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Research Article

Effect of Ultraviolet Stabilizers on Rubber-Based Automotive Sealing Profiles

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ABSTRACT

The sealing profiles for many visible and invisible automotive applications such as doors, windows, hoods and trunks are made of synthetic ethylene propylene diene monomer (EPDM) rubber. This combination of ethylene, propylene and unsaturated diene molecules exhibits high mechanical properties and forms a water-proof structure. With the progress of time, color change, cracking and staining can be observed on the surface of the sealing profiles used on the visible regions exposed to the sun due to the effect of high-intensity ultraviolet (UV) radiation and sunlight. The aim of this study was to investigate the effect of the UV stabilizers widely used in the plastics industry on the UV resistance of EPDM rubber. UV stabilizers protect the polymers against to UV radiation by reacting with the free radicals that are formed when a high energy UV photon causes a chemical bond in the polymer to break or by absorbing potentially destructive UV radiation. Plates of EPDM rubber were prepared by adding different types of UV stabilizers at different rates to an available EPDM formula. The effects of the UV stabilizers on the EPDM plates were measured by mechanical tests and the internationally recognized Florida outdoor aging test with climate conditions of high-intensity sunlight, high-intensity UV, and high temperature and humidity levels.

Keywords: *EPDM, UV, UV Stabilizers, Sealing profiles*

Ultraviyole Stabilizatörlerin Kauçuk Esaslı Otomotiv Sızdırmazlık Profilleri Üzerindeki Etkisi

ÖZET

Kapı, cam, kaput ve bagaj gibi aracın görünür ve görünmez birçok bölgesinde kullanılan sızdırmazlık profilleri; sentetik etilen propilen dien monomer (EPDM) kauçuktan üretilmektedir. Etilen, propilen ve doymamış dien moleküllerinin bu kombinasyonu, yüksek mekanik özellikler sergiler ve su geçirmez bir yapı oluşturur. Güneş ışığına maruz kalan görünür bölgede kullanılan sızdırmaz profillerin yüzeyinde, yüksek yoğunluklu ultraviyole (UV) radyasyonun ve güneş ışığının etkisiyle, zamanla renk değişimi, çatlama ve lekelenme gözlemlenebilir. Bu

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çalışmanın amacı, plastik endüstrisinde yaygın olarak kullanılan UV stabilizatörlerin EPDM kauçuğunun UV dayanımına olan etkisini araştırmaktır. UV stabilizatörleri, polimerde meydana gelen kimyasal bağ kırılımı nedeni ile oluşan serbest radikaller ile tepkimeye girerek veya UV ışımayı absorbe ederek polimeri UV ışınlarına karşı korur. Mevcut EPDM formülasyonuna farklı tip ve farklı oranlarda UV stabilizatörler eklenerek EPDM hamur plakaları oluşturulmuştur. UV stabilizatörlerin EPDM plakaları üzerindeki etkileri; mekanik testler ve yüksek yoğunluklu güneş ışığı, yüksek yoğunluklu UV ile yüksek sıcaklık/nem içeren iklim koşullarına sahip ve uluslararası alanda tanınmış Florida açık hava yaşlanma testi ile ölçülmüştür.

Anahtar Kelimeler: *EPDM, UV, UV Stabilizatörleri, Sızdırmazlık Profilleri*

I. INTRODUCTION

Ethylene-propylene-diene monomer (EPDM) rubber is a type of synthetic rubber formed by the addition of a diene monomer during the copolymerization of ethylene and propylene. EPDM rubber is one of the most widely used synthetic rubbers and used in many applications such as automotive sector, sport sector, glass-run channels, gaskets, lines, hoses, cordons and barriers. The reason of extensively usage is its high mechanical properties, very low unsaturation and its backbone [1-7]. It can be reinforced with different kinds of fillers to improve its properties [8-12].

The EPDM rubber is the fastest growing elastomer and the sealing profiles for many visible and invisible automotive applications such as doors, windows, hoods and trunks are made of it. Despite many good physical and mechanical properties the photo-stability of EPDM is inherently low [13]; therefore, when these materials are exposed to natural or artificial aging, color change, cracking, surface staining and reduction of mechanical properties are observed [14]. The small number of impurities found within the rubber are sufficient to initiate photo-degradation, despite weak UV absorption. Consequently, carbon black is used in the formulation of sealing profiles as carbon black decelerates the photo-degradation of cured elastomers [15]. However, carbon black is not sufficient and appropriate fillers are necessary in addition to carbon black for longer stability.

There are different ways to protect the polymers against photo-degradation such as the addition of UV-absorbers, antioxidants and photo-stabilizers (UV stabilizers) [16]. Practice shows that when the polymer contains a photostabilizer, the oxidation rate is much reduced but the stabilizers should be well dissolved and well diffused in the polymer matrix [17].

A classification of UV stabilizers as follows: UV screeners (absorbers or pigments, UVA), excited state deactivators (quencher), hydroperoxide decomposers and radical scavengers (Hindered Amine Light Stabilizer, HALS). HALS are very effective photostabilizers for a variety of polymers [18, 19] and react with the free radicals that are formed when a high energy UV photon causes a chemical bond in the polymer to break.

ortho-Hydroxyphenyl benzotriazoles are commonly used as UV absorbers (UVAs). They absorb potentially destructive UV radiation and dissipate the energy on a subpico-second time scale [20-25]. Some reasearches show that the weathering resistance of organic materials can be improved by protecting their surface with both UV absorber (UVA) and a radical scavenger (HALS) [26].

The hindered amine light stabilizers (HALS) and UV absorbers (UVAs) such as benzotriazole and benzophenones are the stabilizers that can be used for EPDM rubber [27].

This study aims to research the influence of fillers on UV-resistance and mechanical properties of EPDM rubber by adding different types of HALS and UVAs as fillers at specific rates to an available rubber formulation. According to results optimum photo stabilizer and optimum amounts can be specified for optimum photo-stability. Thus, EPDM rubber formulation that can pass the internationally recognized Florida outdoor aging test with climate conditions of high-intensity sunlight, high-intensity UV, and high temperature and humidity levels can be designed.

II. MATERIAL AND METHOD

A. MATERIAL

The material used in this study was ethylene-propylene-diene monomer (EPDM) compound, made by Standard Profile by using rubber-grade chemicals as shown in Table 1.

The HALS triazine derivative (Flamestab NOR 116) and bis (1-octyloxy-2,2,6,-tetramethyl-4-piperidyl) sebacate (Tinuvin-123) and the UVAs 2-(2H-benzotriazol-2-yl)-p-cresol (Tinuvin-P), 3-(3-(2H-benzotriazole-2-yl)-5-t-butyl-4-hydroxyphenyl propionate (Tinuvin-213) and 2-(2H-benzzotriazol-2-yl)4,6-bis(1-ethyl-1-phenylethylphenol) (Tinuvin-234) were supplied by the BASF company.

Table 1. *Compounding Receipe of EPDM Rubber*

Compounding Ingredients	**Phr**
EPDM	100
Carbon Black + White filler	175
Process Oil	65
Small Chemicals	10
Sulphur (S) + Accelerators	6.5
UVAs or HALS	0.5 – 1.0 – 1.5 – 2.0

B. METHOD

An artificial weathering test, appearance control, mechanical tests and permanent set control were applied to prepared EPDM plates. 21 different EPDM rubber plates that were prepared by adding different types of UV stabilizers at different rates to an available EPDM formula. The composition of the plates is given in Table 2.

Table 2. Composition of the plates.

EPDM Plates	EPDM (+vulcanizers)	Tinuvin-P	Tinuvin-213	Tinuvin-234	Flamestab NOR 116	Tinuvin-123
1	x					
2	x	0.5 phr				
3	x	1.0 phr				
4	x	1.5 phr				
5	x	2.0 phr				
6	x		0.5 phr			
7	x		1.0 phr			
8	x		1.5 phr			
9	x		2.0 phr			
10	x			0.5 phr		
11	x			1.0 phr		
12	x			1.5 phr		
13	x			2.0 phr		
14	x				0.5 phr	
15	x				1.0 phr	
16	x				1.5 phr	
17	x				2.0 phr	
18	x					0.5 phr
19	x					1.0 phr
20	x					1.5 phr
21	x					2.0 phr

B.1. The weathering (Florida) test

The weathering test was carried out via weathering equipment (Atlas Ci4000) according to PV3930, Florida weathering standard. The samples were exposed for 100 h and 250 h. The cycle consisted of UV (λ = 340) radiation at 65 ºC and relative humidity (60 – 80%). The irradiance intensity was 0.50 W.m-2.

B.2. Appearance studies

The sample appearance change was first evaluated visually and then with gloss values of plates. The gloss values were determined by a gloss meter (BYK) using a 60º incidence angle.
B.3. Evaluation of mechanical properties

The mechanical properties were analyzed by tensile strength, tear strength, elongation and hardness tests. The tensile strength and elongation tests were specified according to DIN 53504 while tear strength test were identified according to DIN ISO 34-1 standards. Mechanical tests were carried out at a temperature of 23 ºC and with test speed of 200 mm/min by using a global test machine (Zwick Roell Z010). The hardness (shore A) values of the aged sides of EPDM plates were determined according to standard named as DIN ISO 7619-1. Five samples were established to test for reliable result.

B.4. Evaluation of thermal aging behavior as permanent set

The permanent set tests were realized by aging 22 h + 2 h at 100 ºC according to DBL 5571. Test specimens were measured with a gauge (Mitutoyo) and calculated using the following equation:

$$\text{Permanent set (\%)} = \frac{hi - hf}{hi - h0} \times 100 \quad (1)$$

where hi is the height of the sample before thermal aging, hf is the height of the sample after aging and h0 is the compression distance. Three samples were specified to test for reliable result.

III. Results and Discussions

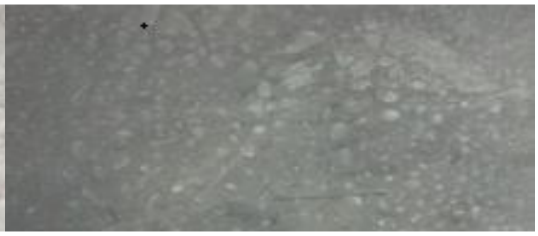
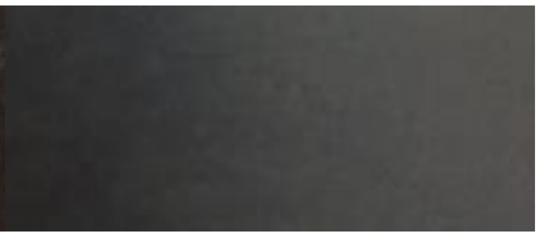
A. CHANGE IN APPEARANCES

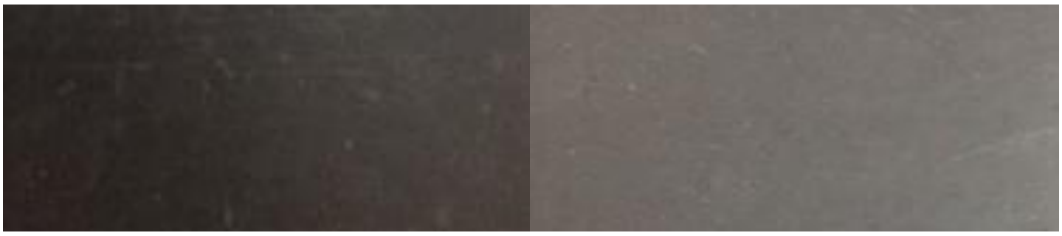
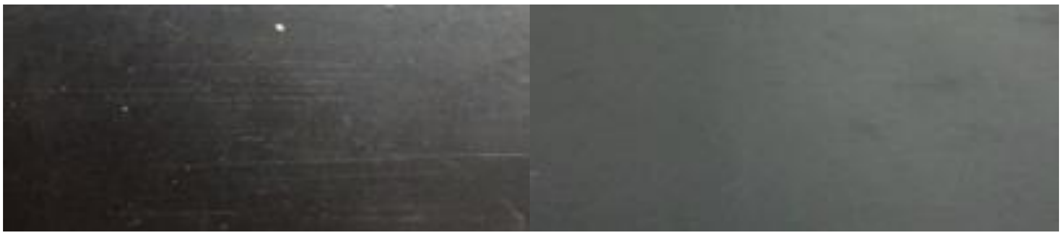
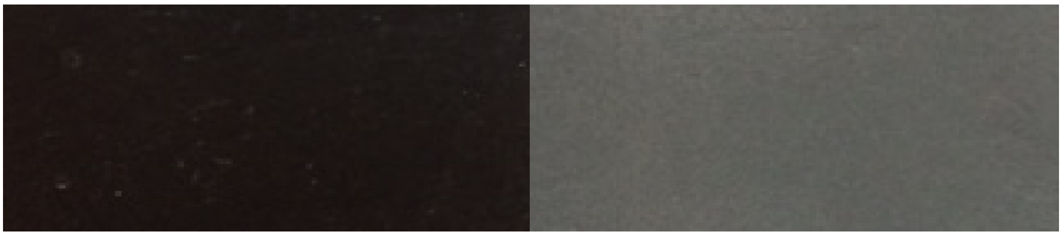
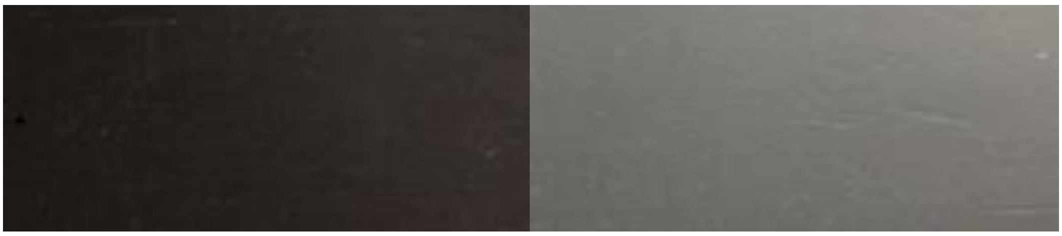
The visual controls were made from the EPDM plates that were exposed to an artificial weathering test for 100 h and 250 h and are presented in Table 3.

Table 3. *Visual control results of EPDM plates.*

EPDM Plate	100 h Florida Aging	250 h Florida Aging
1		

2		
3		
4		
5		
6		
7		
8		

9		
10		
11		
12		
13		
14		
15		

16	
17	
18	
19	
20	
21	

Surface cracks and color changes can be observed on the surfaces after 100 h and 250 h of Florida aging until EPDM plate 14. The surfaces of plates 14 through 21 were more protected against UV-light than those of the others.

Surface optical properties of materials are characterized by a term of gloss. Gloss values are measured by a machine which has a reflection ability and a incidence angle. The effect of UV-stabilizer types and rates on gloss values of EPDM plates is presented in Figure 1.

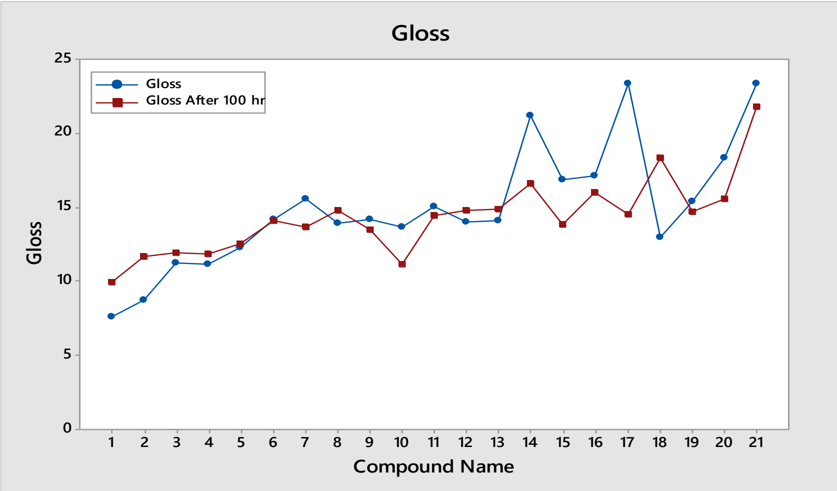


Figure 1. *UV stabilizers effect on surface gloss*

It can be observed that the gloss values of plates 14 through 21 are higher than those of the other plates before and after aging, which means that plates 14 through 21 reflected more light than the other plates because of their smoother surfaces.

B. EVALUATION OF MECHANICAL PROPERTIES

The UV-stabilizer types and rates effect on the mechanical properties are represented by the comparison of the tensile strength, tear strength, elongation, and hardness values of EPDM plates. As presented in Figure 2 and Figure 3, the tensile and tear strength values of the plates are very similar; thus, it can be observed that they did not depend on the type or rate of the UV stabilizers.

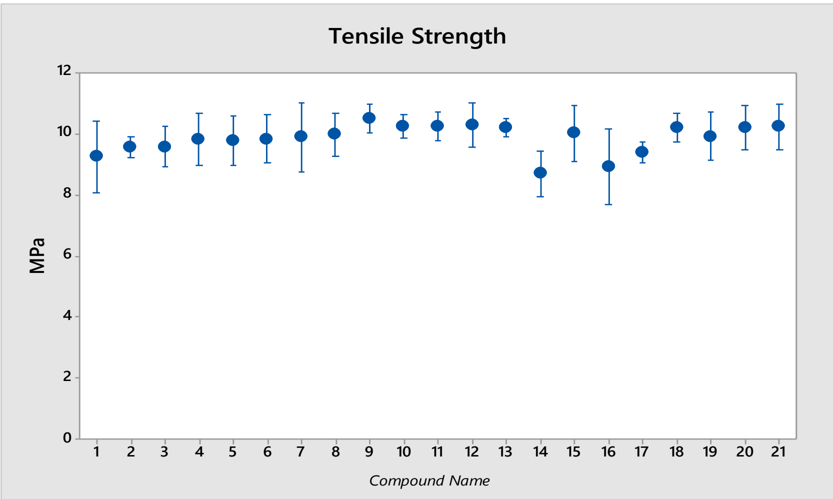


Figure 2. *UV stabilizers effect on the mechanical properties such as tensile strength*

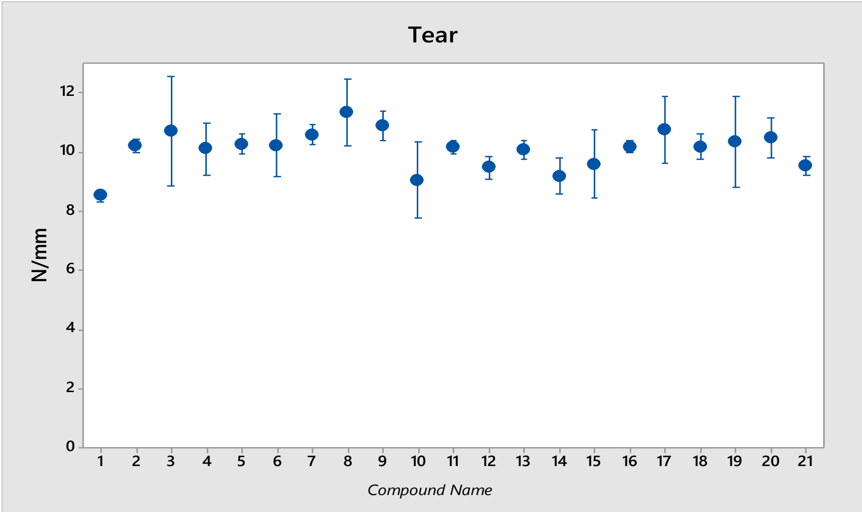


Figure 3. *UV stabilizers effect on the mechanical properties such as tear strength*

The effects of the type and rate of UV stabilizers on the elongation and hardness values are presented in Figures 4 and 5, respectively.

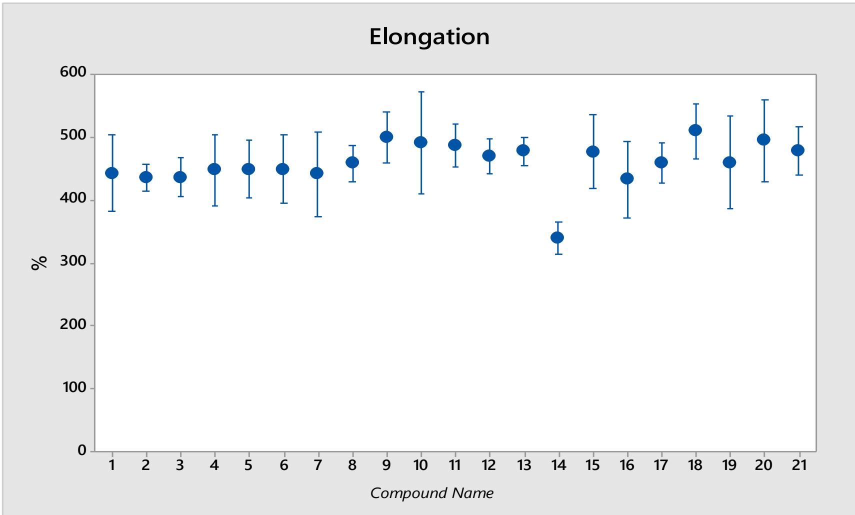


Figure 4. *UV stabilizers effect on elongation behavior*

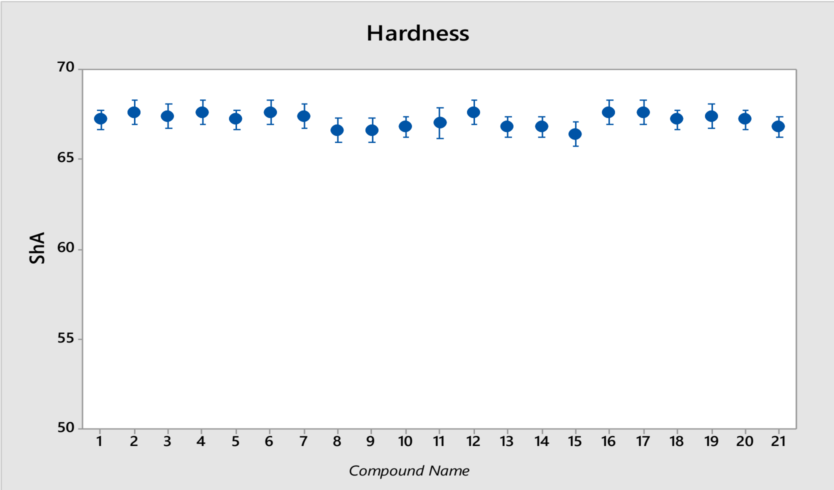


Figure 5. *UV stabilizers effect on hardness*

Figure 4 shows that Flamestab material causes decreasing in elongation behavior when it is used in a ratio of 0.5 phr but other plates have similar elongation values. Similarly, as seen on Figure 5 hardness values are very similar. From this it can be interpreted that they did not depend on the types and rates of UV stabilizers.

C. EVALUATION OF THERMAL AGING BEHAVIOR AS PERMANENT SET

The effect of the UV-stabilizer rates and types on the thermal aging and compression behavior of the EPDM are represented as a permanent set. The permanent deformations of the EPDM plates were calculated after thermal aging at a specific compression.

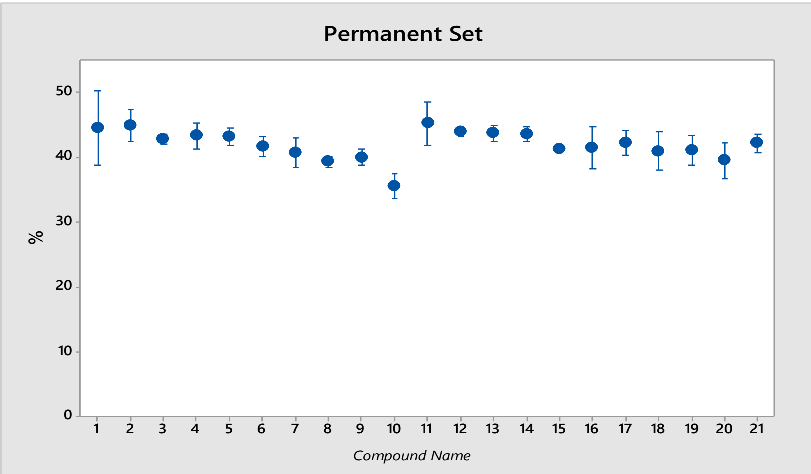


Figure 6. *UV stabilizers effect on compression behavior*

Figure 6 shows the comparison of the permanent set values of the EPDM plates. It can be observed from the similar values that the thermal aging and compression behavior of the EPDM rubber did not depend on the types or rates of UV stabilizers.

IV. CONCLUSION

The comparison curves of the tensile and tear strength, elongation and hardness values showed that types and rates of UV stabilizers had no effect on the mechanical properties of the EPDM rubber used in the production of sealing profiles for the automotive sector. Similarly, the permanent set results of the EPDM plates prepared by adding different types of UV stabilizers at different rates illustrated that the UV stabilizers did not change the thermal aging behavior of the EPDM rubber.

From the visual analysis of the change in appearance it was observed that the HALS materials had protected the surface against artificial weathering better than the UVA materials. Cracks and color changes could be seen on the surface of the plates prepared with UVA materials like in the available EPDM plates. In comparison, the HALS material made the surfaces smoother than the UVA materials, which resulted in more reflection and correspondingly, higher gloss values. Consequently, the Flamestab NOR 116 used to prepare the EPDM plates 14 through 17 showed the best results and will be analyzed more extensively in a future study.

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