



UV AGING EXAMINATION OF WINDSHIELD HOLDER RUBBER

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RESEARCH ARTICLE

ABSTRACT: The aim of this research is to examine the UV aging properties of windshield holder rubber materials used in public transportation vehicles, with a particular focus on the structural changes induced by UV light and their effects on mechanical properties. During the research, various rubber compounds were prepared, and their mechanical properties were measured in both fresh and UV-aged terms. The mechanical tests included measurements of tensile strength, elongation at break, modulus at 100% elongation (M100), and Shore A hardness. Based on the results, it was determined that UV aging significantly impacts the mechanical properties of the rubbers. UV exposure leads to a decrease in tensile strength and elongation at break, while the Shore A hardness increases. These changes can be attributed to free radical formation and the modification of polymer cross-links within the material structure. Comparison of different compounds revealed that some rubber blends exhibit better resistance to UV-induced aging, thereby possessing a longer lifespan. These findings contribute to the development and manufacture of sunlight-resistant rubber products and are beneficial for professionals working in rubber manufacturing and material testing. In summary, UV aging studies help to better understand the long-term behavior of windshield holder rubbers and provide opportunities for optimizing products against the effects of UV light.

KEY WORDS: *UV aging, Windshield holder rubber, Mechanical properties, Rubber compounds, Public transportation vehicles*

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ISTRAŽIVANJE STARENJA GUME DRŽAČA VETROBRANSKOG STAKLA ZBOG UV ZRAČENJA

REZIME: Cilj ovog istraživanja je da se ispituju karakteristike gumenih materijala za držače vetrobrana koji se koriste u vozilima javnog prevoza, sa posebnim fokusom na strukturne promene izazvane starenjem usled UV zračenja i njihov uticaj na mehanička svojstva. Tokom istraživanja pripremljena su različita jedinjenja gume i merena su im mehanička svojstva kako nove tako i ostarele gume usled UV zračenja. Mehanička ispitivanja su obuhvatila merenja: zatezne čvrstoće, izduženja pri lomu, modula elastičnosti pri 100% izduženju (M100) i tvrdoće po Šoru A. Na osnovu rezultata utvrđeno je da starenje izazvano UV zračenjem značajno utiče na mehanička svojstva gume. Izlaganje UV zračenju dovodi do smanjenja zatezne čvrstoće i izduženja pri prekidu, dok se tvrdoća po Šoru A povećava. Ove promene se mogu pripisati formiranju slobodnih radikala i modifikaciji polimernih poprečnih veza unutar strukture materijala. Poređenje različitih jedinjenja otkrilo je da neke mešavine gumene pokazuju bolju otpornost na starenje izazvano UV zračenjem, čime imaju duži životni vek. Ova otkrića doprinose razvoju i proizvodnji gumenih proizvoda otpornih na sunčevu svetlost i korisna su za profesionalce koji rade u proizvodnji gume i ispitivanju materijala. Ukratko, studije starenja zbog UV zračenja pomažu da se bolje razume dugoročno ponašanje gume za držače vetrobrana i pružaju mogućnosti za optimizaciju proizvoda koji sprečavaju staranje usled UV zračenja.

KLJUČNE REČI: *starenje usled UV zračenja, guma za držač vetrobrana, mehaničke karakteristike, mešavina gume, vozila javnog prevoza*

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INTRODUCTION

The Ethylene propylene diene monomer rubber (EPDM) is composed of ethylene and propylene monomers, with a small percentage of a diene monomer incorporated into the polymer, retaining one of its double bonds even after polymerization. Since EPDM rubbers contain three monomers, they carry the favorable properties of all three materials. Polyethylene is suitable for producing elastomers with low internal friction, but it is highly crystalline due to its regular structure. This regularity can be disrupted by the presence of methyl groups from the polypropylene chain, which face outward. This is typically achieved with a propylene content of 30-40% by weight, though other proportions can also be used. For sulfur vulcanization to be at least partially feasible, the role of the double bond from the diene monomer is crucial. Despite this, vulcanization is predominantly performed with peroxides, following a radical mechanism that does not require the presence of double bonds. Nevertheless, since EPDM rubbers contain double bonds, traditional sulfur vulcanization is also possible.[1]

In the production of EPDM rubber, the ethylene, propylene, and difunctional monomer are most often polymerized using solution polymerization in aliphatic hydrocarbons (typically pentane or hexane) with a Ziegler-Natta catalyst composed of vanadium chloride and alkyl-aluminum. After the polymerization process, the difunctional monomer groups present in small percentages are randomly and statistically distributed throughout the polymer.[1]

The most important advantage of EPDM rubber is its chemical resistance, which is due to the predominance of strong carbon-carbon and carbon-hydrogen sigma bonds, requiring high energy to break. As a result, EPDM rubbers exhibit excellent resistance to chemicals, heat, light, and ozone, and their highly non-polar nature ensures exceptional water resistance. On the other hand, this non-polarity also means that EPDM rubbers have weak resistance to organic solvents, and their mechanical properties are inferior to those of NR rubbers due to the lack of polysulfide bridges in peroxide vulcanization. Additionally, unlike CR rubbers, EPDM rubbers are not flame-resistant and cannot be used in fire-hazardous environments.[1]

When using vulcanizates made from EPDM rubber, we primarily take advantage of their resistance to ozone, chemicals, heat, and light. This makes them ideal for use in the automotive industry, for example, in windshield wipers and bumpers, as well as in the cable industry due to their good insulating properties. They are also widely used as raw materials for compensators, pipes, and other insulating materials.[1]

The most important application of EPDM rubbers is in the production of sealing materials, especially for securing windows in buses, trains, and passenger vehicles. In this application, the vulcanizate must withstand both high and low temperatures, as well as UV light from the sun and the resulting ozone concentration in the atmosphere. EPDM rubbers are excellently suited for manufacturing such materials, offering significantly longer lifespans than similar products made from other types of rubber.[2]

1 PHYSICAL TESTING METHODS FOR VULCANIZATES

Rubber is often described as a "black box" by rubber industry professionals, as identifying root causes after a failed production process is not an easy task. The challenge lies in the

difficulty, or rather impossibility, of measuring the molecular structure of cross-linked rubber. This is because the cross-linked molecule cannot be dissolved (liquid chromatography methods are not applicable), and it does not possess a regular crystalline structure (X-ray diffraction methods are also ruled out). Nevertheless, the process of vulcanizing rubber compounds, as well as the physical testing of fully vulcanized rubber, can provide valuable insights. When performed correctly, these tests offer significant information about the quality of the finished products and any changes in their properties. In this chapter, we will focus on these physical testing methods.[1]

1.1 Tensile Test

One of the most important physical tests in the rubber industry is the tensile strength test. In this test, after cutting the appropriate test specimen (usually a dumbbell-shaped form, but it can also be a ring-shaped one) from a vulcanized sheet, the ends of the specimen are fixed in the grips of a load cell. The lower grip remains stationary, while the upper one moves at a constant speed, stretching the specimen longitudinally. As a result, the specimen elongates and eventually breaks. The modulus required for breaking is called the tensile strength, usually expressed in MPa, calculated by dividing the force required to break the specimen (in newtons) by the cross-sectional area at the point of fracture (in mm²). This variable accurately indicates the amount of force or modulus that the vulcanizate can withstand, which simulates the resistance of products made from the vulcanizate to tensile and stretching forces. To achieve high tensile strength, a sufficient amount of additives (e.g., carbon black, silica) must be incorporated, as unfilled vulcanizates typically exhibit very low tensile strength.[1]

In addition to measuring tensile strength, elongation at break can also be determined, which indicates how much the specimen has stretched, as a percentage of its original length, until the point of breakage.[1] Extensometers are required to monitor the distance between the grips, ensuring precise measurement of displacement. Elongation at break provides insight into how much a given vulcanizate can be stretched before it ruptures.[3]

When rubber is stretched, internal stress develops within the material, causing it to break at its weakest point. This rupture occurs due to the inhomogeneous distribution of the material and the formation of weak surfaces, primarily caused by the uneven distribution of compound components and the irregular, statistical nature of the rubber's cross-linked structure. Remarkably, the elongation at break in rubbers can often reach several hundred percent. This is because vulcanized rubber, as a cross-linked polymer, has an extremely high molecular weight, resulting in a wide temperature range for its hyperelastic state. This state is largely characterized by viscoelasticity, which enables part of the force applied to the material to be absorbed and the remainder to be elastically reflected after the material deforms. Consequently, even after significant deformational force, the deformation of the material is partially reversible, allowing the specimen to nearly regain its original shape even after being stretched with considerable force.[1]

Tensile strength testing of rubbers is typically performed according to ISO 37, which accepts both ring-shaped and dumbbell-shaped test specimens. In our case, we used dumbbell-shaped specimens, with a schematic drawing shown in Figure 1. The advantage of the dumbbell shape is that the narrow part of the specimen experiences relatively uniform deformation, leading to reproducible results. According to the standard, the length of the specimen (denoted as part 1 in Figure 1.) should be 20 ± 0.5 mm or 25 ± 0.5 mm, and if these lengths are not possible, a length of 10 ± 0.5 mm can be used, with a thickness of 2.0 ± 0.2 mm. For smaller specimens, a thickness of 1.0 ± 0.1 mm is also acceptable. The test

specimen is typically vulcanized directly from the rubber compound in a laboratory vulcanizing press, where cross-linking occurs according to the formulation at a given temperature and duration.[9] It is essential to wait at least 16 hours after vulcanization before performing the test, as prescribed by ISO 23529, to allow the vulcanizate to relax and reach its final molecular structure at room temperature. To obtain reliable results in accordance with the standard, at least three tests must be conducted.[4]

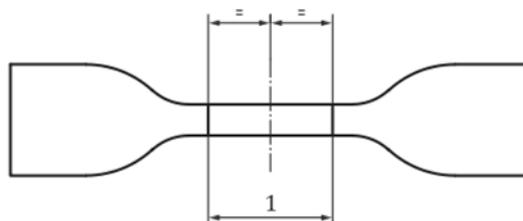


Figure 1. ISO 37 test specimen shape for tensile testing of elastomers – 1. The gauge length of the specimen [5].

Considering that the tensile strength of ebonite, which has a dense sulfur cross-linked structure, significantly exceeds that of soft rubber, it can be stated that the tensile strength of a vulcanizate increases with the increase in cross-link density.[1]

1.2 Hardness Testing

For hardness measurement, both in industry and laboratories, there are various methods available (such as Mohs, Rockwell, Brinell scales, etc.), but in the plastics and rubber industry, Shore hardness is the most widely used, specifically Shore A and Shore D, which operate on a scale from 0 to 100. In Shore hardness testing, a needle is pressed into the specimen, and the depth of penetration determines the Shore hardness. The harder the material, the more it resists the needle, resulting in a higher Shore hardness value.[1] Generally, it is noted that Shore scales are most accurate in the mid-range, while measurements near the extremes (close to 0 or 100) are less reliable (according to the ISO 48-4 standard, below 20 and above 90), and in such cases, switching to another scale is recommended. For the best reproducibility in the plastics and rubber industry, Shore hardness testing is typically conducted in accordance with the ISO 48-4 standard. According to this standard, Shore A and D measurements are usually performed on a solid vulcanized disc with a minimum thickness of 6 mm.[6]

In the rubber industry, Shore A hardness measurement is most commonly performed, using a truncated cone-shaped indenter, meaning the tip of the needle is flat. When testing the hardness of rubber, the Shore A reading should be taken after 3 seconds, as the elastic rubber can continue to deform if more time passes, potentially skewing the results. It is worth noting that 1 unit of Shore hardness corresponds to a spring force of 75 mN.[6]

2 AGING OF RUBBER DUE TO LIGHT EXPOSURE

As is well known, a significant portion of the light coming from the sun falls within the UV range. According to the electromagnetic spectrum of light, the wavelength of UV light (100-380 nm) is shorter than that of visible light (~380-780 nm), which means it carries more energy than visible light. The energy of UV light reaches a level sufficient to break primary chemical bonds, a process also observed in polymers and rubber. As a result, high-energy UV radiation acts as an initiator for various unwanted reactions, leading to the breaking of

carbon-carbon, sulfur-sulfur, and carbon-sulfur bonds. Depending on the composition of the mixture, this can cause the vulcanizate to soften and become sticky, or it may harden and crack, taking on a texture similar to that of elephant skin. Unfortunately, the exact molecular structural changes are difficult to determine because cross-linked polymers cannot be analyzed using classical or instrumental analytical methods. The light resistance of rubber can be significantly improved by adding various additives. One of the best and most commonly used materials for this purpose is carbon black, which has excellent light-absorbing properties. Carbon black absorbs the incoming light and disperses it evenly, reducing the light's intensity and thereby increasing the UV resistance of the compound.[1]

The effect of sunlight can be measured in several ways. One option is to expose the vulcanized test specimen to natural sunlight, but a more efficient and reproducible method is to use UV chambers. In such equipment, the wavelength range and intensity of the applied light can be adjusted, and by increasing the intensity, the exposure time can be shortened. The applied irradiation time can then be converted, using literature data, into an equivalent amount of sunlight exposure, taking into account specific climatic conditions.[1]

2.1 Energy of Solar Radiation

To model the energy and effects of UV light from the sun, we will use UV lamps operating at specific wavelengths and intensities. The energy per square meter (energy density) can be calculated as a function of exposure time. The obtained value can then be compared with data from the literature, using two locations with different geographical characteristics as a reference. In this case, we will consider Hungary (humid continental climate) and Florida in the United States (subtropical climate). According to the literature, one year of solar radiation in Hungary corresponds to an energy density of 2015 kJ/m², while in Florida, it reaches 2800 kJ/m² [7].

2.2 Compounds Used

The manufacturer provided us with four different EPDM rubber-based vulcanizate compositions, the exact formulations of which were not disclosed due to business confidentiality. However, we do know that the EPDM rubber-based compounds are suitable for the production of sealing materials. To differentiate between the formulations, we labeled them as I., II., III., and IV.

2.3 Equipment Used

For the sunlight simulation tests, we utilized UV lamps, exposing rubber test specimens for 0, 400, 800, 1200, and 1600 hours for each compound type. The exposure process was conducted using an ATLAS Material Testing Solutions LLC UV Test device. The chamber temperature was kept constant at 50 °C, with an irradiation intensity of 1.5 W/m². The device was equipped with eight UVA-340 fluorescent tubes, and the wavelength of the irradiation was 340 nm.

For tensile strength tests, we used an Instron 4482 R5900 machine, equipped with a video extensometer. The test specimens were cut in a dumbbell shape according to the ISO 37 standard, with a gauge length of 25 mm for the extensometer. During the test, the crosshead speed was 500 mm/min, and the preloading was conducted with a force of 1 N at 10 mm/min. The grip distance was set to 50 mm. The test was performed under controlled laboratory conditions at a temperature of 23 °C ± 2 °C.

For Shore A hardness measurements, we used a Zwick Shore A hardness tester mounted on a stand.

3 TENSIL TEST RESULT

The measurements were performed after 0, 400, 800, 1200, and 1600 hours of UV exposure, and the data were recorded. During the evaluation, the average of the measurements was considered. Standard deviation values were also taken into account in the assessment of the measurement results. The width of the vulcanized and die-cut test specimens was fixed at 6 mm, while the thickness was measured each time.

Table 1 Tensile test results

Sample	UV	Modulus M100 [MPa]	Tensile stress at Maximum Load [MPa]	Tensile strain [%]
	[h]			
I.	0	3.8	10.7	329
	400	4.4	10.9	283
	800	4.6	10.8	266
	1200	4.4	10.1	258
	1600	4.8	10.2	239
II.	0	3.0	8.0	310
	400	3.2	8.1	302
	800	3.3	8.1	295
	1200	3.5	8.4	294
	1600	3.5	8.0	267
III.	0	7.3	12.0	199
	400	7.8	11.6	173
	800	8.7	11.6	150
	1200	7.8	10.8	155
	1600	8.5	10.7	136
IV.	0	6.2	7.4	127
	400	7.0	8.3	124
	800	6.6	7.6	121
	1200	6.7	7.8	120
	1600	7.3	8.0	114

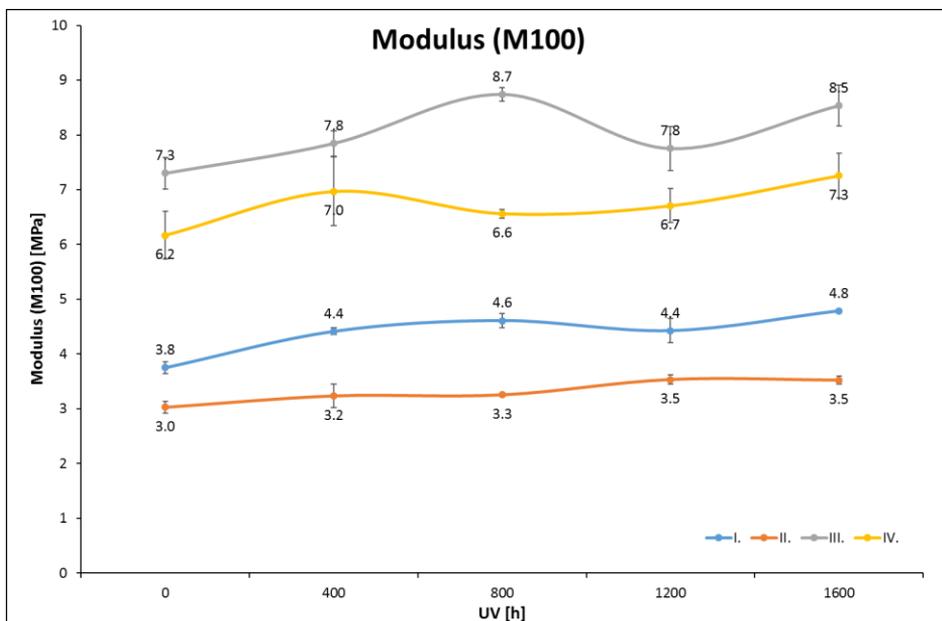


Figure 2. Modulus (M100)

In the case of the modulus, we observed an increasing trend for all samples as a result of aging. The largest percentage difference between the averages was found in Sample I, with an increase of 27.5%, while Samples II, III, and IV showed increases of 16-17%.

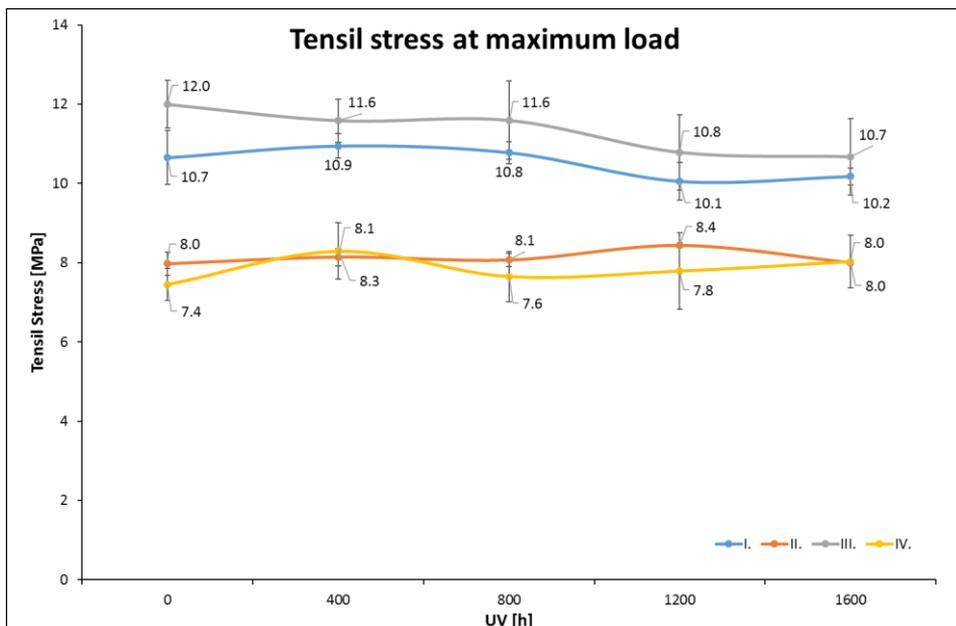


Figure 3 Tensile stress at maximum load

When examining the average values of the tensile stress corresponding to the maximum force, considering the standard deviation, no clear difference or trend can be identified.

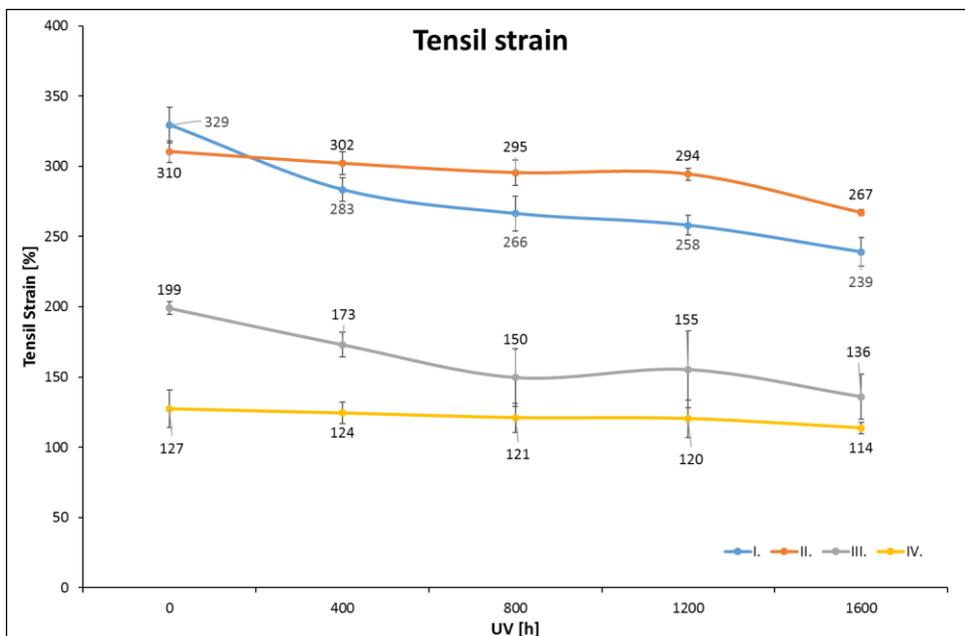


Figure 4. Tensile strain

The elongation at break values show a decreasing trend, with Sample I exhibiting a 27% decrease and Sample III a 32% decrease. For Samples IV and II, the decreases were 11% and 14%, respectively.

Table 2 Shore A

Sample	UV [h]	Shore A	
		Value	Standard deviation
I.	0	70.3	0.5
	400	71.1	0.7
	800	71.6	0.5
	1200	71.8	0.4
	1600	72.5	0.5
II.	0	67.3	0.7
	400	67.6	0.5
	800	68.1	0.3
	1200	68.0	0.0
	1600	68.7	0.5
III.	0	83.6	0.5
	400	83.8	0.4
	800	84.2	0.4
	1200	84.4	0.5
	1600	85.0	0.0
IV.	0	84.2	0.4
	400	85.2	0.4
	800	86.0	0.0
	1200	86.0	0.0
	1600	86.2	0.4

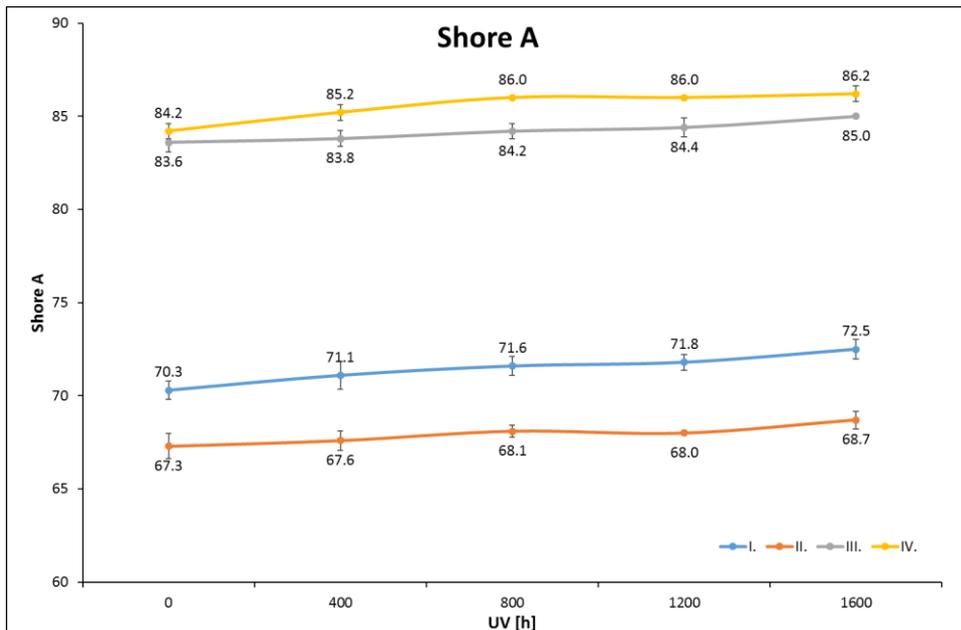


Figure 5. Shore A

The Shore A hardness values across the different compounds showed an increase ranging from 1.5% to 3.2%. This increase is acceptable for future applications.

4 CONCLUSIONS

During the 1600-hour UV aging process, we conducted mechanical tests on samples taken at various time intervals. Our goal was to assess how resistant each compound is to UV radiation and to what extent they change. Samples I and III were the most sensitive to UV radiation, while Samples II and IV were less affected. We recommend further development of the formulation used in Samples II and IV for the windshield sealing material.

Overall, this study demonstrates the varying levels of UV resistance among the tested rubber compounds. By identifying the compounds that show greater resilience, manufacturers can focus on optimizing these formulations for enhanced durability in real-world applications. The findings also highlight the importance of continuous testing and material development to ensure the longevity of rubber materials exposed to UV radiation in transportation settings.

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