. The mechanical properties of the ethylene propylene diene rubber compounds with 0.5 phr sulfur or 5 phr dicumyl peroxide as the curing agent were examined. Ethylene propylene diene rubber with dicumyl peroxide had a higher hardness and elongation at break as well as a lower tensile strength but the compression set was similar. Sulfur and dicumyl peroxide had significant effects on the damping properties of the ethylene propylene diene rubber compound. This suggests that sulfur and dicumyl peroxide affect the damping of the ethylene propylene diene rubber compounds. Tan δ increased remarkably when dicumyl peroxide was used, suggesting that dicumyl peroxide is a better curing agent for improving the damping of ethylene propylene diene rubber compounds than sulfur.

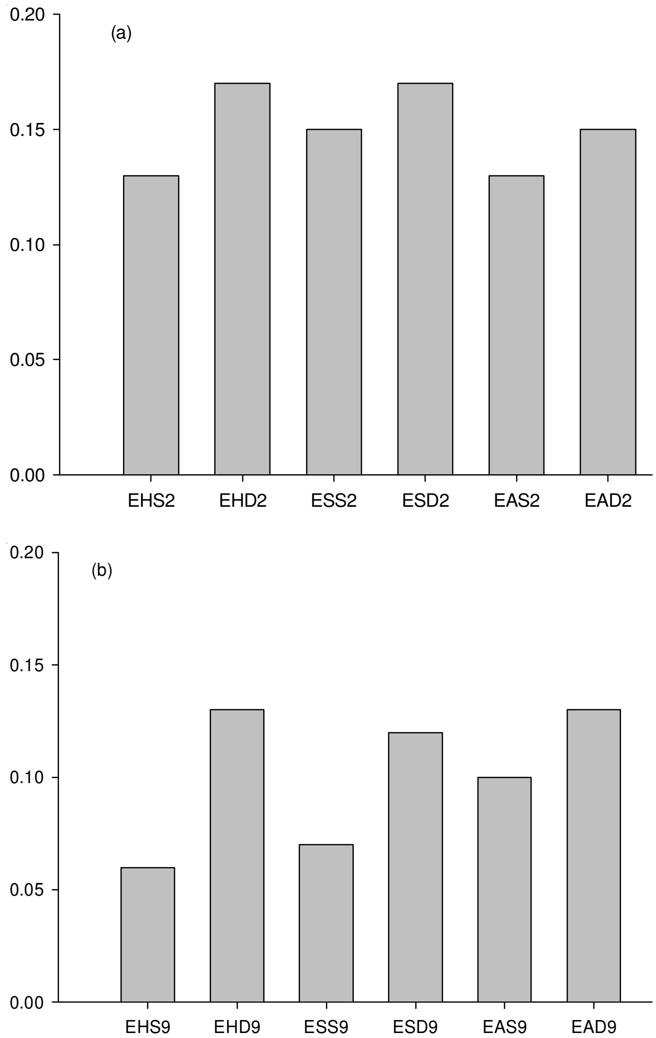


Fig. 5. Tan δ of the different prepared samples (a) KEP-220 and (b) KEP-960 at 25 °C

Conclusion

The mechanical and damping properties of ethylene propylene diene rubber and different compounds were examined. The measurements were conducted using a durometer, UTM and dynamic mechanical analysis. The mechanical properties (hardness, tensile strength and elongation at break) of ethylene propylene diene rubber were improved at high ethylene contents. Among the three fillers, the increase in heat resistance was most significant for acetylene black filled ethylene propylene diene rubber compounds. Curing agents sulfur and dicumyl peroxide affected the mechanical and damping properties of ethylene propylene diene rubber compounds. Compounds using peroxide as the curing agent showed superior mechanical properties, lower compression set and higher tan delta values than sulfur. Furthermore, dynamic mechanical analysis indicated that the tan delta of the ethylene propylene diene rubber compounds obtained was enhanced by compounding with dicumyl peroxide.

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