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ARAŞTIRMA MAKALESİ **RESEARCH PAPER**

Chemical Modification of Black Carbon Black for Coloring

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Abstract: Sealing profiles that are mainly used to prevent the ingress of water, noise, dust and air in the automotive industry are produced from synthetic Ethylene-propylene-diene monomer (EPDM) rubber. Although EPDM rubber is preferred due to its high mechanical properties and waterproof structure, it is necessary to reinforce it with various additives due to the requirements for profiles in automotive manufacturers' specifications. One of the fillers used to keep the fluidity at the desired level during production and to improve the mechanical properties and UV resistance of the profiles is carbon black (CB) and has the highest contribution rate in the EPDM rubber formulation. Due to its high amount in the rubber formulation, it allows the rubber formulation and subsequently the sealing profiles produced with this formulation to be produced only in black. However, recently, automotive manufacturers have demanded different color profiles in line with the demands of end users. Solubility and reactivity of CB is low and it tends to aggregate. In order for CB to be colored, its surface must be activated and polarized using different chemicals. This study aimed to oxidize the surface of CB with different chemicals and make it reactive. The highest oxidation level was determined after chemical analysis. Thus, the first step thus obtaining the first colored sealing profile that has not yet been produced in our country and in the world was taken in producing colored CB and subsequently colored EPDM rubber with a dye agent suitable for the structure.

Keywords: Carbon black oxidation, colored carbon black, colored EPDM, colored sealing profiles, EPDM.

Renklendirmek için Karbon Siyahının Kimyasal Modifikasyonu

Öz: Otomotiv sektöründe temel olarak su, gürültü, toz ve havanın içeri girmesini engellemek amacıyla kullanılan sızdırmazlık profilleri sentetik Etilen-propilen-dien monomer (EPDM) kauçuktan üretilmektedir. EPDM kauçuk, yüksek mekanik özellikleri ve su geçirmez yapısı nedeniyle tercih edilmesine rağmen, otomotiv üreticilerinin şartnamelerinde profillere yönelik talepleri nedeniyle çeşitli katkı maddeleri ile güçlendirilmesi gerekmektedir. Üretim esnasında akışkanlığın istenilen seviyede tutulması, profillerin mekanik özelliklerinin ve UV dayanımının artırılması amacıyla kullanılan dolgu maddelerinden biri de karbon siyahıdır (CB) ve EPDM kauçuk formülasyonunda en yüksek katkı oranına sahiptir. Kauçuk formülasyonunda yüksek miktarda bulunması sebebiyle kauçuk formülasyonunun ve dolayısıyla bu formülasyonla üretilen sızdırmazlık profillerinin sadece siyah renkte üretilmesine olanak sağlamaktadır. Ancak son dönemde otomotiv üreticileri, son kullanıcıların talepleri doğrultusunda farklı renk profilleri talep etmeye başlamıştır. CB'nin çözünürlüğü ve reaktivitesi düşüktür ve agregasyona eğilimlidir. CB'nin renklendirilebilmesi için yüzeyinin çeşitli kimyasallar kullanılarak aktifleştirilmesi ve polarize edilmesi gerekmektedir. Bu çalışmada CB'nin yüzeyinin farklı kimyasallar ile okside edilmesi ve reaktif hale getirilmesi amaçlanmıştır. Oksidasyon seviyesi en yüksek olan kimyasal analizler sonrası tespit edilmiştir. Böylece yapıya uygun boya ajanı ile renkli CB ve akabinde renkli EPDM kauçuğun üretilmesinin dolayısıyla ülkemizde ve dünyada henüz üretilmemiş ilk renkli sızdırmazlık profilinin elde edilebilmesinin ilk adımı atılmış olmuştur.

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Anahtar kelimeler: EPDM, Karbon siyahı oksidasyonu, Renklendirilmiş karbon siyahı, Renkli EPDM, Renkli sızdırmazlık profilleri.

INTRODUCTION

Almost all motor vehicles, from commercial to prestige vehicles, have an exterior plastic or fiberglass body with numerous panels and movable and/or fixed windows on the side doors. For this reason, there is a need for retaining tape designs to close and seal the gaps between one body panel and another and/or between moving/fixed windows and the body panel. These tape designs are called sealing profiles and are used in all automotive classes (Keeney, 2002). Sealing profiles are designed as glass channels, interior and exterior scraper profiles, roof profiles, interior and exterior door profiles, trunk seals, dust seals, pole profiles, fixed triangle profiles, convertible vehicle seals and hood profiles (Freise, 2002).

It offers comfort to end users by preventing the entry of water, air, noise and dust, ensuring that the moving windows on the vehicle operate silently with minimum friction force, and offers an aesthetic appearance by completing the design on visible surfaces. In addition, by preventing air inflow and outflow, it reduces the need for air conditioning and saves energy. Thus, sealing profiles developed with advanced technologies indirectly contribute to vehicle performance through energy saving (Standard Profile, 2024).

Synthetic ethylene propylene diene monomer rubber (EPDM), created with a combination of ethylene, propylene and unsaturated diene molecules is used in the production of sealing profiles due to its high mechanical properties, waterproof structure, low glass transition temperature, flexibility and permanent deformation values, high performance against atmospheric aging, oxidation, heat, ozone and low temperatures. Since the EPDM molecule is unsaturated due to the third monomer diene, it can be mixed with other polymers and can be reinforced with different fillers to improve its properties, as well as vulcanized with sulfur or peroxide systems (Lonkar et al., 2007; Mazlum et al., 2015; Eroglu et al., 2006; Markovic et al., 2000; Quanlin et al., 2007; Therias et al., 2006; Kumar et al., 2007; Jestin et al., 2000).

The most commonly used filling material in EPDM rubber is carbon black (Alp et al., 2019). Carbon black is used to improve the mechanical properties of EPDM rubber, ensure its conductivity and fluidity, and increase UV resistance (Du et al., 2019; Wang et al., 2019; Pereira et al., 2019). Due to the use of high amounts of carbon black, EPDM rubber plates and therefore sealing profiles are produced in black as a single color. However, recently, sealing profiles in different colors have been produced in line with the demands of automotive manufacturers and end users. Since even adding 1% of carbon black turns the profiles black, this is currently only possible with colored coating on the surface of the profile. However, coating the surface not only brings additional processes and additional labor to production, but also creates additional specifications and requirements in the final product. For this reason, the demand of sealing profile manufacturers is to directly color the EPDM rubber and therefore produce the profile to be produced in color. According to research, in order to achieve this, it is necessary to either bind the dye that will color the profile to the EPDM rubber, or to produce colored carbon black by binding the dye to carbon black, and thus produce colored profile with the EPDM rubber formula that adds colored carbon black.

Carbon black are structurally complex particles and consist of irregularly shaped aggregates ranging in size from tens of nanometers to several hundred nanometers (Zhu et al., 2012). Carbon black has excellent chemical stability, heat resistance, electrical conductivity, darkness and safe properties. Therefore, they are good components for dark dyes used for coatings (Li et al., 2001), plastics (Grunlan et al., 2002), inks (Belmont & Adams, 1998), and inkjet (Belmont et al., 1996) applications. Many of these applications require good dispersion and the solvent system is often water-based for environmental and cost reasons. However, the stability and dispersion of carbon black in aqueous solution are very poor. Carbon black particles are prone to agglomeration cause to their low hydrophilicity, Therefore, surface modification is of great importance to increase the hydrophilicity of carbon black and/or activate its surface.

Various methods have been reported for surface modification and functionalization of carbon black, including oxidation, graft polymerization, surface coating, and dispersant modification (Jeguirim et al., 2005; Paredes et al., 2005; Li et al., 2005; Qi et al., 2007). Jeguirim et al., (2005) studied the oxidation mechanism of carbon black with NO_2. Paredes et al., (2005) increased the hydrophilicity of carbon black by plasma modification. Li et al., (2001) grafted hydrophilic polyacrylate-g-carbon black synthesized by free radical polymerization of acrylate monomers on the carbon black surface and exhibited excellent hydrophilicity and dispersibility. Li et al., (2005) prepared polyvinyl alcohol-encapsulated hydrophilic carbon black and polyacrylamide-encapsulated hydrophilic carbon black. Qi et al., (2007) used peptides as dispersants and binders to disperse carbon black. However, most of the above methods have limitations such as long reactions, complex equipment, harsh and costly reaction conditions, and high toxicity. Therefore, the oxidation method with easy, environmentally friendly and economical chemicals was chosen for this study for the surface modification of carbon black.

Recently, automotive manufacturers want sealing profiles to be colored in line with end-consumer demands.

Due to the high amount of carbon black used as a filler in EPDM rubber used in sealing profiles, profiles can only be produced in black. The low solubility and reactivity of carbon black and its tendency to aggregation prevent the binding of a coloring agent to its structure. Therefore, the aim of this study is to activate and polarize the surface of carbon black using various chemicals in order to color it. To this end, carbon black was first oxidized and its surface was reactive with dopamine (Zhu et al., 2012), hydroxymethyl (Li et al., 2001), hydrogen peroxide (Gomez de la Fuente et al., 2005; Curtis et al., 2000; Razdyakonova et al., 2015), potassium permanganate (Cheng et al., 2015; Alp et al., 2019) and nitric acid. After the oxidized carbon black samples obtained from these applications are washed and dried, TGA and FTIR analyzes were performed in comparison with the unoxidized carbon black samples, and if deemed necessary, solid NMR analysis will be performed. According to the results obtained from this study, it is planned to select the most suitable dye for the structure of oxidized carbon black and stick it to the surface of carbon black. Thus, by coloring the carbon black, it will be possible to produce EPDM rubber with colored carbon black.

MATERIAL AND METHOD

In this study, carbon black, which is currently used by Standard Profil and supplied by DOW Chemical Company, USA, was used. The chemicals to be used for the modifications were potassium permanganate for analysis EMSURE® ACS,Reag. Ph Eur, 105082.0250 and nitric acid 65% for analysis (max. 0.005ppm Hg) EMSURE® ISO, 100452.2500, supplied by Merck/Turkey. 10% HCHO (formaldehyde) aqueous solution (pH: 10) and H2O2 (10% v/v) (hydrogen peroxide) were supplied by Tura Laboratory.

The modifications shown in Table 1 were applied to the carbon black, and all modifications were repeated 3 times. Chemical characterization of the surface-modified carbon blacks to be obtained modifications was performed by FTIR and thermal characterization was performed by TGA analyzes.

Chemical Characterization: FTIR analyses were applied to both the current CB and the CBs obtained after the modifications detailed below. FTIR spectroscopy is a powerful tool for monitoring vibrational energy levels in regions of different molecules. Changes in chemical properties are often monitored by FTIR spectroscopy, which is a very sensitive and non-destructive technique. Infrared spectroscopic analysis of untreated and chemically treated CBs was performed using Shimadzu IRPrestige 21 spectrometer. FTIR spectra were recorded in the range of 450–4000 cm^{-1} at room temperature. The resolution was 4 cm−1 and the number of scans to record IR spectra was 32. To record IR spectra, CBs were cut into small pieces and placed in a boiling tube and heated to semiliquid state. A drop of the liquid was applied between two circular NaCl disks to form a transparent film, and the NaCl disks were placed in the IR cell and the spectra were recorded (Gunasekaran et al., 2007).

Modification with H_2O_2: 5, 10 and 15 g of CB were oxidized by mixing with 10% (v/v) H_2O_2 at room temperature for 48 hours, then filtered, washed with plenty of water and dried at 120°C for 24 hours (Gomez de la Fuente et al., 2005; Curtis et al., 2000; Razdyakonova et al., 2015). FTIR analysis was applied to CB after modification.

Modification with HCOH: After 5, 10 and 15 g of CB were oxidized with 10% HCOH aqueous solution, the pH was adjusted to 10 with NaOH. It was mixed at 50°C for 1 hour, filtered, washed, and analyzed after drying at 120°C for 24 hours (Amornwachirabodee et al., 2018). FTIR analysis was applied to CB after modification.

Modification with $KMnO_4$

20 g of CB was oxidized with 2, 4 and 8 g of $KMnO_4$ in the presence of 4 N H_2SO_4 by stirring for 1 hour at room temperature, then filtered and washed. It was analyzed after drying at 105 °C for 24 hours (Cheng et al., 2015; Alp et al., 2019). FTIR analysis was applied to CB after modification.

Modification with HNO_3: 10 g of CB was oxidized by mixing with 30% and 65% HNO_3 by weight for 4 hours, then filtered and washed. It was analyzed after drying at 110 °C for 24 hours (Jeguirim et al., 2005). FTIR analysis was applied to CB after modification.

Table 1. Actualized modifications.

Modification	Oxidant	Method
1	Formaldehyde (HCOH)	CB is treated with formaldehyde under alkaline conditions. CB is mixed with 10% HCOH aqueous solution. The mixture is stirred at pH=10 for 1 hour at 50 °C. Hydroxymethylated CB is washed with water and dried.
2	Hydrogen peroxide (H_2O_2)	CB is mixed with H_2O_2 solution (10% v/v) at room temperature for 48 hours. The mixture is dried at 120 °C for 24 hours.
3	Potassium Permanganate ($KMnO_4$)	20 g of CB is treated with $KMnO_4$ (4 N H_2SO_4) solution in an acidic environment. The color of permanganate disappears quickly. After 1 hour, the entire amount of permanganate has reacted. CB is obtained after filtering and washing.
4	Nitric acid (HNO_3)	100 g of carbon black are suspended in 500 ml of aqueous nitric acid with a concentration of 30% by weight. It is boiled for 4 hours. Heating is stopped after 4 hours of gentle boiling and carbon black is precipitated. The supernatant liquid is absorbed and replaced with water. After filtration, a non-shedding suspension is obtained. It is vacuum filtered and washed.

Thermal Characterization: TGA analysis measures the rate or rate of mass change in a material as a function of temperature or time under controlled atmospheric conditions. It is used to determine the composition of additive masterbatches and polymer products, as well as to analyze the effects of additives that modify the degradation behavior of the polymer, such as antioxidants. Analysis were done with Shimadzu DTG 60 test machine in a dynamic nitrogen atmosphere of 75 ml/min with a heating rate of 20℃/min. TGA thermograms were analyzed in three regions: 300 °C to 400 °C, 400 °C to 500 °C, and 600 °C to 700 °C.

For further study, the products taken from 4 different modifications and the analysis results will be evaluated with the company in order to select an appropriate modification method. After the carbon black is modified with the most suitable chemical, a suitable dye can be attached and the carbon black can be colored. Elemental Analysis, FTIR, SEM-EDX and TGA-DSC analyzes will be performed for dye-bonded carbon black. In line with these analysis results, the existing EPDM rubber formulation shown in Table 2 will be prepared with the colored carbon black obtained. The resulting mixtures will be mixed in a laboratory type mixer and passed through a laboratory type cylinder and EPDM rubber plates will be optained by pressing at 190 °C for 8 minutes to cure in a laboratory type press.

Table 2. EPDM rubber formulation.

Components	%
EPDM	29.9
Carbon Black (Colored)	36.1
White Fill	7.5
Oil	21.1
Activators	3.3
Sulfur and Vulcanizators	2.1

RESULTS AND DISCUSSION

Chemical Characterization

The carbon black imported and used by the company was directly analyzed and the result is given in Figure 1.

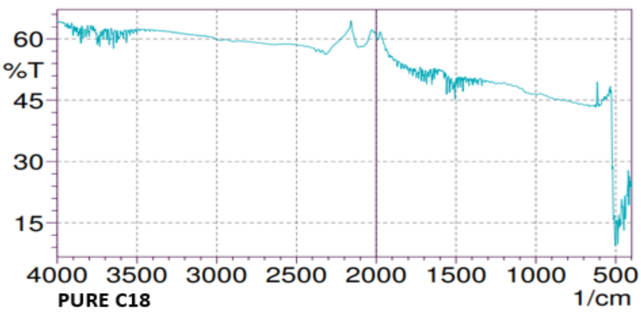

Figure 1. FTIR analysis of current CB.

Modification with H_2O_2: Comparison of H_2O_2-oxidized CB with current CB is given in Figure 2. Oxidation of 5, 10 or 15 g of CB with H_2O_2 did not cause any changes on the surface. Curtis et al., (2019) found that solutions containing >30% aqueous hydrogen peroxide, not 10% as here, provided the highest degree of oxidation. Similarly, Gomez et al., (2005) treated PtRu nanoparticles deposited on a substrate on carbon black with H_2O_2 to increase electrooxidation activity, but it was found that it did not have a direct effect on the carbon black surface.

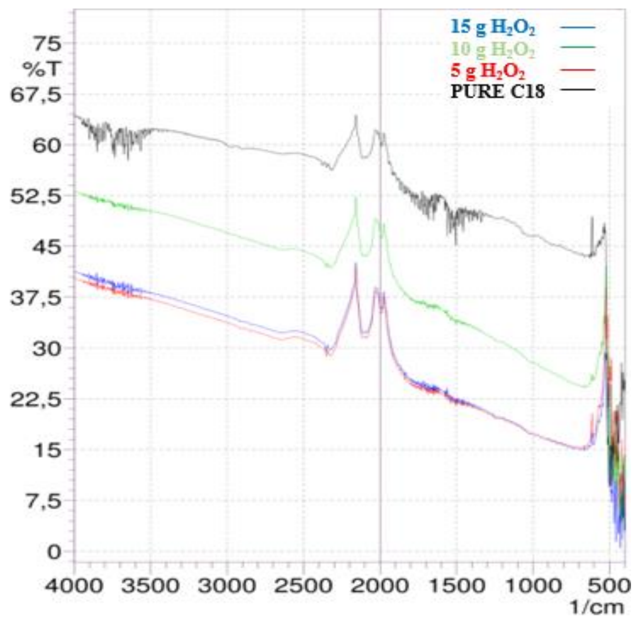

Figure 2. FTIR comparison of H_2O_2-oxidized CB/current CB.

Modification with HCOH: Comparison of HCOH-oxidized CB with current CB is given in Figure 3. Yuan et al., (2014) first hydroxymethylated the prepared CB nanoparticles with a formaldehyde solution and then oxidized using concentrated nitric acid to introduce hydroxyl and carboxy acid groups onto the CB surface. These hydrophilic groups were beneficial to break up large CB particles into smaller particles and significantly improved the dispersion of CB nanoparticles in aqueous media. In this study, oxidation of 5, 10 or 15 g of CB with HCOH did not cause any changes on the surface.

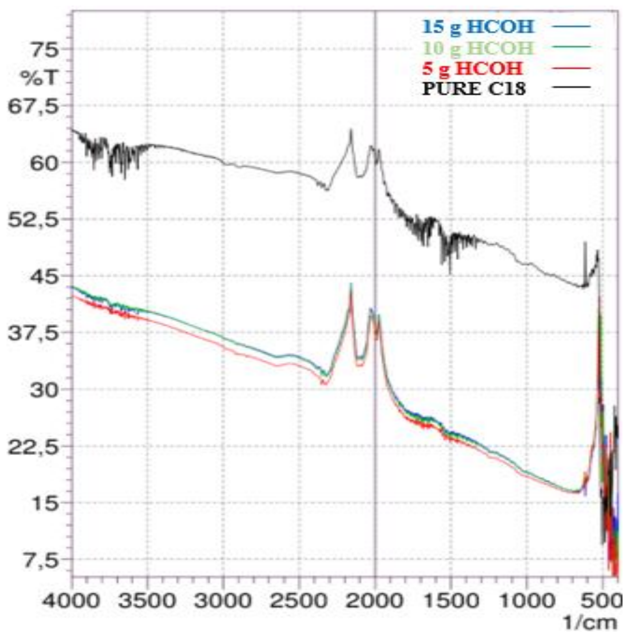

Figure 3. FTIR comparison of HCOH-oxidized CB/current CB.

Modification with $KMnO_4$: Figure 4 shows the FTIR analysis of CB oxidized with $KMnO_4$ compared to the FTIR analysis of unoxidized carbon black. When 20 g of CB is treated with 8 g of $KMnO_4$ in an acidic environment, oxidation is observed on the surface of the CB. Alp et al., (2019) oxidized the surface of carbon black obtained from end-of-life waste tires by adding potassium permanganate using the Improved Hummers method.

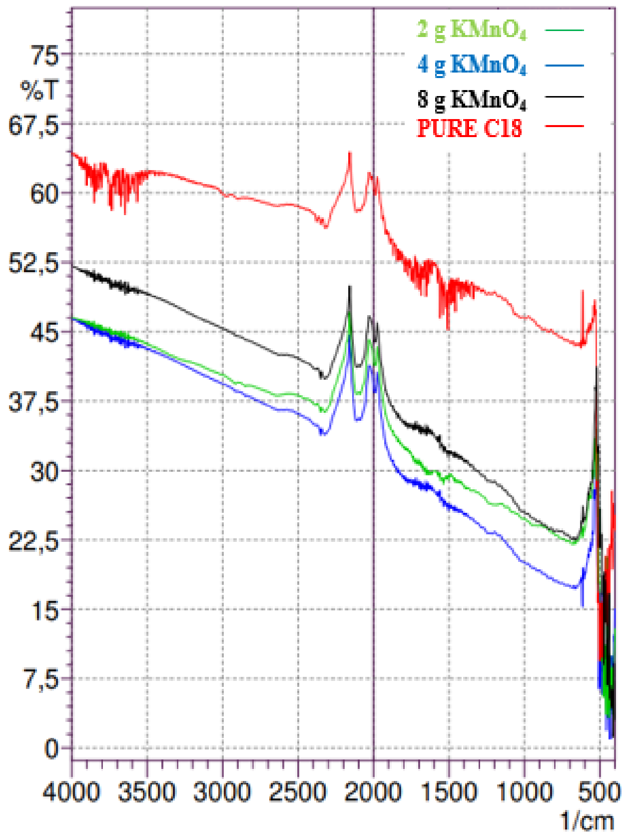

Figure 4. FTIR comparison of $KMnO_4$-oxidized CB/current CB.

Modification with HNO_3: Figure 5 shows the FTIR analysis of CB oxidized with 30 and 65% HNO_3 in comparison with the FTIR analysis of unoxidized carbon black. While no change was observed on the surface of carbon black with 30% HNO_3 solution, shifts in the peaks were observed after oxidation with 65% HNO_3 solution. Cheng et al., (2015) found that modified CB with 65% HNO_3 or 20% HNO_3 + 1.58% $KMnO_4$ had very good adsorption and complexation properties for metal ions in water compared to CB. As a result, 10 g of CB can be oxidized with 65% nitric acid.

Thermal Characterization

Modification with H_2O_2: The TGA graph of CB oxidized with H_2O_2 and the graph of unoxidized CB is given in Figure 6. In the last region, CB degradation and mass consumption occured. As seen from the graph, the thermal stability of carbon black increases when treated with H_2O_2.

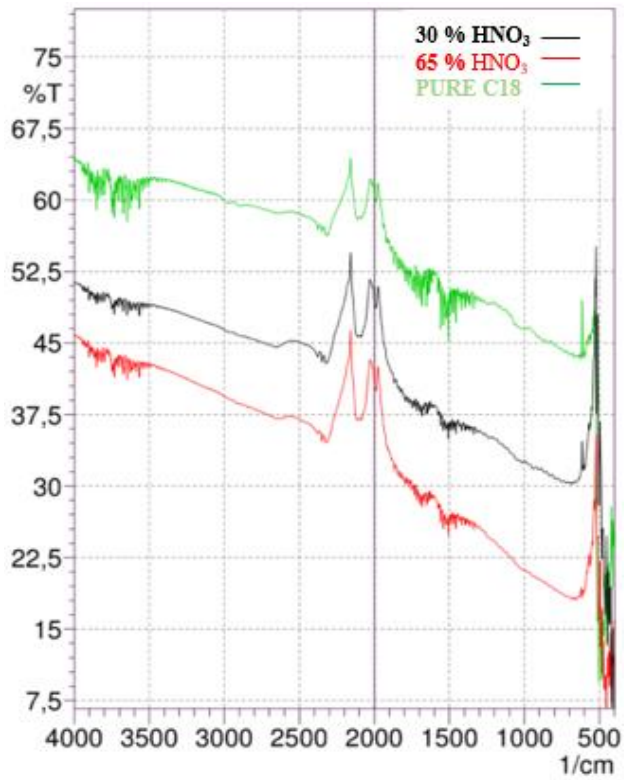

Figure 5. FTIR comparison of HNO_3-oxidized CB/current CB.

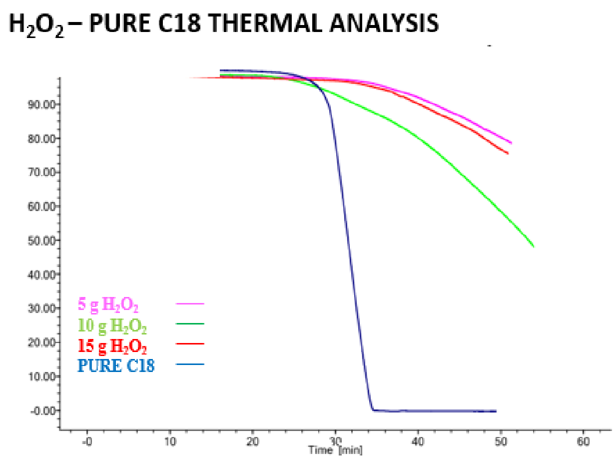

Figure 6. TGA comparison of H_2O_2-oxidized CB/current CB.

Modification with HCOH: The TGA graph of CB oxidized with HCOH and the graph of unoxidized CB is given in Figure 7. In the last region of unoxidized CB, degradation and mass consumption occured. As seen from the graph, the thermal stability of CB increases when treated with HCOH.

Modification with $KMnO_4$: The TGA graph of CB oxidized with $KMnO_4$ and the graph of unoxidized CB is given in Figure 8. In the last region of unoxidized CB, carbon black degradation and mass consumption occured.

As seen from the graph, the thermal stability of CB decreases when treated with $KMnO_4$.

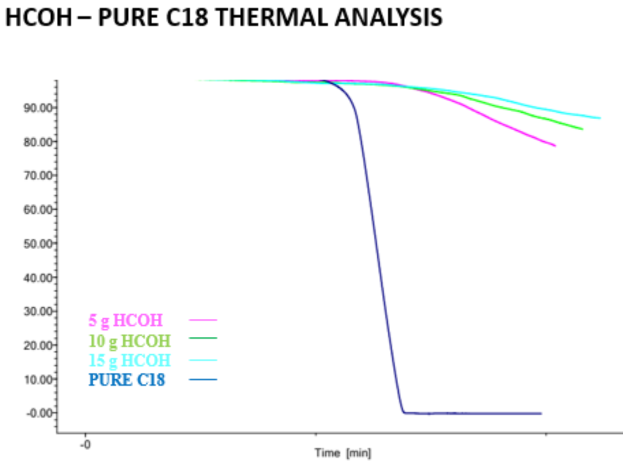

Figure 7. TGA comparison of HCOH-oxidized CB/current CB.

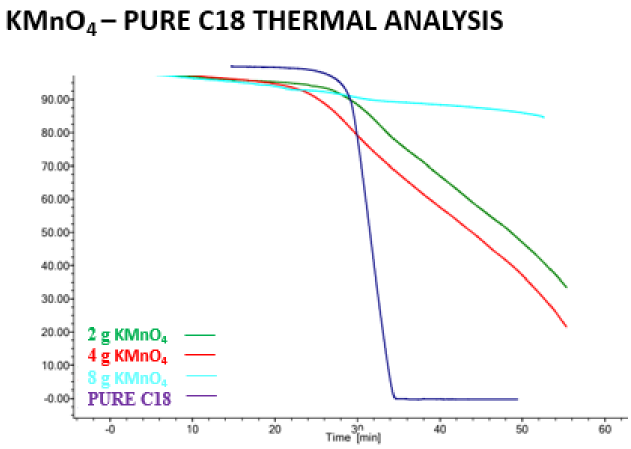

Figure 8. TGA comparison of $KMnO_4$-oxidized CB/current CB.

Modification with HNO_3: The TGA graph of CB oxidized with HNO_3 and the graph of unoxidized CB is given in Figure 9. In the last region, CB degradation and mass consumption occured. As seen from the graph, the thermal stability of CB increases when treated with HNO_3.

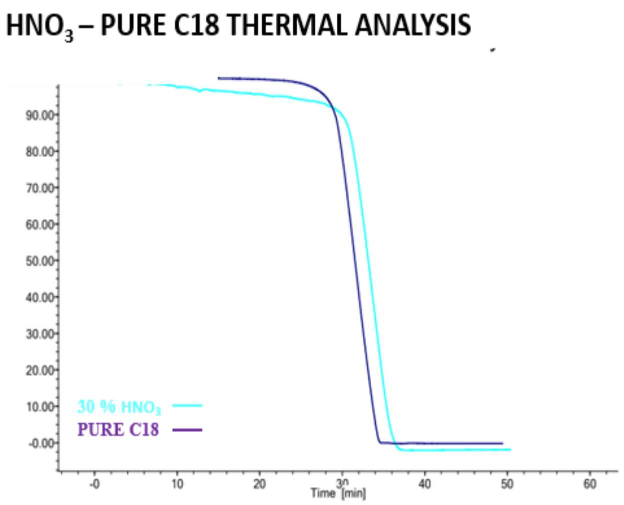

Figure 9. TGA comparison of HNO_3-oxidized CB/current CB.

CONCLUSION

It was aimed to carry out the surface modification of CB for the preliminary stage of the colored sealing profile design, which is a highly innovative product that will be produced as a first in the world. 4 different chemicals (H_2O_2, HCOH, $KMnO_4$ and HNO_3) were used for surface modification and the results were compared with FTIR and TGA analyses. As a result; no change was observed on the surface of CB when it was treated with H_2O_2 and HCOH. In order to oxidize the CB surface with these chemicals, the experiments should be repeated by increasing the amounts. As a result of the study, the highest oxidation of carbon black occurred when treated with 8 g $KMnO_4$ or 65% wt HNO_3 solution in acidic medium. In the next stage, a suitable dye that can be bonded to the modified CB surface will be selected and bonded to the surface. Then, using the company's infrastructure, an EPDM rubber formulation will be designed from dye-bonded CB, and in this way, a colored sealing profile will be produced in the long term, a first in the world.

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REFERENCES

Amornwachirabodee, K., et al. (2018). Oxidized Carbon Black: Preparation, Characterization and Application in Antibody Delivery across Cell Membrane. *Scientific Reports*, ***8***, 2489-2499.

Alp, R.B., Dilmac O.F. & Simsek, B. (2019). Grafit ve ömrünü tamamlamış atık lastikten elde edilen karbon siyahının iyileştirilmiş Hummers yöntemi ile oksidasyonu. *International Journal of Advances in Engineering and Pure Sciences*, ***3***, 238-244.

Belmont, J. & Adams, C. (1998). Non-aqueous inks and coatings containing modified carbon products. *US Patent* 5.713.988.

Belmont, J., Johnson, J. & Adams, C. (1996). Ink jet ink formulations containing carbonblack products. *US Patent* 5.571.311.

Cheng, J., Yu, Y., Li, T., Liu, Y. & Lu, C. (2015). A Comparing Study on Copper Adsorption on Nanoscale Carbon Black Modified by Different Kinds of Acid. *International Journal of Nanoscience*, ***14***(1-2), 1-6.

Curtis, J.C., Taylor, R.L. & Joyce, G.A. (2000). Hydrogen Peroxide Oxidation of Carbon Black. US6120594A.

Du, X., Zhang, Y., Pan, X., Meng, F., You, J. & Wang, Z. (2019). Preparation and properties of modified porous starch/ carbon black/natural rubber composites. *Composites Part B: Engineering*, ***156***, 1-7.

Eroglu, A.M., Albayrak, G., Aydin, I., Eren, M. & Gurkaynak, M.A. (2006). Investigation of the effect of carbon black particle size used in EPDM based mixtures on the vulcanisation and physical properties of final product. *7th National Chemical Engineering Congress*, Eskisehir.

Freise, C.K. (2002). *Handbuch der Karosseriedichtungen: Inhaltsverzeichnis.* Wolfsburg, Germany.

Gomez de la Fuente, J.L., et al. (2005). Enhanced methanol electrooxidation activity of PtRu nanoparticles supported on H_2O_2-functionalized carbon black. *Carbon*, ***43***, 3002-3039.

Grunlan, C., Gerberich, W.W. & Francis, L.F. (2002). Lowering the percolation thresholdof conductive composites using particulate polymer microstructure. *Journal of Applied Polymer Science*, ***80***, 692-705.

Gunasekaran, S., Natarajan, R.K. & Kala, A. (2007). FTIR spectra and mechanical strength analysis of some selected rubber derivatives. *Spectrochimica Acta Part A*, ***68***, 323-330.

Jeguirim, M., Tschamber, V., Brilhac, J.F. & Ehrburger, P. (2005). Oxidation mechanism of carbon black by NO_2: effect of water vapor. *Fuel*, ***84***, 1949-1956.

Jestin, F.D., Lacoste, J., Oudin, N.B., Cardinet, C. & Lemaire, J. (2000). Photo, thermal and natural ageing of ethylenepropylene-diene monomer rubber used in automotive applications. Influence of carbon black, crosslinking and stabilizing agents. *Polymer Degradation and Stability*, ***67,*** 469-477.

Keeney, J.D. (2002). Automotive Vehicle Seal and Decorative Trim Strip. *U.S. Patent* 6 422 571**.**

Kumar, B., Rana, S. & Singh, R.P. (2007). Photo-oxidation of EPDM/layered double hydroxides composites: Influence of layered hydroxides and stabilizers. *Express Polymer Letters,* ***1***(11), 748-754.

Li, H.Y., Chen, H.Z., Xu, W.J., Yuan, F., Wang, J.R. & Wang, M. (2005). Polymer-encapsulated hydrophilic carbon black nanoparticles free from aggregation. *Colloid Surface A*, ***254***, 173-178.

Li, W., Xie, Z.M. & Li, Z.M. (2001). Synthesis, characterization of polyacrylate-g-carbonblack and its application to soap-free waterborne coating. *Journal of Applied Polymer Science*, ***81***, 1100-1106.

Lonkar, S.P., Rana, S., Singh, R.P., Lacoste, J., Gardette, J.L., Jestin, F. & Brocorde, E. (2007). Synthesis, characterization, and performance evaluation of polymeric HALS in ethylene-propylenediene terpolymer (EPDM). *Journal of Macromolecular Science, Part A,* ***42***(1), 1037-1046.

Markovic, M.G., Choudhury, N.R., Dimopoulos, M. & Matisons, J.G. (2000). Weatherability of coated EPDM rubber compound by controlled uv irradiation. *Polymer Degradation and Stability*, ***69***, 157-168.

Mazlum, U., Vahapoglu, V. & Karadeniz, S. (2015). Experimental investigation of the stress relaxation behaviours of EPDM synthetic rubbers. *Sigma Journal of Engineering and Natural Sciences*, ***33***(3), 365-375.

Paredes, J.I., Gracia, M., Martínez Alonso, A. & Tascón, J.M.D. (2005). Nanoscale investigation of the structural and chemical changes induced by oxidation on carbon black surfaces: a scanning probe microscopy approach. *Colloid Interface Science*, ***288***, 190-199.

Pereira, T.D.S., Mauruto de Oliveira, G.C., Santos, F.A., Raymundo-Pereira, P.A., Oliveira, O.N. & Janegitz, B.C. (2019). Use of zein microspheres to anchor carbon black and hemoglobin in electrochemical biosensors to detect hydrogen peroxide in cosmetic products, food and biological fluids. *Talanta*, ***194***, 737-744.

Qi, M., O'Brien, J.P. & Yang, J. (2007). A recombinant triblock protein polymer with dispersant and binding properties for digital printing. *Peptide Science*, ***90***, 28-36.

Quanlin, Z., Xiaogang, L. & Jin, G. (2007). Aging of ethylene-propylene-diene monomer in artificial weathering environment. *Polymer Degradation and Stability*, ***92***, 1841-1846.

Razdyakonova, G.I., Kokhanovskaya, O.A. & Likholobov, V.A. (2015). Influence of environmental conditions on carbon black oxidation by reactive oxygen intermediates. *Procedia Engineering*, ***113***, 43-50.

Standard Profile (2024). http://www.standardprofil.com/ (27 May 2024).

Therias, S.M., Fanton, E., Tomer, N.S., Rana, S., Singh, R.P. & Gardette, J.L. (2006). Photooxidation of vulcanized EPDM/ montmorillonite nanocomposites. *Polymer Degradation and Stability*, ***91***, 3033-3039.

Wang, R., Li, W., Liu, L., Qian, Y., Liu, F., Chen, M., Guo, Y. & Liu, L. (2019). Carbon black/graphene-modified aluminum foil cathode current collectors for lithium ion batteries with enhanced electrochemical performances. *Journal of Electroanalytical Chemistry*, ***833***, 63-69.

Yuan, J.J., Hong, R.Y., Wang, Y.Q. & Feng, W.G. (2014). Low-temperature plasma preparation and application of carbon black nanoparticles. *Chemical Engineering Journal*, **253**, 107-120.

Zhu, L., Lu, Y., Wang, Y., Zhang, L. & Wang, W. (2012). Preparation and characterization of dopamine-decorated hydrophilic carbon black. *Applied Surface Science*, ***258,*** 5387-5393.