Effect of UV-radiation on IR, BR, and SBR elastomers FT-IR spectra

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DOI: https://doi.org/10.14314/polimery.2024.11.3

Abstract: The effect of UV radiation on infrared spectra (FT-IR) and mass change of elastomers (IR, BR, SBR) was studied. It was found that with the extension of the UV radiation time the intensity of bands originating from hydroxyl and carbonyl groups increased. Carbonyl groups were identified in SBR after 30 h of exposure, while in IR and BR after 18 h. It was shown that SBR was characterized by the highest resistance to UV radiation.

Keywords: rubber, elastomers, UV radiation, degradation, FT-IR.

Wpływ promieniowania UV na widma FT-IR elastomerów IR, BR i SBR

Streszczenie: Zbadano wpływ promieniowania UV na widma w podczerwieni (FT-IR) i zmianę masy elastomerów (IR, BR, SBR). Stwierdzono, że wraz z wydłużeniem czasu działania promieniowania UV zwiększała się intensywność pasm pochodzących od grup hydroksylowych i karbonylowych. Grupy karbonylowe zidentyfikowano w SBR po 30 h ekspozycji, natomiast w IR i BR po 18 h. Wykazano, że największą odpornością na promieniowanie UV charakteryzował się SBR.

Słowa kluczowe: kauczuk, elastomery, promieniowanie UV, degradacja, FT-IR.

Elastomers are a highly essential group of materials that find an application in the form of sealings, tires, products for medicine, industrial technologies, agriculture, military, electronics, etc. The main reason of their widespread application is their viscoelastic behaviour [1, 2].

Elastomers are flexible with substantial extension when stretched [1, 2]. These materials can exist in nature, for instance natural rubber (NR) or can be manufactured synthetically. Most of the synthetic rubbers were produced at the beginning of the 20th century, e.g. styrene-butadiene rubber. The isoprene rubber (IR) was synthetized in 1950s according to Ziegler-Natta catalysts. The isoprene rubber can be manufactured within four conformations: *cis*-1,4-; *trans*-1,4-; 1,2-; and 3,4-. As a mirror to the natural rubber, there is a request to achieve similar physical properties. For many years, it was believed that the content of *cis*-1,4-polyisoprene units (<99.9 %) can fully mimic the properties of natural rubber. Despite of that, it was recently said that NR is a nanocomposite formed by proteins and lipids, and the fact is that NR nanomatrix structure gives its extraordinary properties [2]. The isoprene rubber has been used in many processes as a natural rubber such as blending with styrene-butadiene rubber or polybutadiene rubber [3]. Polybutadiene rubber (BR) with a high *cis*-1,4-unit content provides a similar viscoelasticity to NR and is one of the largest produced rubbers worldwide [4, 5]. Thanks to excellent mechanical properties and usability of copolymer styrene-butadiene rubber (SBR), it is highly applicable in many areas, for instance silent blocks, vibration absorbers, or shoes. Styrene-butadiene rubber attains good crack and weather resistance also [6, 7].

A crucial factor that controls the behaviour of numerous elastomers is the natural environment [8]. During the exposition of elastomeric materials to the natural environment, the degradation based on oxygen, UV-radiation, and aging is pronounced. As a function of UV-radiation's propagation depth, the distribution of photo-oxidation products onto elastomeric materials will be non-uniform. Elastomers undergo a significant modification due to the presence of heat, ozone, light, and oxygen throughout the environmental impact [8, 9]. As its reported, the oxidative degradation can cause a softening of polybutadiene rubber and chain scission, respectively, and both hardening and softening of styrene-butadiene rubber [9]. Due

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to the tendency of free radicals to arise, when rubber is exposed to conditions mentioned above, the hardening of the SBR is produced. Besides these two scenarios, the cracking, charring, and colour fading is perceived. The study [10] proved that the SBR microstructure is significantly changed due to the UV-radiation. Cracks, wrinkles, rough and broken surface structures can be easily formed. In addition, the UV-radiation modifies the elastomer surface by creating carbonyl, carboxyl and hydroxyl moieties [9, 11].

The main objective of this work was to analyse the changes in chemical composition of isoprene rubber (IR), butadiene rubber (BR), and styrene-butadiene rubber (SBR) exposed to the UV-radiation within several cycles for 90 h using infrared spectroscopy (FT-IR). Furthermore, after each cycle the change of mass was determined.

EXPERIMENTAL PART

Materials

In this work, the following materials were used:

– isoprene rubber (IR) (Nizhnekamskneftekhim Inc., Nizhnekamsk, Russia) with a 99.7 wt% content of *cis*-1,4-unit and Mooney viscosity ML(1+4)100°C: 67–76 MU;

– Polybutadiene rubber (BR 1) (Synthetic Rubber Factory, Voronezh, Russia) manufactured within solution polymerization using Ti catalytic system; Mooney viscosity ML(1+4)100°C: 40–50 MU;

– Polybutadiene rubber (BR 2) (LG Chem, Ltd, Seosan-SI, South Korea) manufactured within solution polymerization using Ni catalytic system; Mooney viscosity ML(1+4)100°C: 41–49 MU;

– Polybutadiene rubber (BR 3) (Synthos PBR s.r.o., Kralupy nad Vltavou, Czech Republic) catalysed with Nd; Mooney viscosity ML(1+4)100°C: 39–49 MU;

– Polybutadiene rubber (BR 4) (Zeon Corporaration, Tokuyama, Japan) interacting with carbon black and catalysed with Li; Mooney viscosity ML(1+4)100°C: 45–55 MU;

– Styrene-butadiene rubber (SBR 1) (Nippon Zeon, Tokuyama, Japan); manufactured within solution; including styrene 25 wt% and vinyl BR 35 wt%, stabilized; Mooney viscosity ML(1+4)100°C: 51–61 MU;

– Styrene-butadiene rubber (SBR 2) (Styron Deutschland GmbH, Schkopau, Gremany): manufactured within solution, including styrene 21 wt% and vinyl BR 62; Mooney viscosity ML(1+4)100°C: 45–55 MU.

Samples preparation

10 mL of heterocyclic organic substance tetrahydrofuran (THF), IR, BR, and SBR elastomers were dissolved for 24 h. Subsequently, a thin film (3.0 mm) of rubber solutions was coated on glass (Fig. 1).

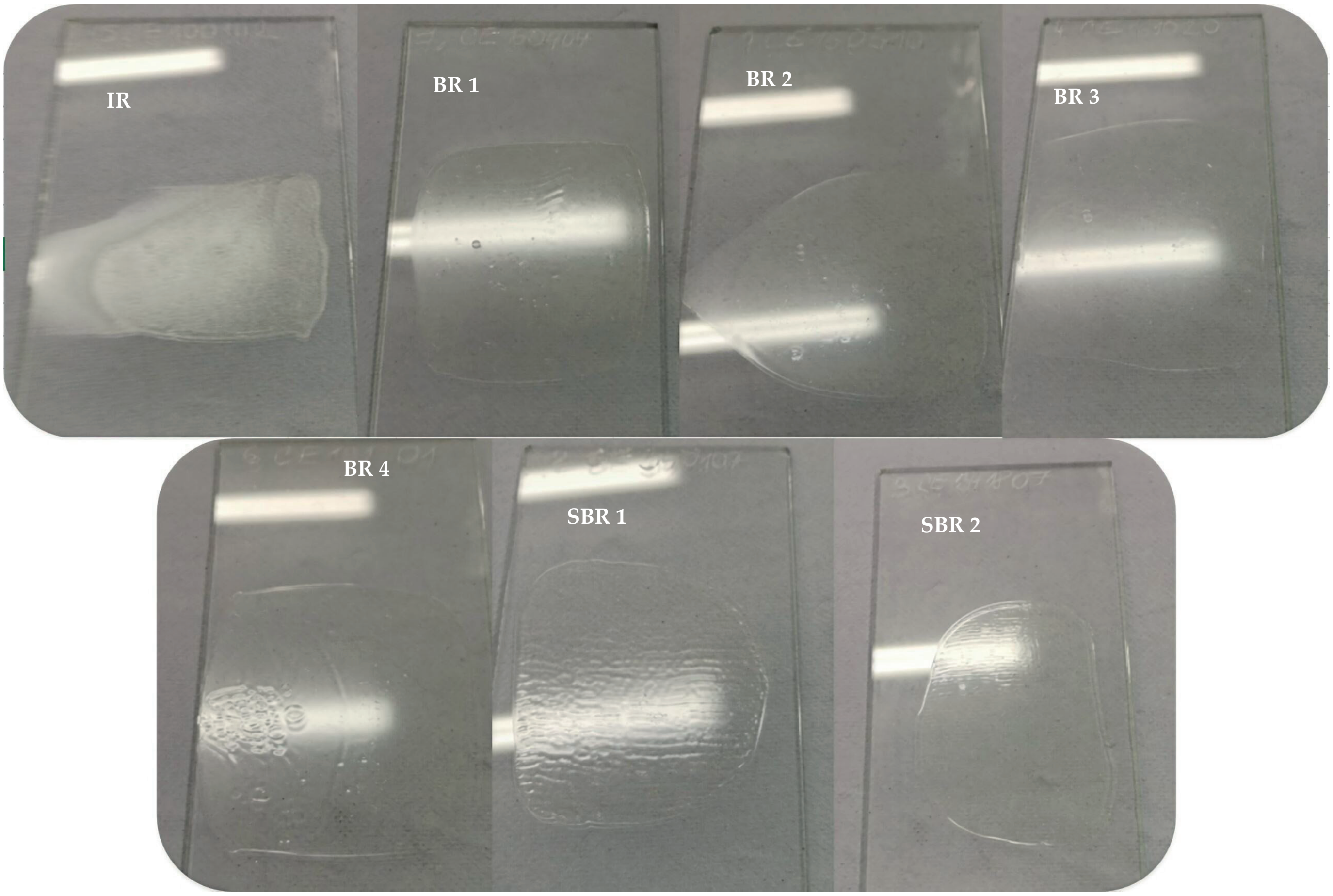

Fig. 1. Thin films of rubber solutions

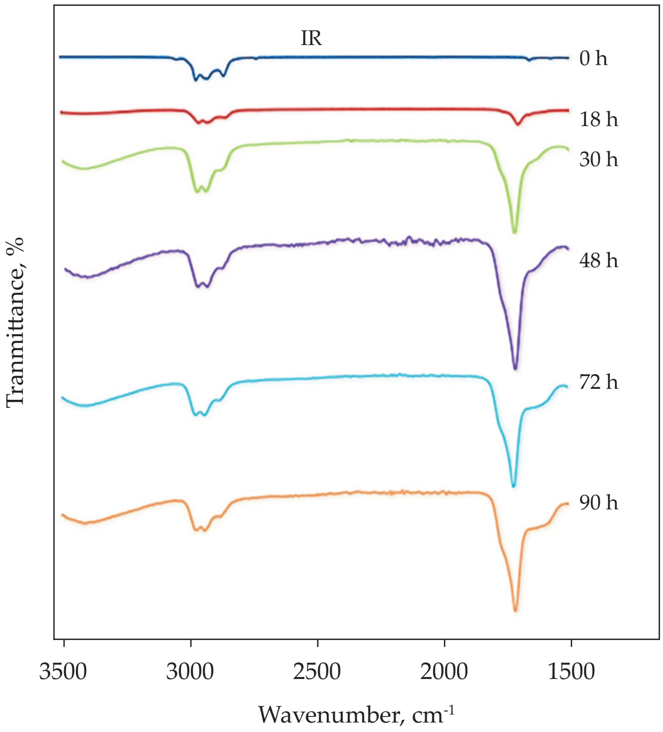

Fig. 2. FT-IR spectra of IR before and after UV irradiation

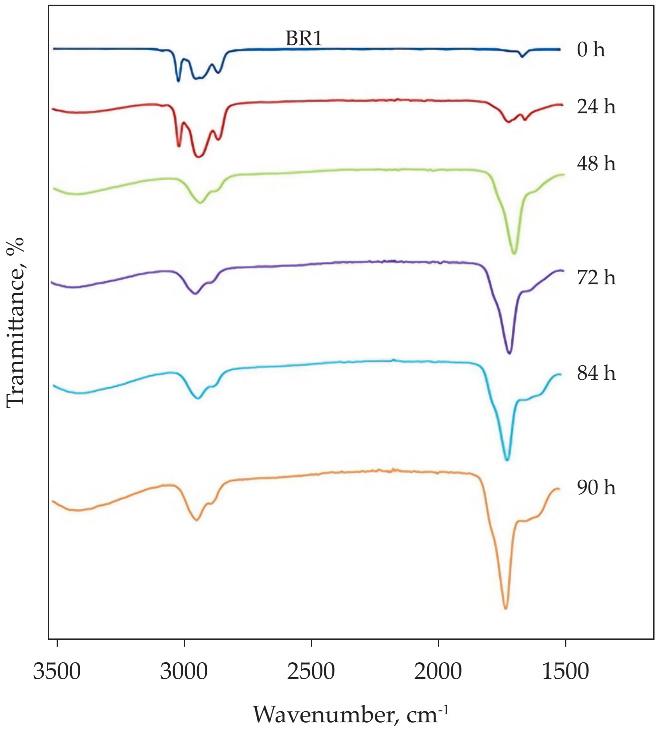

Fig. 3. FT-IR spectra of BR 1 before and after UV irradiation

Methods

UV-radiation chamber Xenotest 440 (Atlas, Illinois, USA) was used to simulate the UV-radiation condition for assembled elastomers. The UV-chamber used Xenologic Lamp Technology equipped with two air cooled xenon bulbs with 2200 W of power. The UV-chamber was provided by 120W/cm^2 irradiation, combined with xenocal senser to measure irradiation. A FT-IR spectrometer Tensor 27 (Tensor Bruker, Vienna, Austria) was utilized to monitor changes in chemical composition and the formation of new functional groups before and after the UV irradiation of synthetic rubber samples. Using FT-IR analysis with an ATR technique, the spectra of individual rubbers were measured before exposure to UV-radiation and at regular 6 h intervals during exposure with a total aging time of 90 hours. For the studied rubber samples, FT-IR spectra were measured after each sampling from the UV-chamber, a graph was generated in the OPUS program and the most important peaks were assigned.

RESULTS AND DISCUSSION

Figure 2 depicts the infrared spectra of the isoprene rubber IR before and after exposition to the UV-radiation. A broad absorption peak corresponding to the stretching vibrations of the hydroxyl group ν(OH) can be observed around 3466–3371 cm^{-1} [11]. This peak appears for the first time after 12 hours of isoprene rubber irradiation in the UV chamber and its intensity visibly increases with the time of exposure. This could be evidence of the increasing number of hydrogen bonds on the surface of isoprene rubber, most likely due to degradation effect caused by UV-radiation. The absorption peaks in the wavelength area between 2978 –2962 cm^{-1} are typical for the stretching vibrations of the methyl and methylene groups ν(CH_2, CH_3) [12, 13, 14]. Due to the presence of –CH_3 bonds inside the structure of the isoprene rubber, the changes in the intensity and shape of related peak can be observed, because of exposure. The highest intensity of related peak was recorded after 12 hours of aging in the UV chamber. A pronounced absorption peak around of ~1720–1709 cm^{-1} can be attributed to the stretching vibrations of carbonyl groups ν(C=O) [15, 16, 17]. The intensity of this peak visibly increases after 30 hours and increases with the time of exposure to UV-radiation. Subsequently, due to the influence of methylation during the degradation process, the shift to lower wavenumbers can be observed.

Figure 3 summarizes the results of BR 1 rubber FT-IR spectra. In the area of 3471–3406 cm^{-1} a broad absorption peak corresponding to the stretching vibrations of hydroxyl groups ν(OH) [9, 15] bounded by hydrogen bonds can be observed, and is likely connected to the intramolecular or intermolecular hydrogen bridges. After 24 h of irradiation in the UV chamber, a more visible increase in the mentioned absorption peak's intensity is noticed. The peaks between 2911 cm^{-1} and 2930 cm^{-1} are typical for stretching vibrations of aliphatic C–H bonds [13, 15]. Due to the presence of –CH_3 bonds in the rubber structure, the intensity of absorption peaks increased. A pronounced absorption peak in the range of 1712–1705 cm^{-1} is cha-

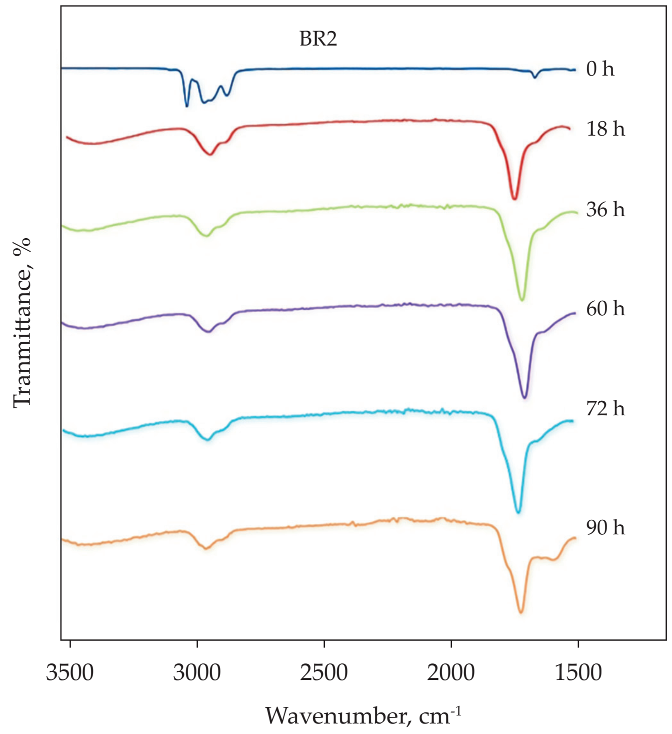

Fig. 4. FT-IR spectra of BR 2 before and after UV irradiation

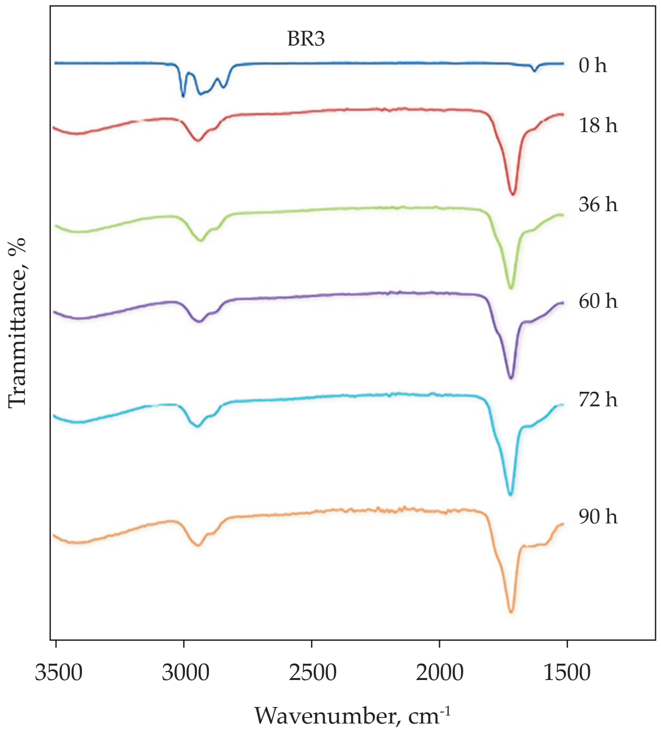

Fig. 5. FT-IR spectra of BR 3 before and after UV irradiation

racteristic for stretching vibrations of carbonyl moieties [9, 15, 17]. Consequently, due to methylation the peak of ν(C=O) stretching vibration shifted to lower wavenumbers.

Figure 4 illustrates the infrared spectra of BR 2 rubber sample before and after UV-radiation. The absorption peak in the range of 3437–3378 cm^{-1} can be associated with the stretching vibrations of hydroxyl groups ν(OH) [11]. After 18 h of irradiation, intensity of this peak increased. In the area of 2964 cm^{-1} to 2910 cm^{-1}, the peaks related to the symmetric and asymmetric stretching vibrations of ν(CH_2, CH_3) groups can be observed [13, 14, 15]. After 12 h

Table 1. Mass change of IR, BR, and SBR after 0-42 h of UV irradiation

Elastomer	Mass, mg							
	0 h	6 h	12 h	18 h	24 h	30 h	36 h	42 h
IR	84503.3	84503.0	84512.6	84517.6	84517.4	84516.4	84517.4	84516.8
BR 1	84118.3	84118.8	84120.2	84120.7	84130.7	84135.3	84135.2	84136.2
BR 2	82791.5	82793.6	82805.7	82810.6	82810.0	82808.7	82809.0	82808.8
BR 3	84344.7	84345.1	84341.6	84345.7	84368.4	84372.3	84372.0	84371.5
BR 4	83796.6	83796.8	83797.4	83806.0	83817.4	83817.6	83817.2	83817.3
SBR 1	82667.6	82663.0	82663.1	82667.7	82675.4	82675.4	82675.5	82675.2
SBR 2	83962.5	83963.2	83963.1	83958.8	83960.3	83966.3	83967.5	8396.7

Table 2. Mass change of IR, BR, and SBR after 48–90 h of UV irradiation

Elastomer	Mass, mg							
	48 h	54 h	60 h	66 h	72 h	78 h	84 h	90 h
IR	84516.1	84516.0	84516.2	84515.9	84515.8	84514.7	84514.7	84514.6
BR 1	84135.3	84134.9	84134.9	84134.8	84134.8	84134.4	84134.3	84134.3
BR 2	82807.8	82794.9	82790.1	82789.8	82789.7	82789.4	82789.1	82789.0
BR 3	84371.0	84371.4	84371.1	84371.4	84371.2	84370.5	84370.5	84369.8
BR 4	83816.9	83816.6	83816.2	83816.3	83816.0	83815.9	83815.9	83815.9
SBR 1	82675.0	82674.9	82674.2	82673.2	82673.1	82673.0	82673.0	82673.0
SBR 2	83966.0	83965.9	83965.9	83965.9	83965.7	83965.6	83965.6	83965.3

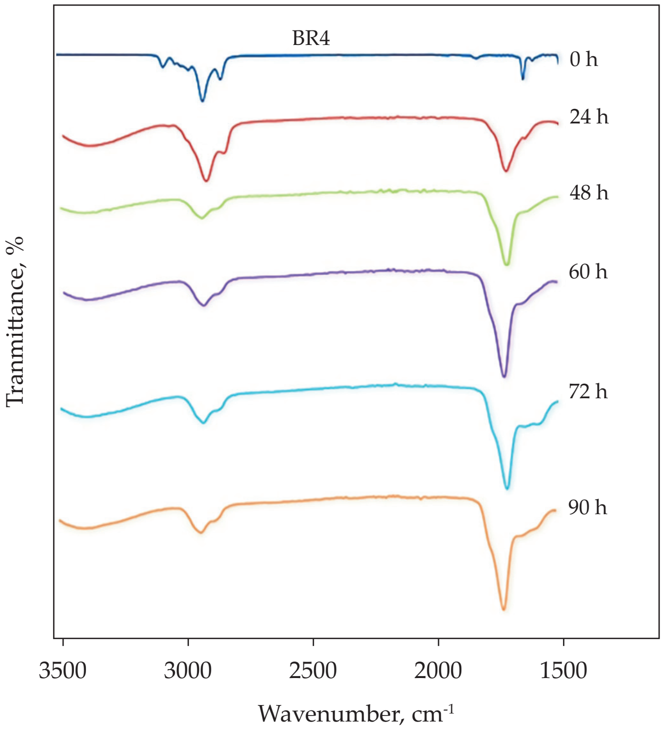

Fig. 6. FT-IR spectra of BR 4 before and after UV irradiation

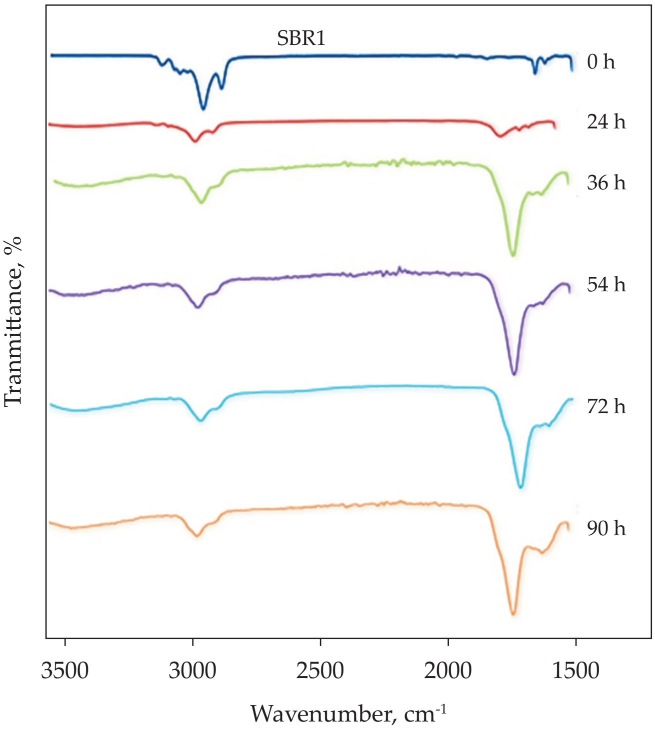

Fig. 7. FT-IR spectra of SBR 1 before and after UV irradiation

of aging, a strong peak corresponding to the stretching vibrations of ν(C=O) was observed in 1714–1705 cm^{-1} [16, 17]. Since 18 h of exposure to UV radiation, a significant increase in intensity was noticed.

The infrared spectra of BR 3 before and after UV-radiation is depicted in Fig. 5. As shown in Fig. 5, already in 12 h of UV exposition, the absorbance peak corresponding to the stretching vibration of ν(OH) was detected [11]. After 18 h, the peak's intensity increased. Between 2930–2895 cm^{-1}, symmetric and asymmetric stretching vibrations of methyl and methylene groups ν(CH_2, CH_3) were identified [15]. As a sign of UV degradation after 18 h of exposition and around 1729 cm^{-1} and 1703 cm^{-1}, the stretching vibrations of ν(C=O) weas distinguished [17, 18]. Along with the UV pronounced degradation, the shift of ν(C=O) stretching vibration peak to lower wavenumbers was observed.

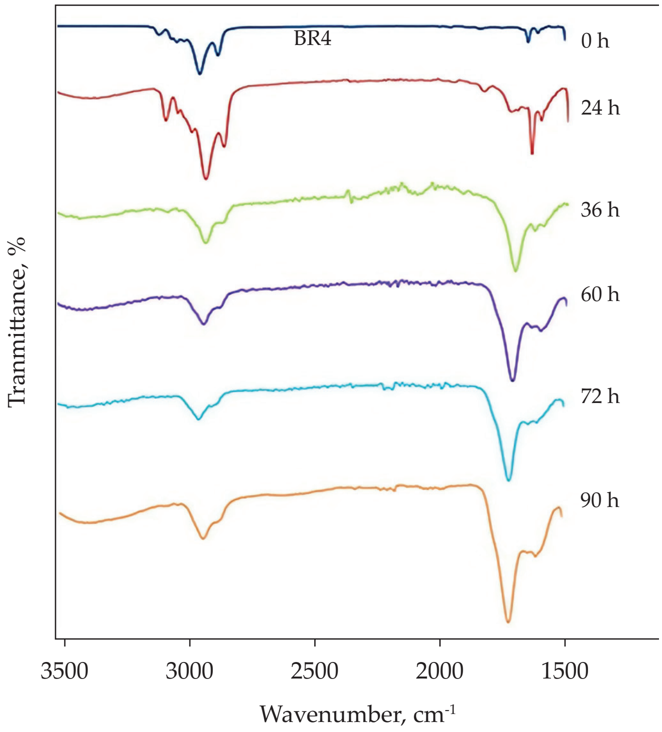

Fig. 8. FT-IR spectra of SBR 2 before and after UV irradiation

In Fig. 6, the infrared spectra of BR 4 can be seen. After 18 h of UV exposure, the absorption peak corresponding to the stretching vibrations of hydroxyl groups ν(OH) was observed between the area of 3447–3383 cm^{-1} [9]. Due to an increase in the number of hydrogen bonds, its intensity increased after 24 h of exposure. Symmetric and asymmetric stretching vibrations of the methyl and methylene groups ν(CH_2, CH_3) can be seen in 2930–2914 cm^{-1} [15]. After 24 h of aging, the absorption peaks related to the stretching vibrations of carbonyl groups ν(C=O) resulting from degradation were identified [16, 17].

Fig. 7 shows the SBR 1 infrared spectra before and after UV exposure. After 12 h of exposure, the absorption peak associated with stretching vibrations of ν(OH) is noticed [9, 15]. After 24 h of irradiation inside the UV chamber, a significant increase in intensity of ν(OH) peak was produced. A symmetric and asymmetric stretching vibrations of ν(CH_2, CH_3) were seen in area of 2931–2915 cm^{-1} [12, 13] along with increasing intensity in time. Herein, after 30 hours of UV-radiation, the stretching vibration of carbonyl groups ν(C=O) was perceived [19, 20]. This fact corresponds to a higher resistance of SBR 1 rubber sample to UV-radiation. Furthermore, a methylation was demonstrated.

As shown in Fig. 8, already after 6 h of UV exposure, the presence of hydroxyl moieties was demonstrated in spectrum of SBR 2. After 24 h, the increase of related peak's intensity was observed. The increase in intensity is the evidence of hydrogen bonds growth due to chemical changes and because of degradation. Herein, after 30 h of UV exposure, the stretching vibrations of carbonyl functional group ν(C=O) were identified [17, 19, 20]. As a result of methylation, a shift of ν(C=O) stretching vibration peak to lower wavenumbers was noticed.

Mass change determination

As can be seen in Table 1 and Table 2, no significant effect of UV-radiation on isoprene rubber, polybutadiene rubber, and styrene-butadiene rubber mass change was observed. Nevertheless, a partial weight gain due to UV degradation was identified for all rubber samples. A comparison of the results shows that BR rubber samples showed the highest weight gain due to UV degradation. In contrast, SBR rubber samples showed the lowest weight gain due to UV degradation, and the IR rubber sample was in the middle.

CONCLUSIONS

The effect of UV-radiation on elastomers, specifically isoprene rubber, polybutadiene rubber, and styrene butadiene rubber were investigated. Analytical method of infrared spectroscopy using ATR technique and determination of weight change before and after UV exposure were used to monitor changes produced by irradiation. All rubber samples were exposed to 90 h of UV irradiation. The significant influence of UV-radiation on the degradation of the elastomer matrix of isoprene, polybutadiene, and styrene-butadiene rubbers was confirmed. With decreasing wavelength of the applied radiation, its energy increased, which is the cause of degradation changes in the rubber matrix. FT-IR proved a change in the chemical composition due to degradation of rubbers after the exposure to UV-radiation. Confirmation of chemical changes in rubbers under the effect of UV-radiation is evident by means of the presence of hydroxyl and carbonyl groups, identified in spectral records. Due to degradation of polymer chains caused by the UV-radiation, the hydroxyl and carbonyl functional groups arise in rubber. After the irradiation, an increase in weight was determined for all rubber samples. BR type rubber attained the highest increase in weight differences. In contrast, SBR samples showed the lowest increase. These results led to the conclusion that among all studied synthetic rubbers, the SBR 1 and SBR 2 rubbers achieved the greatest resistance to the degradation by UV-radiation. This conclusion was also confirmed by the evaluation of changes in the chemical composition using the infrared spectroscopy, where the presence of carbonyl groups was confirmed after 30 h of exposure.

ACKNOWLEDGEMENT

This work was supported by the APVV-23-0342-VV-E and Science Grant Agency – project VEGA 1/0265/24.

Authors contribution

D.O. – conceptualization, supervision, investigation, validation, writing-original draft, review; M.P. – methodology, validation, supervision, review; S.Ď. – writing-original draft, investigation, references; T.K. – visualization, methodology, supervision, I.L. – validation, investigation, refences; M.Š. – writing-original draft, methodology, investigation, conceptualization; S.L. – validation, investigation, refences.

Funding

This work was supported by the APVV-23-0342-VV-E and Science Grant Agency – project VEGA 1/0265/24.

Conflict of interest

The authors declare no conflict of interest.

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Received 29 IX 2024.
Accepted 12 X 2024.