

Effect of selected vegetable oils on the properties of acrylonitrile-butadiene rubber vulcanizates

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Abstract: In this study, we study if vegetable oils such as olive and orange oil, which are natural products devoid of any toxic effects, can function as multipurpose additives (processing aids, plasticizers and antioxidants) in acrylonitrile-butadiene rubber (NBR) containing 20 phr of carbon black (HAF). Dioctyl phthalate (DOP) and polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) were used as a reference plasticizer and antioxidant respectively. Rheometric and swelling characteristics were studied. The mechanical and dielectric properties before and after thermo-oxidative aging for different time periods up to 264 h at 100 °C were also studied. The physico-mechanical results indicated that olive and orange oils impart good mechanical properties to NBR vulcanizates. Furthermore, they improve aging resistance and increase hardness. Dielectric relaxation spectra were used to study the relaxation behavior of these samples as function of frequency (0.1 Hz to 5 MHz) at different temperatures. The obtained data were interpreted on the basis of electrode polarization and provide evidence that the recorded relaxation phenomena include contributions from both the polymeric matrix and the presence of the reinforcing phase. According to the available mechanical and electrical results, it is suggested that olive and orange oils may be used as multipurpose additives in nitrile rubber.

Keywords: vegetable oils (olive and orange oil), acrylonitrile-butadiene rubber, aging resistance, mechanical and dielectric properties.

Wpływ dodatku wybranych olejów roślinnych na właściwości wulkanizatów kauczuku akrylonitrylo-butadienowego

Streszczenie: Badano możliwość zastosowania naturalnych, nietoksycznych olejów roślinnych — oleju z oliwek i oleju z pomarańczy — jako wielofunkcyjnych dodatków (substancji pomocniczych, plastyfikatorów, przeciwutleniaczy) do kauczuku akrylonitrylo-butadienowego (NBR), zawierającego 20 phr sadzy węglowej (HAF). Porównawczo, w kompozycjach użyto ftalanu dioktylu (DOP) i polimeryzowanej 2,2,4-trimetylo-1,2-dihydrohinoliny w charakterze, odpowiednio, plastyfikatora i przeciwutleniacza. Wyznaczono charakterystykę reometryczną i pęcznienia próbek wytworzonych wulkanizatów, ponadto badano ich mechaniczne oraz dielektryczne właściwości przed i po starzeniu termiczno-oksydacyjnym w ciągu 264 h w temp. 100 °C. Wyniki wykazały, że oleje oliwkowy i pomarańczowy korzystnie poprawiają właściwości fizyko-mechaniczne wulkanizatów NBR, ponadto zwiększają odporność na starzenie oraz twardość. Na podstawie polaryzacji elektrodowej oceniono też przebieg procesu relaksacji wytworzonych próbek w funkcji częstotliwości (od 0,1 Hz do 5 MHz) w różnej temperaturze. Stwierdzono, że obserwowane procesy relaksacyjne dotyczą zarówno matrycy polimerowej, jak i składników wzmocnienia.

Słowa kluczowe: oleje roślinne (oliwkowy i pomarańczowy), kauczuk akrylonitrylo-butadienowy, odporność na starzenie, właściwości mechaniczne, właściwości dielektryczne.

Vegetable and petroleum oils are added to rubber compounds as softeners to facilitate the addition and dis-

persion of the other solid compounding ingredients, as well as to enhance the processing properties for extrusion, calendaring, *etc.* Tack (stickiness) is another property achieved by adding softeners and it is essential for many applications, such as tire building. Oil products are used as plasticizers for plastics to render them plastic or flexible during processing. Vegetable oils are esters and have a higher molecular weight compared to conventional synthetic esters. Moreover, they contain free fatty acids that can function as coactivators. Almost all vegetable oils contain phenolic compounds like tocopherols,

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which are potential antioxidants and can protect the elastomers from oxidation. Therefore, vegetable oils can be potential multipurpose ingredients in rubber.

The conventional compounding of rubber contains rubber, sulfur, activator, accelerator, filler, processing aid *etc.* The main function of the processing aid or physical plasticizer is to modify the physical properties of either the compounded rubber or the finished vulcanizate. The processing aid must be compatible with the rubber and the compounding ingredients. Petroleum based process oils *viz.* aromatic, naphthenic and paraffin oils are generally used in the rubber as process aids and extenders [1]. Generally used plasticizers include mineral oils, synthetic esters and some natural products such as wood rosin and animal glue [2]. The petroleum-based oils are used quite extensively in rubber compounds. Fast depleting petroleum resources call for the exploration of alternative materials. Vegetable oils are a potential substitute for mineral oils in this regard. The renewable nature of the source and the presence of other natural products such as tocopherols and free fatty acids can be advantageous in rubber compounds. Rice-bran oil has been used as a processing aid in acrylonitrile-butadiene (NBR), polychloroprene (CR) [1] and styrene-butadiene (SBR) rubbers [3]. Castor oil has been used as a plasticizer in natural rubber (NR), nitrocellulose, polystyrene films and rubber containing bound acrylonitrile or styrene [4, 5]. Lima *et al.* substituted dioctyl phthalate (DOP) by dehydrated castor oil in acrylonitrile-butadiene rubber [6]. They reported an increased plasticizing efficiency without affecting the physicochemical properties and aging resistance. Ashraf *et al.* reported the improvement of the physical and mechanical properties of poly(methyl methacrylate) (PMMA) by blending with dehydrated castor oil [7].

Vegetable oils have been used, especially drying oils and their derivatives, as additives in plastics and elastomers. Vulcanized vegetable oil (factice) was used in elastomers for low temperature flexibility and low hardness. Epoxidized linseed oil was used as a vulcanizing agent in carboxylated nitrile rubber – ionomer blends [4]. Linseed oil, as such, was used as a multipurpose additive in NBR to improve its mechanical properties and processability and also to reduce cure time [8]. Soya bean oil was used as a plasticizer in NR [9] and as a plasticizing agent in cold vulcanized rubber. Blown soya bean oil was used as a plasticizer in ester gums [4].

Virgin olive oil is a vegetable oil that can be obtained directly from olive fruit using only mechanical extraction and which can be consumed without further treatment. Its chemical composition consists of several major and minor components. The major components include glycerols, representing more than 98 % of the total oil weight. Minor components, which amount to about 2 % of the total oil, include more than 230 chemical compounds, *e.g.* aliphatic and triterpenic alcohols, sterols, hydrocarbons, volatile compounds and antioxidants. The main antioxidants of virgin olive oil are carotenes and

phenolic compounds, including lipophilic and hydrophilic phenols [10]. While the lipophilic phenols, among which are tocopherols, can be found in other vegetable oils, some hydrophilic phenols of virgin olive oil are not generally present in other oils and fats [10, 11]. Orange constitutes about 60 % of the total citrus world production. In 2008, 3.23 million tons of citrus fruit were produced in Egypt, including 2.14 million tons of orange. A large portion of this production is addressed to the industrial extraction of citrus juice, which leads to large amounts of residues, including peel and segment membranes. Peels represent between 50 to 65 % of the total weight of the fruits and remain as the primary byproduct. Citrus fruits and juices are an important source of bioactive compounds including antioxidants such as ascorbic acid, flavonoids, phenolic compounds and pectins [12].

The dielectric properties relate to the ability of a material to polarize under the influence of an electric field [13]. The complex dielectric permittivity ϵ^* ($\epsilon^* = \epsilon' - i\epsilon''$), which is a measure of the specimen's response to the applied field, is a frequency dependent complex function that provides information on the dynamic processes of the material. The real part (ϵ') represents the energy storage to the material, while the imaginary part (ϵ'') represents the energy loss due to polarization and ionic conduction. Rubber-based composites with excellent dielectric performance are currently very popular topics in the field of materials science and have received increasing attention [14, 15]. Rubbers are presently used as the most suitable materials for energy storage applications because of their features such as high electric breakdown field, low dielectric loss, easy processing, and low cost [15]. However, the permittivity of common NBR is high (*i.e.*, $\epsilon' > 14$) [16, 17]. Thus, a key issue is to enhance the permittivity of NBR while retaining other excellent performances and to evaluate the effect of olive and orange oils as a multipurpose ingredient for a typical acrylonitrile-butadiene rubber (NBR) containing 20 phr of carbon black. The processability, mechanical, thermal, morphology and dielectric properties of these compounds were studied and compared with dioctyl phthalate oil (DOP) and polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) as plasticizer and antioxidant, respectively.

EXPERIMENTAL PART

Materials

– Acrylonitrile-butadiene rubber (bound acrylonitrile content 32 %, specific gravity 1.17 ± 0.005) was supplied by Bayer AG, Germany.

– Stearic acid and zinc oxide (ZnO) with specific gravity 0.9–0.97 and 5.55–5.61, respectively, at 15 °C were used as activators. We used high abrasion furnace carbon black (HAF), N-330, specific gravity 1.78–1.82, particle size of 40 nm. Dioctyl phthalate (DOP), specific gravity 0.985–0.987, boiling point 384 °C was used as plasticizer.

N-cyclohexyl-2-benzothiazole sulfenamide (CBS), pale gray powder, with specific gravity of 1.27–1.31 at room temperature (25 ± 1 °C), melting point 95–100 °C was used as an accelerator. Elemental sulfur, fine pale yellow powder, with specific gravity of 2.04–2.06 at room temperature, was used as a vulcanizing agent. Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) was used as an antioxidant. Cold pressed olive oil was obtained from National Research Center, Giza, Egypt.

Extraction of orange peel oil

The oil was extracted by applying the cold-pressing method. Citrus fruit was peeled manually and the peels were then shredded to a size of 0.3–2.0 cm with a citrus peel shredder. Cold expressing of peels was performed at ambient temperature. The obtained extraction mixture was centrifuged for 45 min at 28–30 °C and at 3000 rpm, using a Hettich Universal centrifuge. After centrifugation, the oil was separated in a separating funnel and dried over anhydrous sodium sulfate. The oil was stored at 4 °C in opaque glass bottles. The physical and chemical properties of the olive and orange oils are given in Table 1.

Table 1. Physical and chemical properties of cold pressed orange peel oils and olive oils

Specifications	Orange peel oil	Virgin olive oil
Specific gravity at 20 °C	0.8456	0.9175
Refractive index at 25 °C	1.4702	1.4731
Viscosity at 28 °C, cP	6.2	56.4
Peroxide value, meq/kg	2	6
Acid value	1.1 mg KOH/ 100 g oil	0.8 mg KOH/ 100 g oil

Preparation of rubber compounds

Rubber was pre-mixed with all compounding ingredients according to ASTM D3182-07 (2012). Mixing was carried out on a laboratory two-roll mill. The speed of the slow roll was 24 rev./min, with a gear ratio of 1:1.4. The compounded rubbers were left overnight before vulcanization. The vulcanization was carried out 152 ± 1 °C in an

Table 2. Formulation of rubber mixes

Ingredients phr ^{a)}	Sample No.					
	D1	D2	Ol1	Ol2	Or1	Or2
DOP	5	5	-	-	-	-
Olive oil	-	-	5	5	-	-
Orange oil	-	-	-	-	5	5
TMQ	-	1	-	1	-	1

Base recipe: NBR, 100; Stearic acid, 2; Zinc Oxide, 5; HAF, 20; CBS, 1.5; Sulphur, 1.5. ^{a)} Part per hundred parts of rubber.

electrically heated press under a pressure of about 4 MPa to obtain vulcanized rubber sheets of 2 mm thickness. The rubber formulations are given in Table 2.

Methods of testing

Rheometric characteristics

M_L (minimum torque), M_H (maximum torque), T_{c90} (optimum cure time), T_{s2} (scorch time) and cure rate index (CRI) were determined according to ASTM D2084-11 using a Monsanto (Akron, OH, USA) oscillating disc rheometer, model 100. The measurements were carried out at 152 ± 1 °C.

Mechanical properties

The tensile strength, stress at 100 % strain and elongation at break of the obtained vulcanizates were tested according to the standard ASTM D412-06a (2013) with a Zwick testing machine. Five measurements were performed for each sample.

Swelling study

Swelling tests were carried out by soaking a specific weight of rubber samples in toluene at room temperature for 24 hours. The equilibrium swelling in toluene (Q %) was determined according to the standard method (ASTM D471-06). The equilibrium swelling Q % could be calculated according to the following equation:

$$Q = [(w_s - w_d)/w_d] \cdot 100 \% \quad (1)$$

where: w_s – the weight of the swelled specimen, w_d – the weight of the dried specimen.

Crosslinking density

The crosslinking density (ν), mol/cm³ of NBR was determined on the basis of solvent-swelling measurements (toluene solvent for 24 h at 25 ± 1 °C) using the Flory–Rehner equation [18, 19].

$$\nu = 0.5/M_c \quad (2)$$

where: M_c – the molecular weight between crosslinks (g/mol)

$$M_c = \left[\frac{-\rho V_s \left(V_r^{\frac{1}{3}} - \frac{2V_r}{f} \right)}{\left[\ln(1 - V_r) + V_r + \chi V_r^2 \right]} \right] \quad (3)$$

where: ρ – the density of rubbers (ρ NBR is 1.17 g/cm³), V_s – the molar volume of the solvent (toluene), f – network functionality, χ – the interaction parameter of rubbers where the χ of (NBR) is 0.39 and V_r – the volume fraction of swollen rubber that can be obtained from the mass and density of rubber samples and the solvent.

Thermal oxidative aging

The aging process was carried out at 100 ± 1 °C in an air circulating oven for different time periods according to ASTM D572-04 (2010). The reported results were averaged from a minimum five specimens.

Hardness

Hardness was measured using the Shore A durometer according to ASTM D2240.

Strain-energy determination

Strain-energy values were obtained by plotting stress-strain curves for vulcanized rubber using unnotched samples, and integrating the area under the curve up to the particular extension used. Simpson's rule [20, 21] was applied to calculate the strain energy. The calculated strain-energies were plotted against the corresponding strain. This curve was used to obtain the strain-energies for particular extensions.

Hysteresis

Hysteresis loss (H_y) is defined as the amount of energy dissipated during cyclic deformation and is determined from the area W_1 (work done during extension) and W_2 (work done during retraction) when the samples are stretched to a certain extent and then allowed to retract at the same rate to the unstretched state:

$$H_y = W_1 - W_2 \quad (4)$$

Scanning electron microscopy (SEM)

SEM was performed using a JXA-840 A electron probe micro-analyzer (Jeol, Japan). The rubber specimen was broken in liquid nitrogen; the cross section surface was then covered with a very thin layer of gold to avoid electrostatic charging during examination.

Thermogravimetric analysis (TGA)

TGA of the composites was carried out using the Perkin Elmer analyzers, USA. Sample weights between 13 and 25 mg were scanned from 50 to 1000 °C using a nitrogen air flow of 50 cm³/min and a heating rate of 10 °C/min⁻¹.

Dielectric measurements

Circular discs were cut out from the sheets of the composites with a diameter of 12 mm for dielectric studies. These studies were carried out using an impedance analyzer (Schlumberger Solartron 1260), an electrometer, amplifier, and measuring cell as described before [22].

Using the impedance analyzer, the permittivity ϵ' , dielectric loss ϵ'' and ac (alternating current) resistance R_{ac} were obtained at different temperatures and different frequencies 0.1 Hz up to 5 MHz. The measurement was automated by interfacing the impedance analyzer with a personal computer through a GPIB cable IEE488. A commercial interfacing and automation software, Lab VIEW, was used for acquisition of data. The error in ϵ' and ϵ'' amounts to 1 % and 3 %, respectively. The temperature of the samples was controlled by a temperature regulator with Pt 100 sensor. The error in temperature measurements amounts to ± 0.5 °C. To avoid moisture, the samples were stored in desiccators in the presence of silica gel. Thereafter the sample was transferred to the measuring cell and left with P₂O₅ until the measurements were carried out.

RESULTS AND DISCUSSION

Processability studies

Processability studies of polymers are important in the case that the product is to be molded. The processability of composites can be determined by evaluating the cure characteristics such as minimum torque M_L , maximum torque M_{Hr} , scorch time T_{s2} , optimum time T_{c90r} and cure rate index CRI [23]. The cure characteristic of NBR/HAF mixes with DOP, olive and orange oils, with and without antioxidants (TMQ), loaded with 20 phr carbon black were determined and are collected in Table 3. The minimum torque value, a measure of the stock viscosity, is lower for all the mixes prepared with olive and orange oils compared to the respective control mixes. This clearly indicates the improved processability afforded by olive and orange oils. The maximum torque developed is higher in mixes containing DOP oil compared to those containing olive and orange oils. The lower torque values might be attributed to the presence of carboxylic groups present in the olive and orange oil as an internal lubricant and the presence of some unsaturation in the oils used. There is no great difference between all the obtained rheological properties such as the optimum cure time, scorch time and cure rate index of mixes.

Physico-mechanical properties of the vulcanizates

The tensile properties of the NBR/HAF vulcanizates (D1, D2, O11, O12, Or1 and Or2) were determined and are summarized in Table 3. It is clearly seen that the tensile strength and stress at 100 % strain are higher for vulcanizates containing olive and orange oils with antioxidants. Hence, olive and orange oils are more compatible with NBR. This may be attributed to the characteristic polarity of the oils. The elongation at break values for all vulcanizates are very similar to each other. Also, it was found that the equilibrium swelling and the determined values of crosslinking density of the investigated vulcanizates

Table 3. Rheometric, swelling characteristics and physico-mechanical properties of rubber vulcanizates

Sample No.	D1	D2	O11	O12	Or1	Or2
Rheometric characteristics at 152 ± 1°C						
M_L , dNm	3.5	3.5	3.0	2.5	2.5	3.0
M_H , dNm	55	49	32.5	28.5	40	35
T_{c90} , min	12.5	12.25	12.0	12.25	12.0	12.0
T_{s2} , min	3.94	3.94	2.75	3.69	3.0	3.0
CRI , min ⁻¹	11.66	12.03	10.81	11.35	11.11	11.11
Physico-mechanical properties at optimum cure time						
TS_b , MPa	14.63 ± 0.2	17.92 ± 0.2	18.50 ± 0.12	19.33 ± 0.16	16.6 ± 0.08	20.14 ± 0.03
E_b , %	533 ± 2	583 ± 2	575 ± 2	544 ± 2	542 ± 2	583 ± 2
S_{e100} , MPa	2.03 ± 0.01	2.54 ± 0.02	2.17 ± 0.01	2.63 ± 0.00	2.71 ± 0.00	2.94 ± 0.00
Q_m , %	156.55 ± 0.70	166.23 ± 0.09	164.31 ± 0.11	172.29 ± 0.04	161.55 ± 0.90	182.50 ± 0.55
ν , mol/g · 10 ⁻⁴	3.37 ± 0.70	3.04 ± 0.09	3.10 ± 0.11	2.86 ± 0.04	3.19 ± 0.90	2.58 ± 0.55
H , Sh A	45.70 ± 0.01	45.80 ± 0.02	58.25 ± 0.01	51.36 ± 0.02	58.00 ± 0.02	55.00 ± 0.02

TS_b – tensile strength, E_b – elongation at break, S_{e100} – stress at 100 % strain, Q_m – equilibrium swelling, ν – crosslinking density, H – hardness.

gave promising results and, consequently, products that confirmed the other tested properties. The hardness values of NBR/HAF vulcanizates containing olive and orange oils are higher than the vulcanizates containing DOP with and without TMQ.

Effect of the thermo-oxidative aging on the physico-mechanical properties of NBR/HAF vulcanizates

The prepared vulcanizates were exposed to thermo-oxidative aging at 100 °C for different time periods

up to 264 hours. The retained values of the tensile properties and hardness of the aged samples were determined and presented in Fig. 1. It can be observed that the retained values of tensile strength and elongation at break decreased up to 168 h aging time, after that time there are little change for these properties (Figs. 1a, 1b). The reductions in the properties are due to partial crosslinking of the elastomer backbone and degradation of the rubber taking place upon aging [24–27]. The vulcanizate containing orange oil without antioxidant (Or1) is more stable than vulcanizates containing DOP, as well as olive oil

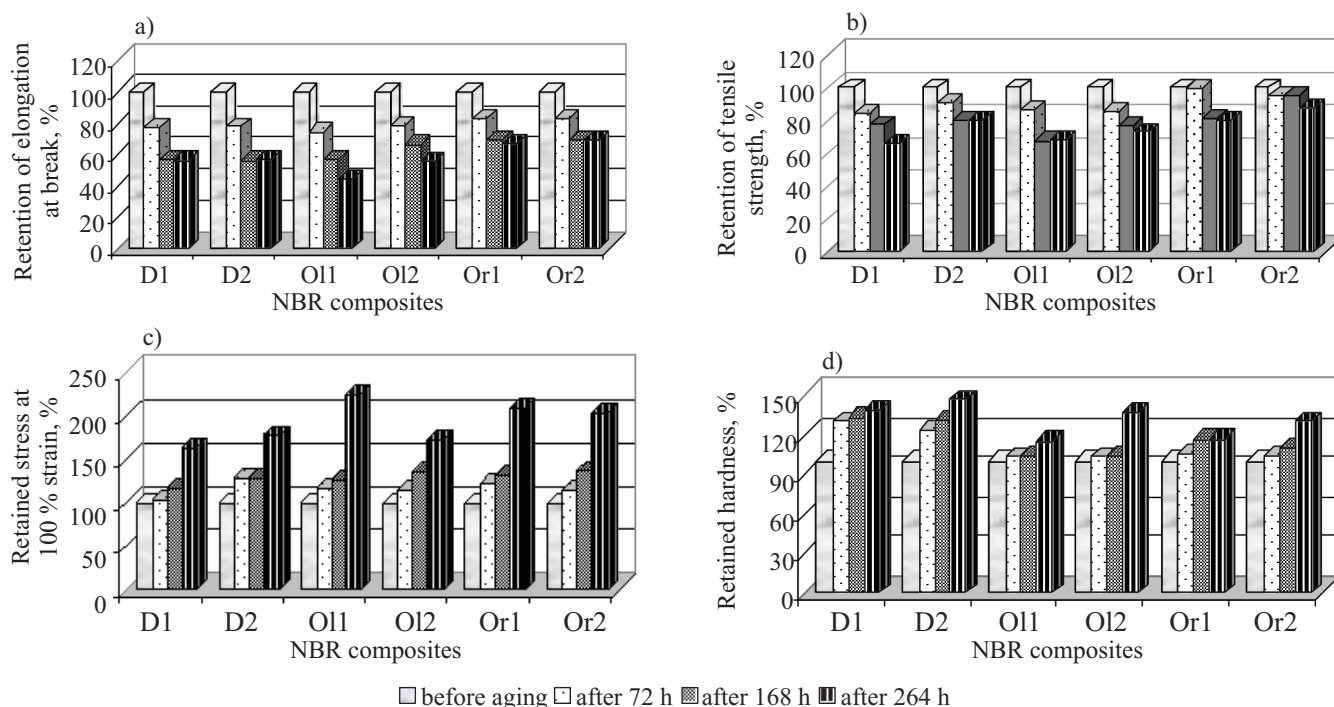


Fig. 1. Influence of oils and aging time on NBR/HAF/oil vulcanizates: a) elongation at break, b) tensile strength, c) stress at 100 % strain, d) hardness

with and without antioxidant (TMQ) (D1, D2, OI1 and OI2). This may be attributed to the effect of phenolic compounds produced from the oxidation of orange oil, which acted as antioxidants and increased the properties after aging. On the other hand, the stress at 100 % strain and hardness values increase with longer aging times and this may be due to the formation of partial additional cross-linking (Figs. 1c & 1d).

Based on these results, it is reasonable to conclude that olive and orange oil can be used as plasticizers and antioxidants in NBR systems.

Stress-strain

Figure 2 shows stress-strain curves of the NBR/HAF vulcanizates (D1, D2, OI1, OI2, Or1 and Or2). The curve obtained for NBR vulcanizates containing DOP and HAF show a low stress and strain at break of around 500 % (D1). The vulcanizates that contain olive or orange oils, and without antioxidant (TMQ), have lower stress properties compared to these that contain TMQ and also give the lowest value of elongation at break. However, the stress and strain of olive or orange oil with TMQ increase considerably. So we presume that oils (olive or orange) with antioxidant properties promote the filler layers to disperse uniformly with a sufficient degree of exfoliation and intercalation of the filler, oils and therefore the rubber matrix becomes strongly reinforced (OI2 and Or2) [4, 28]. Based on the obtained data, it can be concluded that the addition of olive or orange oil to rubber improves the physical properties and this is confirmed by the calculated strain energy. Consequently, the energy absorbed per unit volume (W) is expected to increase in deforming rubber vulcanizates. Thus the energy absorbed can be written as [29, 30]:

$$W = \int \sigma(\epsilon) d\epsilon \quad (5)$$

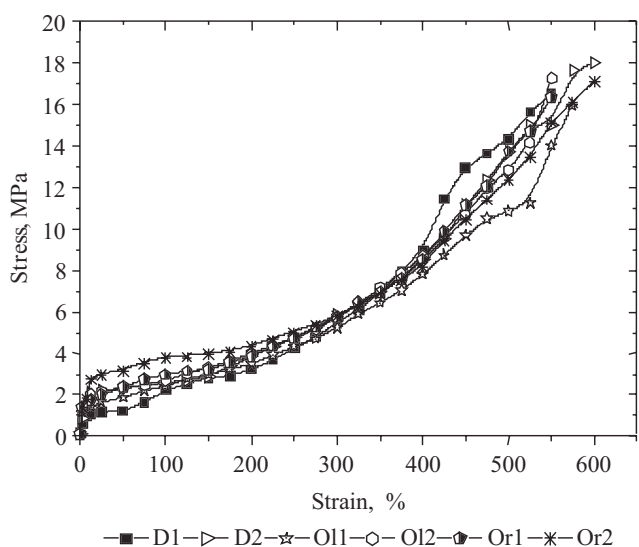


Fig. 2. Stress-strain curves of NBR/HAF vulcanizates containing different oils

where: σ – stress as a function of the strain ϵ . Therefore, the larger the area under the stress-strain curve, the higher the energy absorption capacity. The vulcanizate D2 has the largest area under the stress-strain curve and, consequently, it has the highest energy absorption. On the other hand, the vulcanizates OI1 and Or1 have the lowest absorption of energy. These findings are in good agreement with the data presented in Table 4, which showed a decrease in the strain energy due to the incorporation of olive or orange oil in rubber vulcanizates without TMQ.

Table 4. Strain energy and the hysteresis loop area for first cycle of deformation to 300 % NBR/oil vulcanizates

Sample No.	Strain energy, W (MJ/m ³)	Hysteresis loop area (H_y) (MJ/m ³)
D1	0.538 ± 0.008	0.0581 ± 0.0017
D2	0.856 ± 0.003	0.1735 ± 0.0013
OI1	0.635 ± 0.004	0.1046 ± 0.0021
OI2	0.738 ± 0.014	0.0937 ± 0.0016
Or1	0.739 ± 0.005	0.1249 ± 0.0140
Or2	0.846 ± 0.012	0.1772 ± 0.0150

Effect of cyclic stress-strain on mechanical properties

Stress softening or cyclic deformations were performed for all NBR/HAF vulcanizates up to 300 % of the elongation. Examples of hysteresis curves are shown in Fig. 3a–c. Furthermore, Fig. 3a–c represents the cyclic stress-strain curves, at room temperature (298 K), for all samples. The values of hysteresis loop area for all NBR vulcanizates for the first stress-strain cycle are shown in Table 4. From these data, it's clear that the hysteresis loop area (H_y) of the samples D1, OI1 and Or1 are smaller than samples D2, OI2 and Or2. This may be due to the increase of filler-matrix interactions by addition of TMQ. The higher hysteresis loop area gives an indication of the extent of energy loss and hence the heat build-up during the cyclic deformation [31–33].

Morphology of the investigated compounds

Scanning electron microscopy provides direct evidence for evaluating the dispersion of HAF particles. It was expected that the addition of oil (plasticizer) or antioxidant (TMQ) would improve the dispersion of filler (HAF) particles in the matrix. In Fig. 4a, (D1) it can be seen that the addition of DOP slightly improved the dispersion of HAF particles and the adhesion between HAF particles and matrix NBR (the domain size range from 1.50 to 2.40 μm). While for NBR/HAF/DOP/TMQ, (D2; Fig. 4b), HAF particles seem to be packed into agglomerates of large size between 1.62 and 6.41 μm , and there are obvious gaps between the HAF particles and NBR. How-

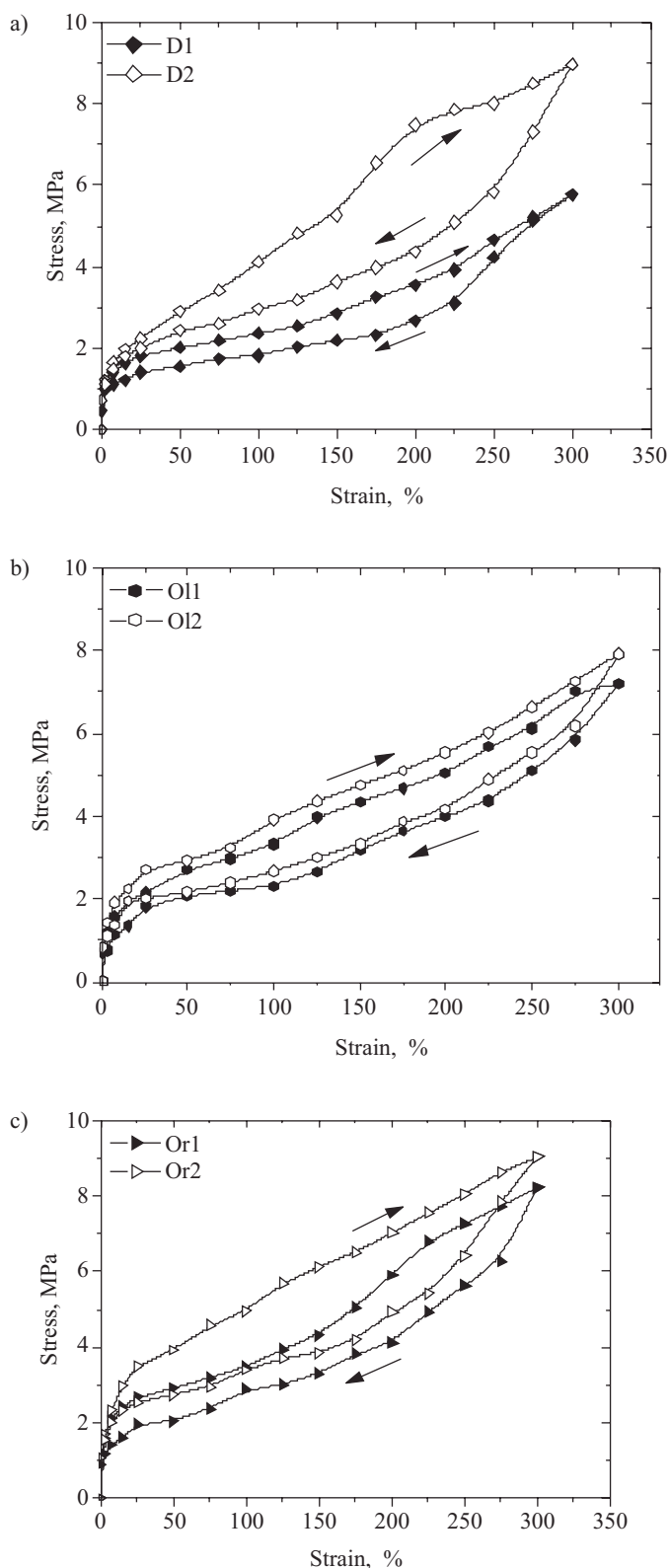


Fig. 3. Hysteresis loop for NBR/HAF vulcanizates: a) D1, D2, b) O11, O12, c) Or1, Or2

ever, in Fig. 4c, (sample O11), the dispersion of HAF is not uniform as several agglomerates can be seen in the photograph (the domain size range from 1.69 to 4.11 μm). The addition of TMQ to NBR/olive/HAF (Fig. 4d) improves the phase morphology and the domains appear to be

more uniformly dispersed (size from 0.77 to 2.65 μm). This can be attributed to the location of TMQ/olive oil at the interfaces between the major phases of NBR and around the microphase (HAF) [34]. On the other hand, a more homogeneous morphology with a finer and more uniform dispersion of the orange oil phase (Or1) in the NBR matrix is observed by SEM (the domain size range from 1.06 to 2.73 μm) (Fig. 4e), whereas a disappearance of HAF agglomerates (sample Or2) is observed (Fig. 4f), particle size in the presence TMQ (range size from 1.23 to 1.74 μm). This suggests that the orange oil may act as an interfacial agent, reducing the interfacial tension with a concomitant breakup of the HAF droplets and, in consequence, a reduction in particle size [35]. Also, it is expected that the hydroxyl group and phenolic acids present in the structure of the orange oil are able to react with NBR/HAF, giving rise to a more homogeneous structure.

Thermal stability

Figure 5 shows the thermo-gravimetric results of vulcanizates D1, O11 and Or1, respectively. All of the studied samples exhibited an initial small weight loss attributed to the elimination of volatile components such as water. Moreover, the improved thermal stability of Or1 is evident from the higher temperature of initiation of degradation (T_i) of these mixes (Table 5). The reasons for the improvement in thermal stability of NBR/oil samples are probably attributed to the increase in physical and chemical crosslink points, attributed to the interaction between the oils and NBR [36]. In addition, olive oil is composed of unsaturated fatty acids and there are also high levels of tocopherol and phenolic compounds. On the other hand, the chemical structure of orange oil is unsaturated. Obviously, in the TGA curve of NBR/HAF/oils, T_{30} , T_{50} and T_{70} were enhanced, the temperature at which 50 % decomposition occurs (T_{50}) is generally considered as the index of thermal stability [37]. Specimens Or1 and O11, respectively, show a noticeable increase in the T_{50} values during decomposition in nitrogen. This may possibly be due to the formation of intermediate, thermally stable structures as a result of thermo-oxidative reactions in their presence (Table 5). The total char residues of O11 or Or1 are higher than the char residue of D1. The char resi-

Table 5. Thermo gravimetric data for NBR/oil vulcanizates

Sample No.	Weight loss temperature, °C					Residual weight, %
	T_i	T_{30}	T_{50}	T_{70}	TF	
D1	324	404	432	544	856	3.653 \pm 0.001
O11	327	412	436	520	676	4.410 \pm 0.002
Or1	331	408	438	528	728	3.911 \pm 0.002

T_i – initial thermal decomposition temperature, T_{30} , T_{50} , T_{70} – temperatures at 30, 50 and 70 weights lose %, TF – final thermal decomposition temperature.

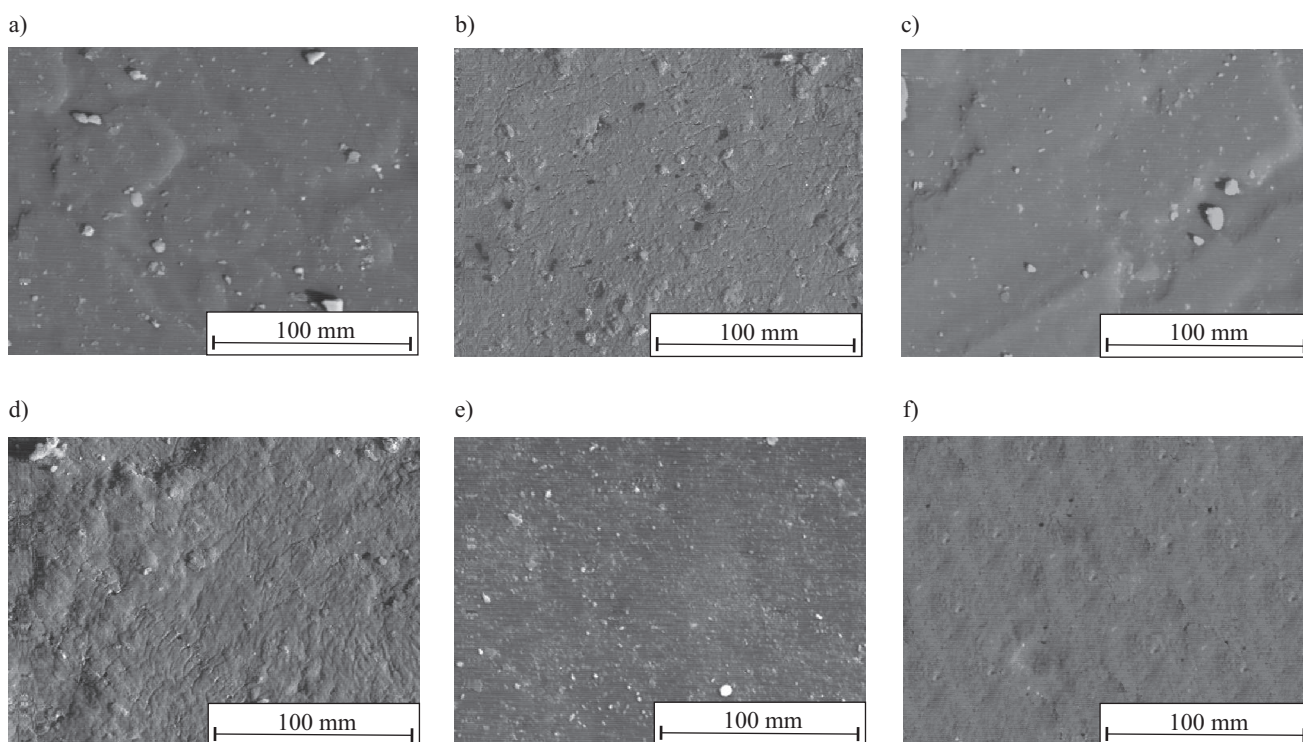


Fig. 4. SEM images of NBR/HAF vulcanizates containing different oils: a) D1, b) D2, c) OI1, d) OI2, e) Or1, f) Or2, magnification $\times 500$

due was probably increased in NBR/oil (olive and orange) vulcanizates due to a synergistic effect of the rubber components leading to more stable product compared to the NBR/HAF/DOP component (Table 5).

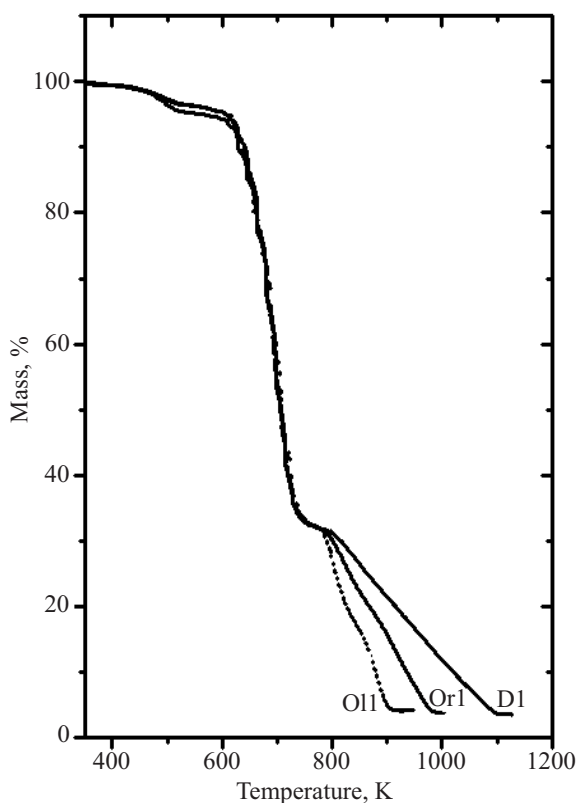


Fig. 5. Thermogravimetric analysis of NBR/HAF vulcanizates containing different oils (D1, OI1, Or1)

Electrical properties of NBR/HAF vulcanizates

The permittivity ϵ' and dielectric loss ϵ'' versus frequency for NBR/HAF vulcanizates with DOP, olive oil, orange oil at different temperatures are shown in Fig. 6. From these figures it is obvious that the magnitude of ϵ' of NBR vulcanizates increased at higher temperatures, especially in the low frequency region due to the contribution of ionic conductivity and the dominant effect of polarization by migrating charges [38]. It is also clear that the permittivity ϵ' of NBR vulcanizates increased at lower frequency, which is a clear indication of low-frequency dispersion [39]. Low frequency dispersion usually causes interfacial polarization due to the increase of the conductivity of the dielectric material and this can be represented by an increase in the dielectric loss ϵ'' in the low frequency region as seen in Fig. 6. Clearly, this figure shows low frequency relaxation, in addition to a clear relaxation peak, corresponding to the segmental orientation of the polymer chains and known as the α -relaxation process in the high frequency region [40]. The α -relaxation process is systematically shifted to higher frequencies at higher temperatures in a manner that is consistent with typical molecular dynamics of all polymer materials at temperatures higher than T_g .

From the same figure, it is also noted that the values of ϵ' and ϵ'' for NBR/HAF/Olive oil vulcanizates are lower than those of NBR/HAF/DOP vulcanizates. This may be due to the lower polarity of olive oil compared to DOP. This lower polarity of olive oil provides lower values of ϵ' and ϵ'' of NBR/olive oil vulcanizates. A double bond in each of the side chains of olive oil, tri-

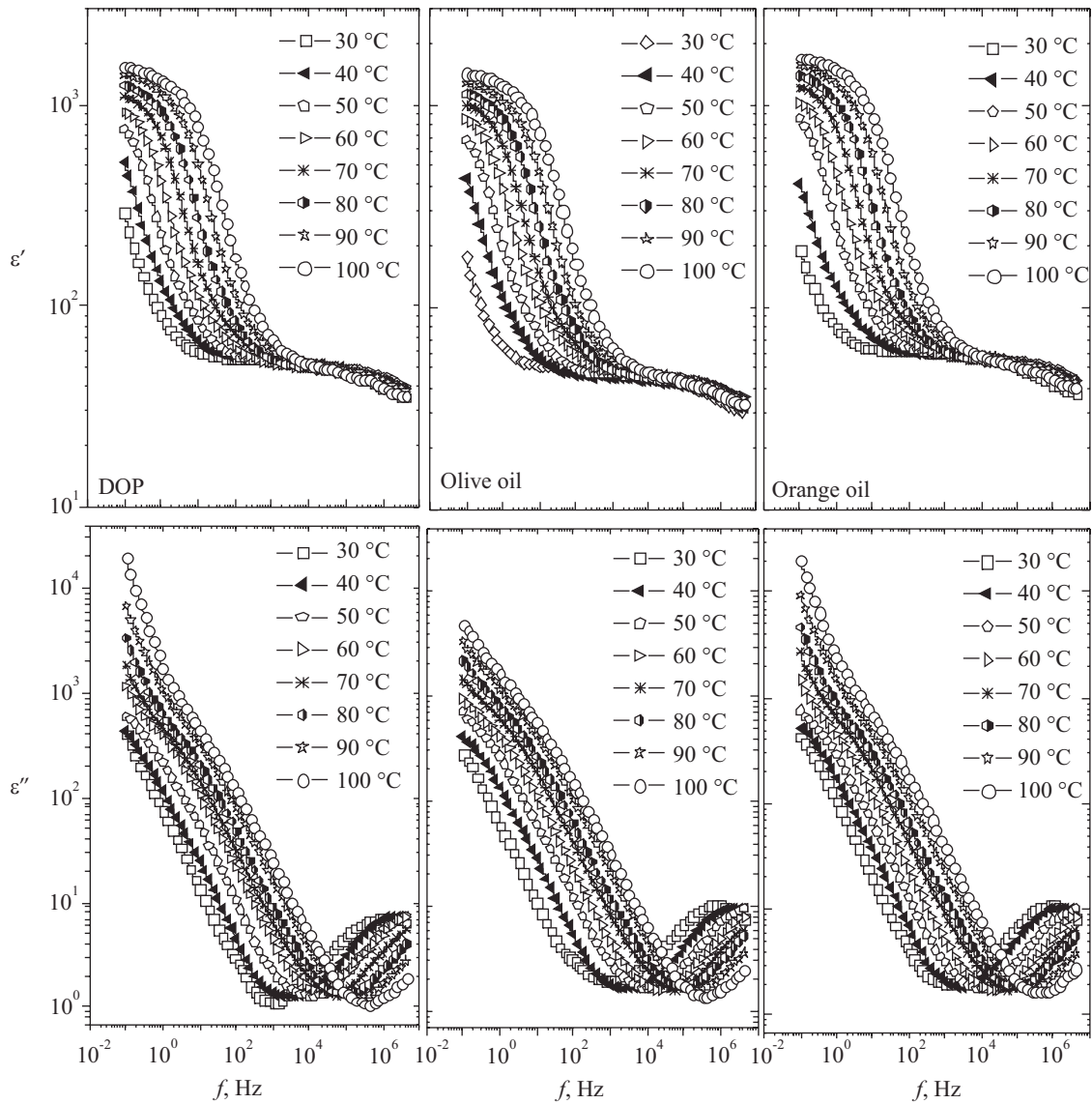


Fig. 6. Influence of oils and temperatures on the permittivity ϵ' and dielectric loss ϵ'' versus frequency of NBR/HAF vulcanizates

olein $C_3H_5(C_{18}CH_{33}O_2)_3$ causes the slight rise in ϵ' and ϵ'' and compensates for its lower polarity. On the other hand, larger values of ϵ' and ϵ'' for NBR/orange oil vulcanizates were observed at low frequencies compared to the other NBR vulcanizates (see Fig. 6). The reasons for this variation in ϵ' and ϵ'' of NBR/HAF vulcanizates with phthalate softeners, olive oil and orange oil are; molecular dipole reorientation and differences in conductivity. Dipole reorientation is thought to be much easier in NBR/orange oil vulcanizates, resulting in larger values of ϵ' and ϵ'' even at high frequencies.

Another reason may be attributed to the high polarity of DOP and orange oil compared to olive oil. However this is confirmed through dc (direct current) — conductivity σ_{dc} (S/m) values calculated from resistance measure-

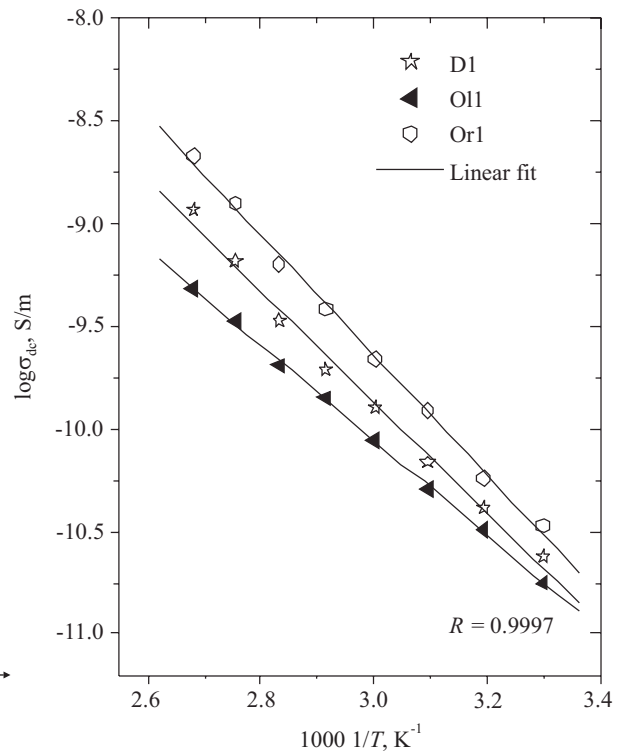


Fig. 7. Influence of oils on the conductivity versus $1000/T$ of NBR/HAF vulcanizates

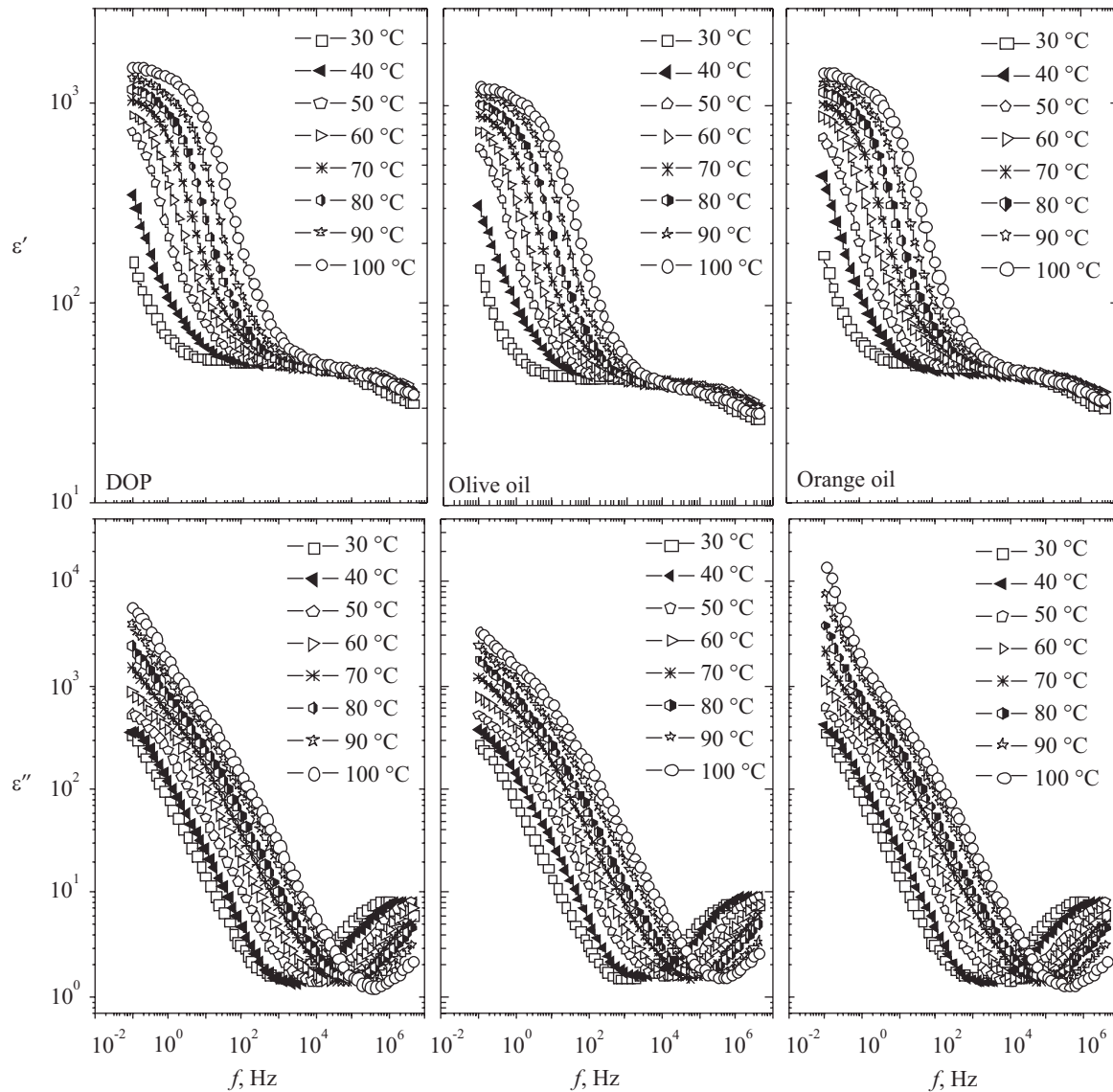


Fig. 8. Influence of oils and temperatures on the permittivity ϵ' and dielectric loss ϵ'' versus frequency of three NBR vulcanizates with TMQ

ments at different temperatures, as can be seen in Fig. 7. This figure shows that the conductivity of NBR/HAF/DOP and orange oil softeners are higher than that of NBR compounded with olive oil and their activation energies calculated using the Arrhenius equation (6) are 22.41 kJ/mol for NBR/DOP, 19.20 kJ/mol for NBR/HAF/olive and 23.92 kJ/mol for NBR/HAF/orange oil. In the NBR samples under consideration, ionic conductance probably results from mobile protons due to the presence of $-C\equiv N$ dipoles, carboxylic groups and other ions obtained from the addition of processing agents; zinc oxide and stearic acid in addition to the softeners. The blocking of ions at the metallic electrodes causes low frequency dispersions of NBR and leads to pronounced relaxation processes at low frequencies. So it can be concluded that, the addition of orange oil resulted in an overall increase of ϵ' and ϵ'' with temperatures due to both dipolar and free charge contributions. Moreover, this increase of the molecular mobility is reflected both by an increase of free

charge mobility and the shift of the peak towards the higher frequency side with a simultaneous increase of its magnitude, especially low frequency relaxation. The overall result is an enhancement of conductivity and dielectric properties on addition of this vegetable oil.

Figure 8 shows the permittivity ϵ' and dielectric loss ϵ'' versus frequency for the three NBR/HAF vulcanizates with TMQ at different temperatures. The values of ϵ' and ϵ'' NBR vulcanizates decreased after incorporating TMQ. This decrease in the values of ϵ' and ϵ'' may be due to the redistribution and/or reduction of the polar groups of NBR.

It is valuable to note that, the values of ϵ' and ϵ'' keep the same ascending order as in Fig. 6 where ϵ' and ϵ'' of orange oil > DOP > olive oil. However, for a particular frequency (100 Hz) and room temperature 30 °C, the values of ϵ' and ϵ'' NBR compounded with orange oil and DOP are higher than those of olive oil (see Fig. 9). These higher values of ϵ' and ϵ'' are due to the increase in dipole orien-

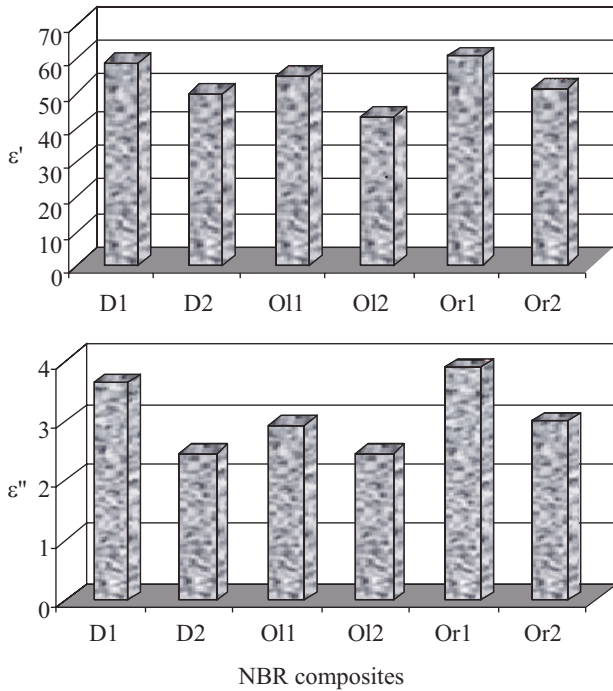


Fig. 9. The influence of oils and temperatures on the values of ϵ' and ϵ'' versus softener type of NBR/HAF vulcanizates at fixed frequency 100 Hz

tation polarization and the presence of interfacial polarization [41]. In addition these, values decreased after incorporating TMQ.

The raw data of the measured NBR/HAF vulcanizates at low frequencies and high temperatures contains significant contribution from dc-conductivity, which leads to masking the underlying relaxation spectra. However, one

can test the experimental data for the existence of relaxation at in a given frequency range by plotting ϵ''_{meas} versus frequency in a log-log plot. If the slope of the curves differs significantly from -1, *i.e.*, if the absolute value of the slope is less than 0.995, then the loss is due to a combination of conductivity and dielectric relaxation. Such a plot for NBR/HAF vulcanizates with DOP at 90 °C as an example for this test is shown in Figure 10a where the absolute values for all slopes are less than 1. This slope can be used to calculate the preliminary approximate value of conductivity allowing us to plot $\log(\epsilon''_{\text{meas}} - \sigma_{\text{dc}}/\epsilon_0\omega)$ (where: $\epsilon_0 = 8.854 \cdot 10^{-12}$ F/m, $\omega = 2\pi f$) versus $\log f$ to highlight loss maxima at low frequencies, as seen in Fig. 10b.

It is also clear that the curves relating ϵ'' and frequency in Figures 6 & 8 are broader than the Debye curve indicating that more than one relaxation process is present [42]. The experimental data can be represented in terms of Havriliak–Negami [43] functions. Examples of fitting the spectra of NBR/DOP vulcanizates at three different temperatures 30, 60 and 90 °C respectively are illustrated graphically in Fig. 11. The fitting procedure gives us two Havriliak–Negami relaxation modes in the available frequency window. From this figure it is noted that the high frequency relaxation shows a much broader relaxation time distribution and lower intensity than the low frequency relaxation. The absorption in the higher frequency region may be due to the segmental orientation of the polymer chains and found elsewhere [44]. While the relatively low frequency process may be due to interfacial polarization (IP) or electrode polarization (EP). This process depends on the sample electrode interface parameters; and is shifted to higher frequency with increasing temperature [45, 46].

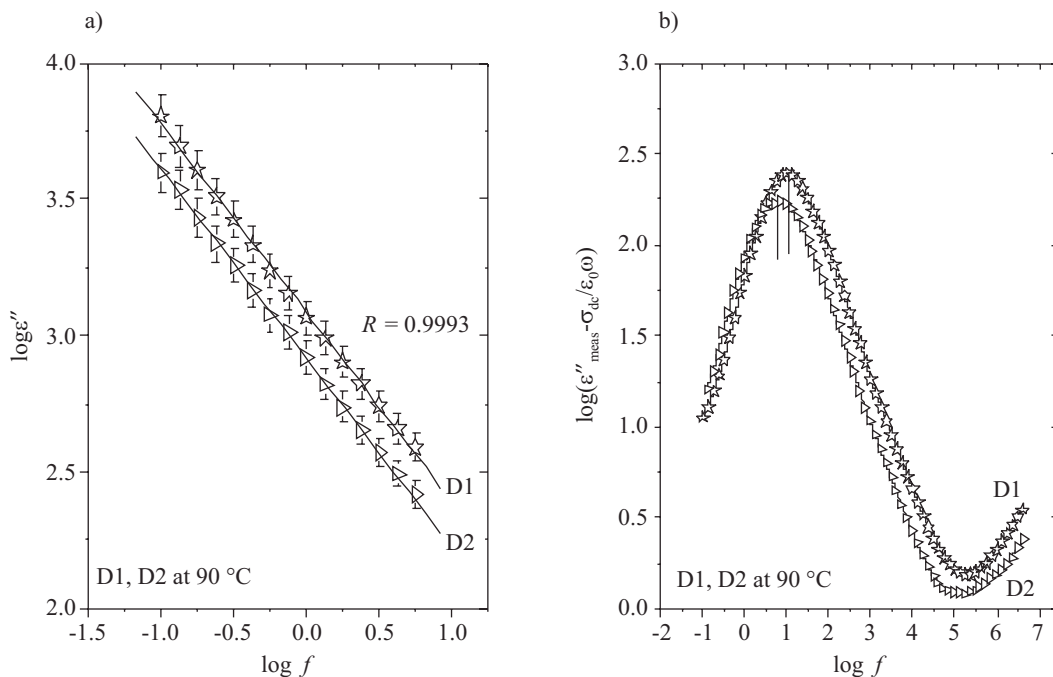


Fig. 10. a) The dielectric loss (ϵ'') versus the frequency (f) on log-log scale for NBR/HAF/DOP at 90 °C, b) $(\epsilon''_{\text{meas}} - \sigma_{\text{dc}}/\epsilon_0\omega)$ versus the frequency (f) on log-log scale for NBR/HAF/DOP at 90 °C

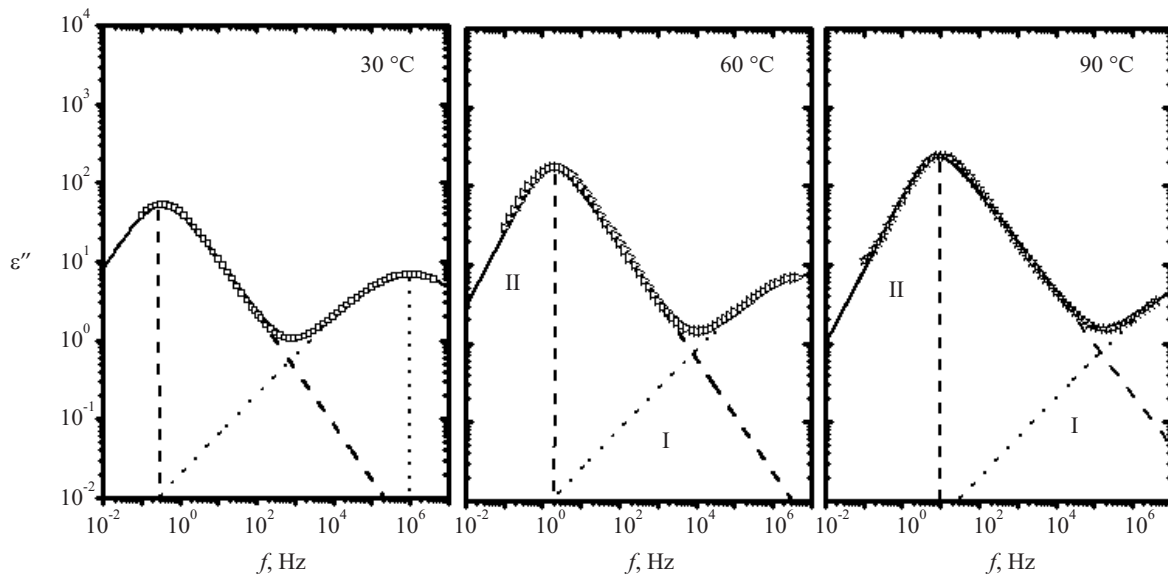


Fig. 11. Analyses of NBR/HAF/DOP at three different temperatures decomposition of two Havriliak-Negami relaxation functions

The temperature dependence of the relaxation process is further analyzed by plotting the frequency of the maximum versus the reciprocal of temperature. Figure 12 shows the plots of NBR/HAF/DOP vulcanizates for the two relaxation processes. The frequency of the maximum increased at higher temperatures due to enhancement of mobility of charge carriers at high temperature. This temperature dependence of dielectric relaxation can be well described by Arrhenius type behavior (see Fig. 12). The plots for the two relaxation processes yield a straight line and from the slope of the line, the activation energy can be calculated using the Arrhenius equation (6):

$$f = f_0 \exp[-E_A/kT] \quad (6)$$

where: E_A – the activation energy, f_0 – pre-exponential factor, k – the Boltzmann constant and T – the absolute

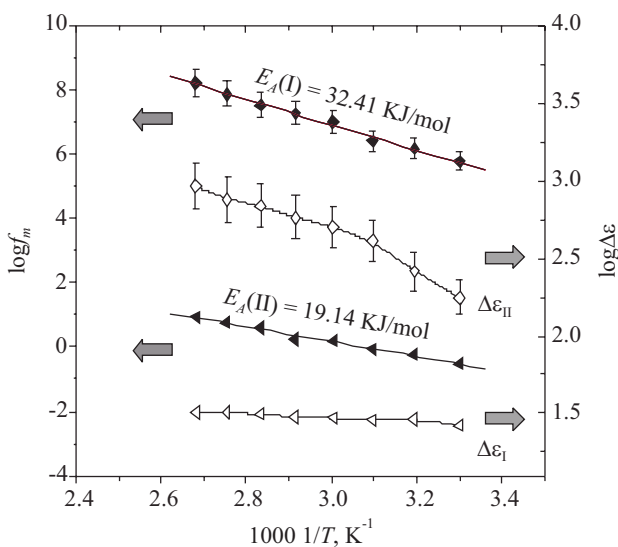


Fig. 12. Characteristic frequency and relaxation strength $\Delta\epsilon$ versus reciprocal of temperature NBR/HAF/DOP

temperature. We calculated values of activation energies of the tested samples before and after thermal aging calculated *via* linear regression of Eq. (6). It is also important to notice that the values of the relaxations strength $\Delta\epsilon_I$ of the first process are nearly the same and not largely affected by the type of softeners. While $\Delta\epsilon_{II}$ of the interfacial process increased with increasing temperature.

In order achieve the overall goal, which is monitoring and evaluating the electrical properties of NBR/HAF vulcanizates, degradation tests must be established for the material. Degradation tests or accelerated thermal aging were carried out for different time periods up to 264 h at 100 °C. The dielectric properties illustrated as function of time for particular frequency 100 Hz in Fig. 13. It is obvious that the vulcanizates containing orange oil or olive oil are more thermal stable than vulcanizates containing DOP. This may be due to the fact that olive oil is found to contain small amounts of tocopherols and phosphatides which are having antioxidant properties. Moreover orange oil oxidized to phenolic compounds, which may also act as antioxidants in the present study olive oil and orange oil may be used as a multipurpose additive in nitrile rubber.

The calculated activation energies of processes I and II of NBR/HAF vulcanizates before and after thermal aging are listed in Table 6. From this table it is clear that, the activation energies of the first process (at higher frequency) were found to be about 32–36 kJ/mol, while they were 19.14–20 kJ/mol for the other process. The highest value of the activation energy of the first process is a clear indication that some sort of interaction between NBR molecules and HAF took place. Such interaction leads to lowering the mobility of the NBR macromolecular segments, whereas the two relaxation processes shifted to lower frequency by incorporating TMQ to NBR vulcanizates (see Figs. 8, 10) and thus increasing the activation energy of the composite [47, 48]. On the other hand the higher

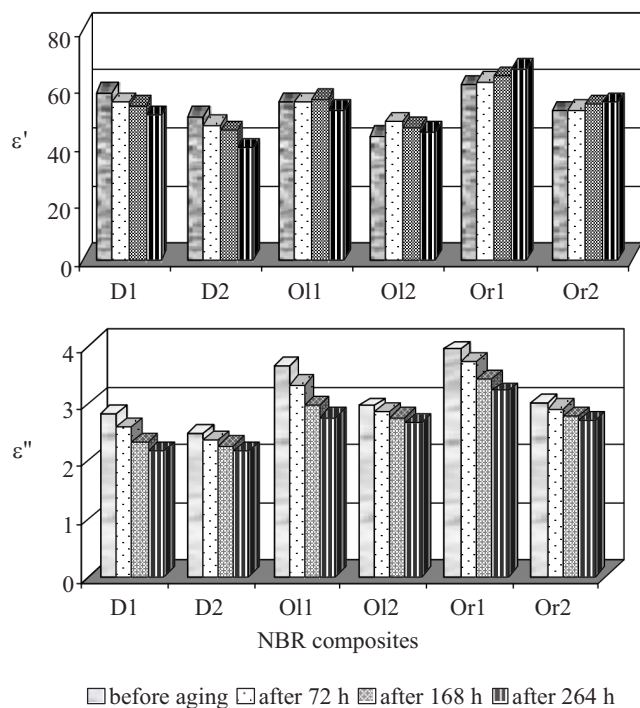


Fig. 13. The values of ϵ' and ϵ'' versus softener type of NBR/HAF vulcanizates at fixed frequency 100 Hz, after thermal aging

values of the activation energy of the interfacial polarization (IP) process denoting the increase of heterogeneity of the composite [49]. These values are in good agreement with the previous reported results.

Table 6. Activation energy of NBR/HAF/oil vulcanizates for the first and second relaxation processes before/after thermal aging at 100 °C

Sample No.	Activation energy (E_A), kJ/mol							
	before aging		after 72 h		after 168 h		after 268 h	
	E_A (I)	E_A (II)	E_A (I)	E_A (II)	E_A (I)	E_A (II)	E_A (I)	E_A (II)
D1	32.41	19.14	33.69	19.09	33.89	19.23	32.61	20.02
D2	33.11	19.50	34.47	18.96	34.82	19.36	32.23	19.67
O11	34.13	18.23	34.83	17.63	34.78	18.40	33.83	18.16
O12	34.55	18.50	34.80	17.75	34.98	17.75	33.34	17.75
Or1	35.40	18.96	36.22	18.33	35.89	19.23	34.26	19.70
Or2	35.77	18.50	36.54	18.66	36.67	18.45	35.60	18.84

CONCLUSIONS

– The olive and orange oils improve the mechanical properties such as modulus, tensile strength of acrylonitrile-butadiene rubber vulcanizates.

– The hardness of NBR/HAF/olive or orange oil vulcanizates was increased.

– The olive and orange oils were found to have multiple effects as good plasticizers and antioxidants for NBR rubber.

– The thermal stability of acrylonitrile-butadiene rubber vulcanizates was enhanced.

– The dielectric results have been explained on the basis of interfacial polarization (IP) and electrode polarization. The analyzed data shows low frequency relaxations due to interfacial polarization in addition to a clear relaxation peak corresponding to the segmental orientation of the polymer chains and known as α -relaxation process.

– The values of ϵ' and ϵ'' of orange take the following ascending order orange oil > DOP > olive oil.

– The experimental data are represented in terms of Havriliak–Negami functions. The analyzed data shows low frequency relaxations due to interfacial polarization in addition to a clear relaxation peak corresponding to the segmental orientation of the polymer chains and known as an α -relaxation process.

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Instytut Chemii Przemysłowej im. prof. I. Mościckiego w Warszawie

opracował ogólnokrajową

BAZĘ APARATURY DO OKREŚLANIA CHARAKTERYSTYKI I PRZETWÓRSTWA POLIMERÓW

będącej w posiadaniu uczelni, instytutów PAN i instytutów badawczych.

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