

The Effect of Tinuvin Derivatives as an Ultraviolet (UV) Stabilizer on EPDM Rubber

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ABSTRACT

Ethylene-propylene-diene monomer (EPDM) is one of the most widely used synthetic rubbers, especially in the automotive industry. Despite its many benefits, the chief weakness of EPDM has been the color change occurring in its products due to ultraviolet (UV) rays. It is recognized that UV energy causes the dissociation of bonds (mostly C-C and C-H) in EPDM materials as well as cracks and color changes on the surface. The aim of this study was to investigate the effect of the Tinuvin derivatives widely used as UV stabilizers in the plastics industry on EPDM rubber. The EPDM rubber plates were prepared by adding Tinuvin-P, Tinuvin-213 and Tinuvin-234 as UV absorbers (UVAs) and Tinuvin-123 as hindered amine light stabilizer (HALS) material at a ratio of 1.0 phr (parts per hundred parts of rubber) to an available EPDM formula. The effects of the Tinuvin derivatives were investigated by the internationally recognized Florida outdoor aging test. The surfaces of the EPDM plates were visually scrutinized and surface morphological changes were examined via scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and Fourier transform infrared (FTIR) spectrometry analyses. The results obtained showed that, unlike in the plastic industry, not all Tinuvin derivatives could be used as UV stabilizers for EPDM products. Of all the tested Tinuvin derivatives, the Tinuvin-123 compound was the most effective, indicating it to be suitable for use as a protective UV stabilizer for EPDM rubber applications. Thus, an important issue such as the UV resistance of sealing profiles made by EPDM rubber has been contributed about the suitability of Tinuvin derivatives.

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1. Introduction

Ethylene-propylene-diene monomer (EPDM) is a type of rubber formed by ethylene propylene and diene molecules [1]. EPDM rubbers are known with their good properties such as high resistance to heat, light and oxidation and high mechanical properties. They can form mixtures without high prices because they can be reinforced and keep the oil [2]. Due to these good properties and its saturated hydrocarbon backbone with the presence of double bonds in the side chains they are one of the most widely used synthetic rubbers [3-5].

This rubber has been generally used in both indoor and outdoor applications [6-8]. Because of its outdoor applications, a study of the photostability of EPDM elastomer is extremely important from the industrial as well as academic point of view [9-12].

The lights come from the sun are emitted in different wave lengths and are expressed as gamma rays, X-rays, ultraviolet (UV) lights, visible lights, infrared lights and radio waves. The UV lights are a special part of the solar spectrum as shorter wavelength than visible light (naturally higher energy) and found in the range of 295-380 nm. Although 97% of them are blocked by the Ozone layer the other 3% may cause damage to human skin for extended exposure. Behind the human skin macromolecular compounds are also effected and degrade when they are exposed to UV light especially below 295 nm wavelength [13]. UV photons have enough energy to split intra- and intermolecular bonds. As a result of absorption of UV light energy by a polymer, primary photochemical products, free radicals, are produced due to the separation of bonds (mostly C-C and C-H) in the molecules. Thus, the first step of photo-oxidation starts as embrittlement at the surface in a depth of more than 100 μm , which is a major cause of surface cracking and deterioration of polymers. Brittle surface causes cracks at low strains that can propagate into and throughout the unaffected material [14]. This process is called as polymer degradation and results in the deterioration of physical properties such as loss of impact strength, changes in colour, cracking, loss of elongation and tensile strength or chalking of the surface [15]. Behind these main effects, degradation also causes macrostructural changes in polymer composites such as loss of some additives within molecules, discoloration of the pigments, deterioration between fiber-polymer matrix [16]. Briefly, polymer degradation starts from the outer surface and continues as propagation into and throughout the bulk of material. At the end carbonyl, carboxyl, hydroxyl, or peroxide groups are introduced into the polymer [17].

There are different ways to protect polymers against photo-oxidation degradation, such as adding pigment light absorbers, antioxidants, and photostabilizers (UV stabilizers) [18]. Ultraviolet stabilizers are classified as UV absorbers (UVAs), deactivators (quenchers), hydroperoxide decomposers and radical scavengers known as hindered amine light stabilizers (HALS). The HALS and UVAs such as benzotriazole and benzophenones are suitable stabilizers for EPDM rubber [19]. The UVAs protect the polymers by absorbing destructive UV radiation, while the HALS material protects by reacting with the free radicals that occur after a high-energy UV photon breaks a chemical bond in a polymer. There are three empirical requirements for an effective stabilizer: high solubility, minimal diffusion and high distribution homogeneity [20].

Tinuvin additives are one of the UV stabilizer groups which enjoy wide use in the plastic industry. Some of them are found as UVAs and some of them are supplied as HALS.

Tinuvin-P, Tinuvin-213 and Tinuvin-234 are benzotriazole derivatives used widely in the plastic industry which act as UVAs [21-33]. They are used to filter off UV light and distribute the energy in the form of heat. They must have a wide range of chemical and physical properties in order to be useful in these applications [34]. However, they can be used as a protective material only for thin polymers such as films and fibers. The main reason is that they need a certain absorption depth (item thickness) to provide good protection for a polymer [35]. There is also a derivative of Tinuvin which has the trade name Tinuvin-123 which acts as a HALS. Tinuvin-123 material is very effective long-term stabilizer thanks to its regenerated molecules that spirit the free radicals away.

The aim of this study was to investigate the effect of the Tinuvin derivatives widely used as UV stabilizers in the plastics industry on EPDM rubber. The addition of large amounts of carbon black (as reinforcing agent) during the vulcanization process greatly modifies EPDM rubbers. This generally results in greatly improved aging properties, which can be further enhanced by the addition of stabilizers [36]. In the sulfur vulcanization process using carbon black, the long-term aging effect of the first reaction with zinc carboxylates before the addition of sulphur may affect the UVA and HALS materials and the efficiency of the stabilizers may be lost at temperatures above 100 °C. For this reason, this study evaluated the Tinuvin-P, Tinuvin-213, Tinuvin-234 and Tinuvin-123 materials described above in terms of their effectiveness as UV stabilizers at high temperatures and their enhancement of long-term aging. Thus, EPDM rubber formulation that can pass the internationally recognized Florida outdoor aging test can be designed. As a result, sealing profiles that can pass Florida outdoor aging that is expected by all big automotive manufacturers can be produced.

2. Materials and Method

2.1. Material

The material used in this study was ethylene-propylene-diene monomer, used by Standard Profile [37]. Compounding was done by employing rubber-grade chemicals. The formulation of the EPDM rubber is given in Table 1.

Table 1. Compounding Recipe of EPDM Rubber.

Compounding Ingredients	Phr (parts per hundred parts of rubber)
EPDM	100
Carbon Black + White filler	175
Process Oil	65
Small Chemicals	10
Sulphur (S) + Accelerators	6.5
Tinuvin Derivatives	1.0

The Tinuvin derivatives selected for investigation as stabilizers were:

- Tinuvin-123: bis (1-octyloxy-2,2,6,-tetramethyl-4-piperidyl) sebacate, a hindered amine light stabilizer (HALS), supplied by BASF corporation
- Tinuvin-P: 2-(2H-benzotriazol-2-yl)-p-cresol, a UV absorber (UVA) of the hydroxyphenol benzotriazole class (225 g mol⁻¹), supplied by BASF corporation
- Tinuvin-213: 3-(3-(2H-benzotriazole-2-yl)-5-t-butyl-4-hydroxyphenyl propionate, a UVA which is a mixture of polyethylene glycol (PEG) and two types of polymeric UVAs, supplied by BASF corporation
- Tinuvin-234: 2-(2H-benzotriazol-2-yl)4,6-bis(1-ethyl-1-phenylethylphenol), a high molecular weight UVA of the hydroxyphenyl benzotriazole class (448 g mol⁻¹), supplied by the BASF corporation.

A total of 25 plates were prepared as five plates for each material by adding 1.0 phr of the Tinuvin derivatives given in Table 2 to the available EPDM formula.

Table 2. Composition of the plates.

EPDM Plates	EPDM (+vulcanizers)	Tinuvin-P	Tinuvin-213	Tinuvin-234	Tinuvin-123
1	x				
2	x	1.0 phr			
3	x		1.0 phr		
4	x			1.0 phr	
5	x				1.0 phr

2.2. Method

An artificial weathering test was run on three EPDM plates for each material and visual control and scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analyses were applied after the weathering test. Our previous study showed that the type of UV stabilizer (e.g., Tinuvin types) had no effect on mechanical properties such as tensile strength, tear strength, elongation behavior, hardness and permanent set values. Thus, Tinuvin-type additives had no effect on the mechanical properties of EPDM rubber used in the production of sealing profiles for the automotive sector [38]. The current study focused on the surface changes of the plates with the introduction of these additives.

2.2.1. Artificial weathering test

Natural weathering tests are commonly used to evaluate the weather-resistant property of materials, but they are time consuming and difficult to reproduce. The artificial weathering test was adopted in order to simulate natural weathering in the laboratory. The test was carried out via weathering equipment (Atlas Ci4000) according to the PV3930 Florida weathering standard. The samples were exposed for 100 h. The cycle consisted of UV ($\lambda = 340$) radiation at 65 °C at a relative humidity of 60 – 80%. The irradiance intensity was 0.50 W/m².

2.2.2. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis

The surface morphology of the degraded samples was characterized using a FEI Quanta FEG 250 optical microscope. The degraded surfaces were sputter-coated with gold and SEM photographs were taken after completion of the 100-h aging treatment. The SEM micrographs were investigated in terms of the EDX spectrum in order to analyze the chemical characterization of the EPDM plates after the weathering test.

2.2.3. Fourier transform infrared spectroscopy analyze (FTIR)



The FTIR spectroscopy analysis was applied to Plate 4 in order to identify the material that had migrated onto the surface after the weathering test. It was performed via the Shimadzu IRPrestige 21 spectrometer.

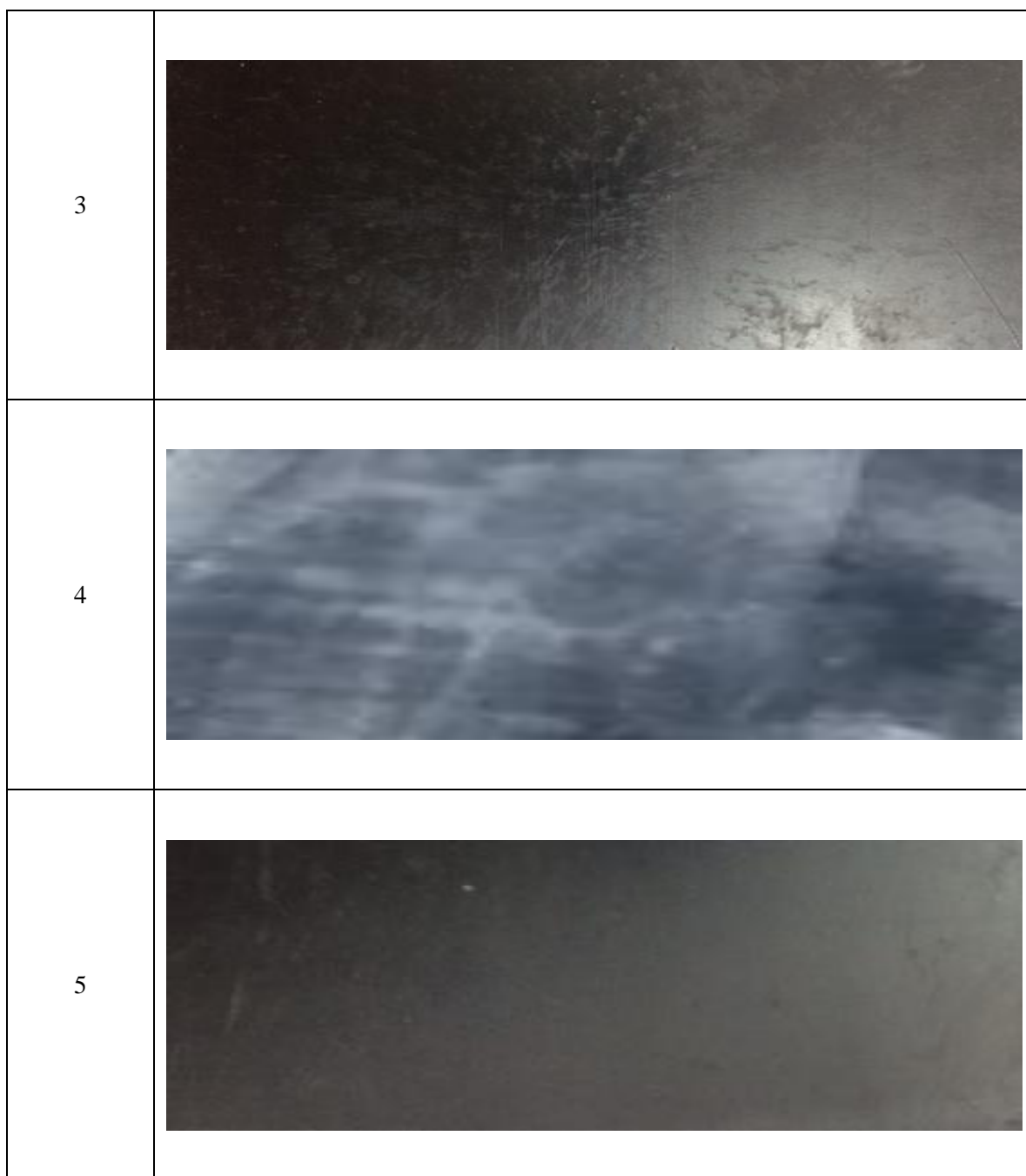
3. Results and Discussions

3.1. Artificial Weathering Test Results

The EPDM plates were evaluated visually after weathering in an artificial environment for 100 h. Table 3 presents the visual control results of the five plates after the Florida aging.

Table 3. Visual control results of EPDM plates.

EPDM Plate	100 h Florida Ageing
1	
2	



Surface cracks were visible on the plates after the Florida artificial weathering. The surface of EPDM Plate 5 is better than the others, indicating that the plates with Tinuvin-123 additive were more protected against UV light than the others. Another notable point is that the Tinuvin material added to Plate 4 had migrated to the surface, which demonstrated that Tinuvin-234 was not a suitable Tinuvin derivative for EPDM rubber.

3.2. Scanning Electron Microscopy Analyze (SEM) and Energy Dispersive X-ray Analyze (EDX)

The SEM photographs in Figure 1 were taken after the Florida weathering. The C amount of all prepared samples was at approximately the same level. The maximum change was found in the amount of nitrogen in Plate 4. The nitrogen content of Tinuvin-234 was 4.58% as calculated by the EDX data and it was discovered that this nitrogen element had migrated to the surface. This was confirmed by the visual control results shown in Table 3 and by the findings of the FTIR analysis.

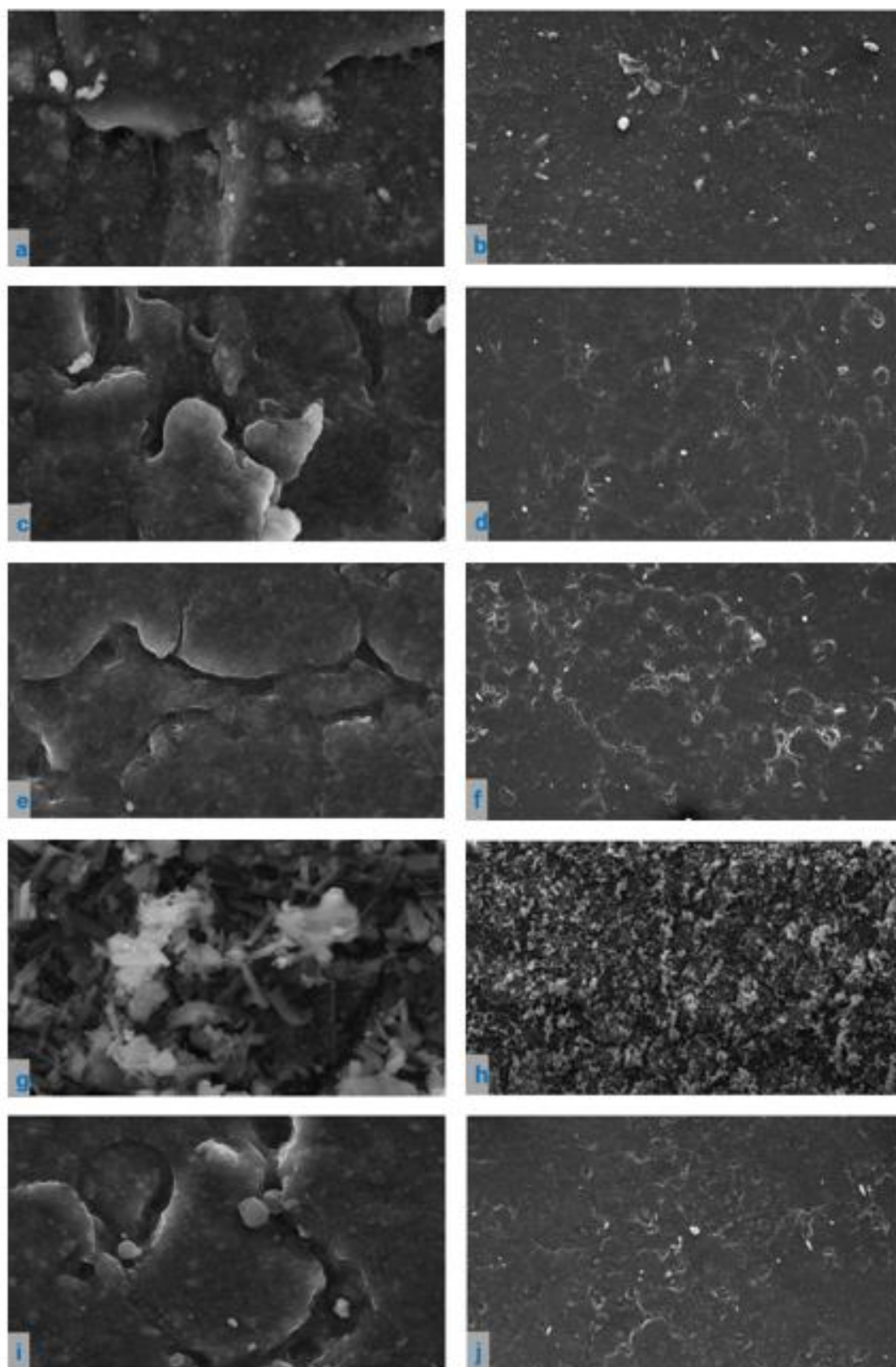


Figure 1. SEM and optical photographs of (a) EPDM plate 1 with 20 μm , (b) EPDM plate 1 with 200 μm , (c) EPDM plate 2 with 20 μm , (d) EPDM plate 2 with 200 μm , (e) EPDM plate 3 with 20 μm , (f) EPDM plate 3

with 200 μm , (g) EPDM plate 4 with 20 μm , (h) EPDM plate 4 with 200 μm , (i) EPDM plate 5 with 20 μm , (f) EPDM plate 5 with 200 μm .

The EDX spectrums of the EPDM plates were investigated to determine the chemical characterization after the weathering test and are shown in Figures 2- 6, respectively. The change in chemical content, especially the nitrogen (N), oxygen (O), sulfur (S) and zinc (Zn) content, is illustrated in the graph in Figure 7.

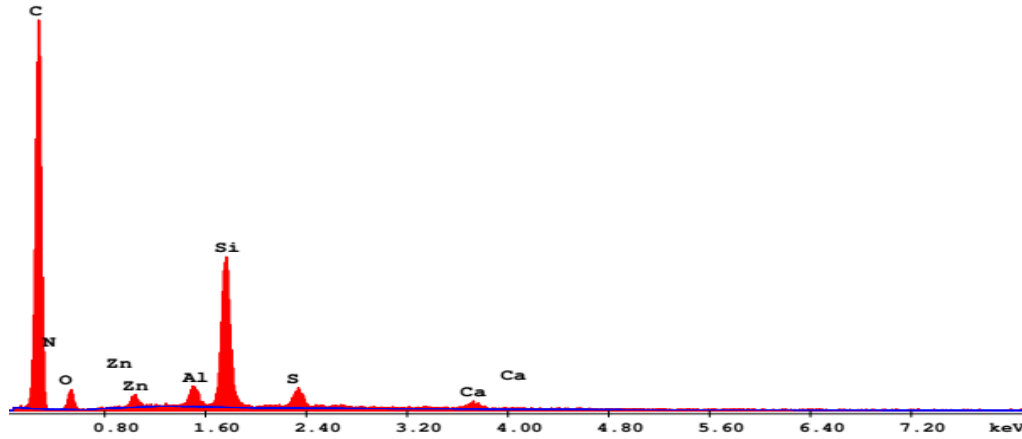


Figure 2. EDX spectrum of EPDM plate 1.

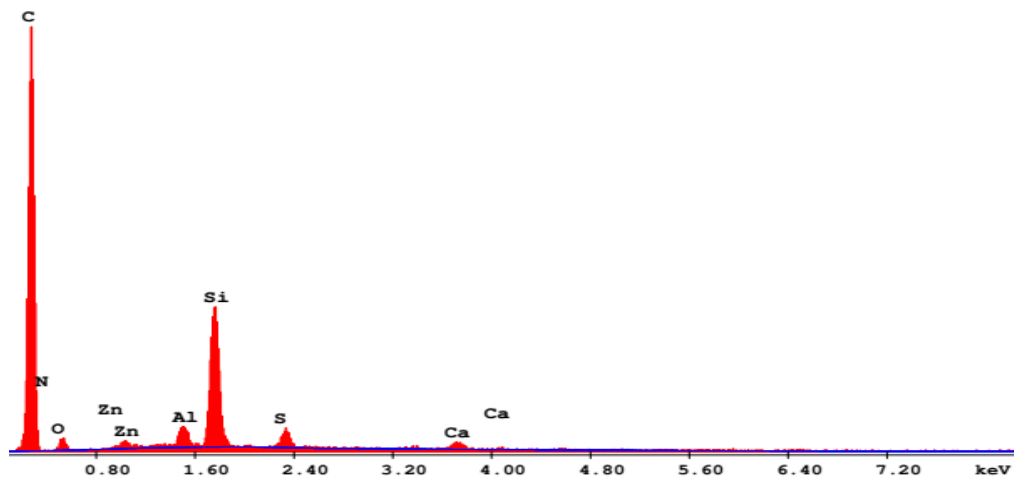


Figure 3. EDX spectrum of EPDM plate 2.

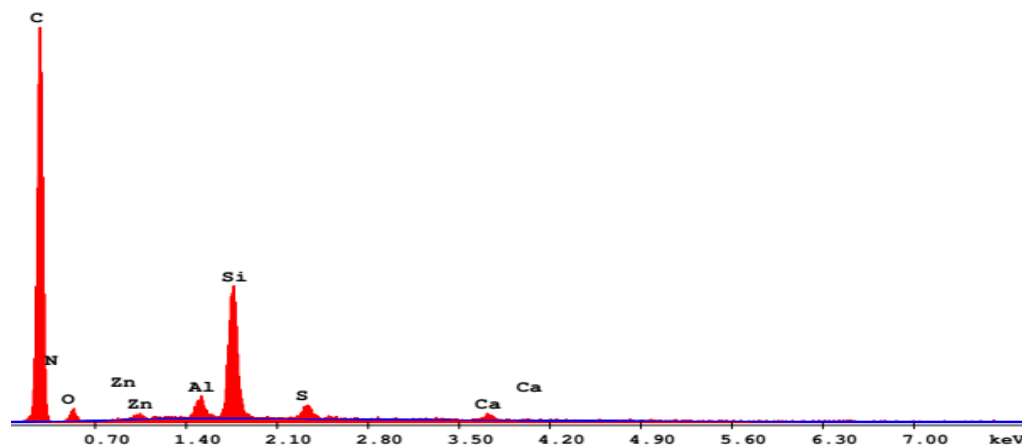


Figure 4. EDX spectrum of EPDM plate 3.

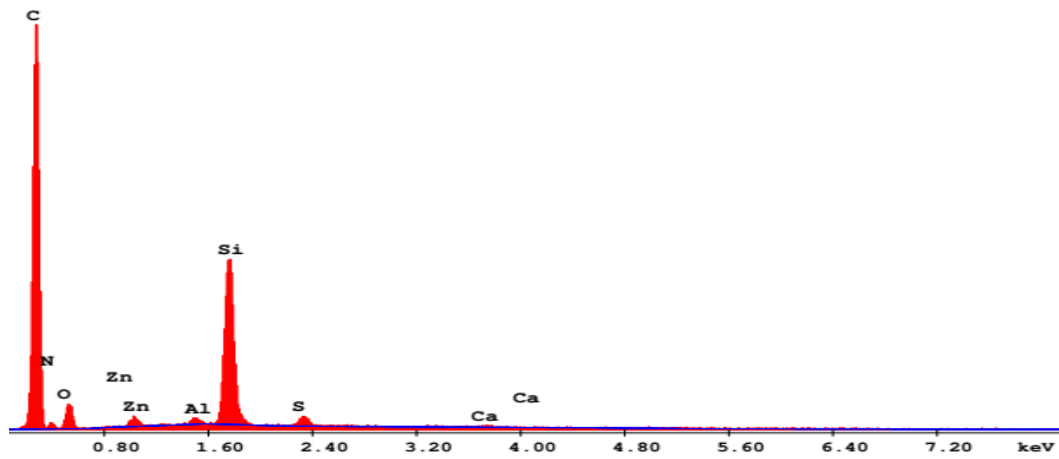


Figure 5. EDX spectrum of EPDM plate 4.

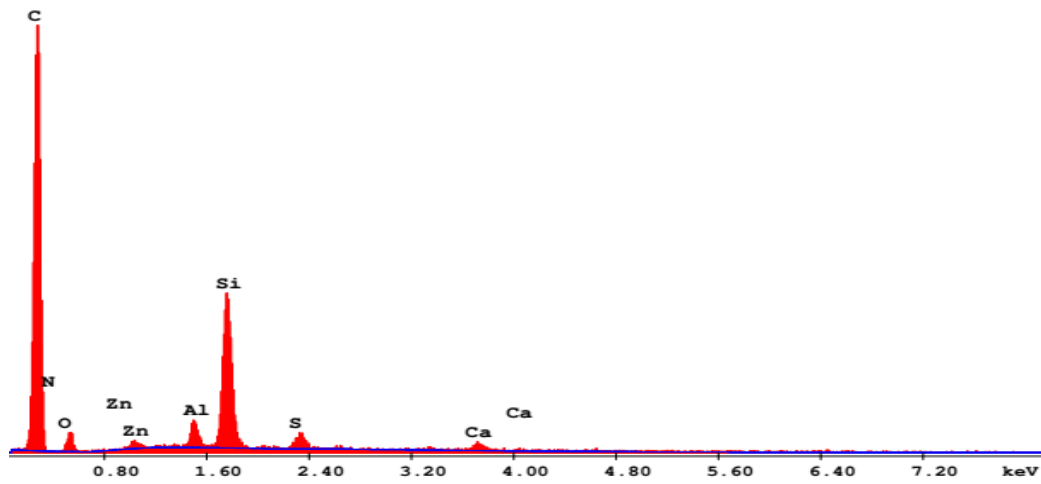


Figure 6. EDX spectrum of EPDM plate 5.

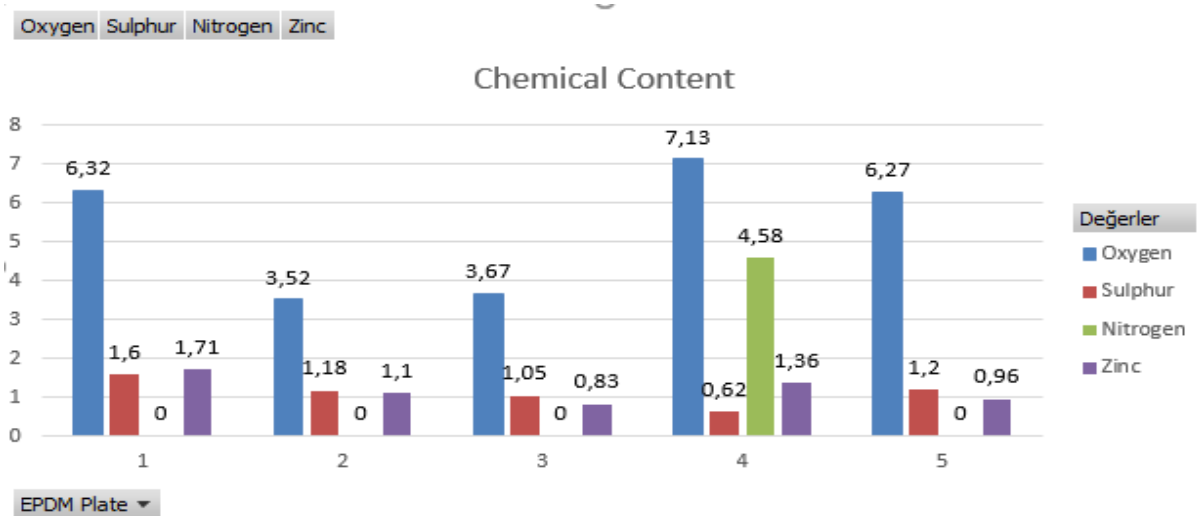


Figure 7. Change in chemical content of EPDM plates

3.3. Fourier Transform Infrared Spectroscopy Analyze (FTIR)

As seen in Table 4, Tinuvin-234 material migrated to the surface, causing whitening on the surface of Plate 4. Therefore, FTIR analysis was applied to Plate 4 to identify the functional groups in the molecular structure. The FTIR analysis is shown in graphic form in Figure 8.

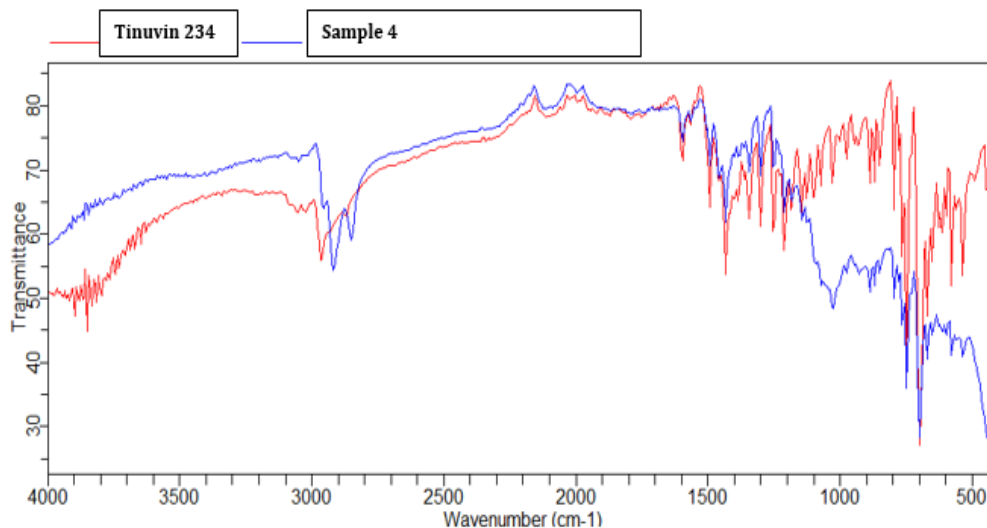


Figure 8. FTIR analyze of EPDM plate 4.

The FTIR results showed that the composition of the material appearing on the surface of Plate 4 was very similar to Tinuvin-234. The peaks at 2900 cm⁻¹ (aromatic –CH), 2800 cm⁻¹ (aliphatic –CH), 1400 cm⁻¹ (aromatic C=C and C=N), 1100 cm⁻¹ (C-C and C-O bonds) clearly indicated that the material which migrated was the Tinuvin-234 molecule.

4. Conclusions

The suitability of Tinuvin derivatives on the UV resistance of EPDM rubber was investigated in order to contribute to an internationally important issue such as the UV resistance of sealing profiles. The outcomes of these investigations can be summarized as follows:

- UV stabilizers can be used for EPDM rubber products.
- Unlike in the plastic industry, not all Tinuvin derivatives can be used as UV stabilizers for EPDM products.
- The visual control results after the artificial weathering test showed that Tinuvin-123 was an effective protective UV stabilizer for EPDM rubber.
- It is clear that Tinuvin-234 is not a good choice as a UV stabilizer for EPDM rubber. Tinuvin-234 appeared on the surface of the samples after the artificial weathering test. This finding was verified by SEM photographs and FTIR and EDX analyses.
- This research indicates that because not all UV stabilizers used in the plastic industry are suitable for EPDM rubber production, substantial research should be carried out before application of these materials.

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