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Influence of blend wax additives on the properties of natural rubber composites containing 2,2,4-trimethyl-1,2-dihydroquinoline as antioxidant

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The paper presents our investigations on the influence of waxes on a very large number of properties of composites based on natural rubber and containing 2,2,4-trimethyl-1,2 dihydroquinoline (TMQ) as an antioxidant. The hypothesis of the present study is that by changing the composition of waxes, respectively wax blends (the ratio between the microcrystalline and the macrocrystalline part) one can control their impact on the properties of rubber mixtures and vulcanizates containing TMQ as antioxidant. Different properties of the composites were studied - rheological, vulcanization, physicomechanical (stress at 100 and 300% deformation, tensile strength, elongation at break, Shore A hardness, tear resistance, etc.), abrasion resistance, thermal and light aging resistance. The combination of TMQ with an optimized mixture of paraffin and microcrystalline waxes can be used successfully for the production of rubber items for various purposes.

Keywords: natural rubber-based composites; wax blends; 2,2,4-trimethyl-1,2-dihydroquinoline; gas chromatographic characterization

INTRODUCTION

For a long time, waxes have been used as additives in rubber processing. They have turned to be cost-effective in terms of internal lubrication energy efficiency; acceleration of the mixing process, improvement of the flow of mixtures and release from matrices. In addition, the elastomeric macromolecules of all rubber compounds based either on natural rubber, butadiene styrene rubber or butadiene acrylonitrile rubber have unsaturation spots (mainly double bonds) which are attacked by atmospheric oxygen, ozone and UV rays [1]. Paraffin and blends being of adaptive molecular structure, are ideal for use as protection against atmospheric influences in rubber processing industry. The migration properties of the former provide continuous oxidative, ultraviolet and ozone protection of finished rubber products [2]. That is why wax blends are a mandatory ingredient in compounds for the production of a number of rubber articles inclusive tire treads.

According to their structure, waxes are divided into macrocrystalline (paraffin) and microcrystalline (ceresin).

Macrocrystalline waxes consist almost entirely of saturated normal hydrocarbons and small amounts of branched hydrocarbons. They are transparent or white in color, hard, shiny and brittle and form large crystals. They differ in melting temperature (relatively low (45-65 ºC)), as well as in the oil content. The number of carbons in their chains ranges from 18 to 50 carbons (commercial paraffins are mostly in the 22 to 38 range) [2].

Microcrystalline waxes are opaque, soft, plastic, sticky and amorphous. They have a higher melting point (65-100ºC). The crystals they form are irregular in shape and small in size. Microwaxes contain significant amounts of branched and cyclic hydrocarbons which distinguish them from paraffins and give them different properties. Microcrystalline waxes have molecular weight higher than that of paraffins with a number of carbons between 30 and 80. The majority have between 45 and 55 carbons [3].

However, wax blends are most commonly used in the rubber processing industry. These are blends of macrocrystalline and microcrystalline waxes. Usually the macrocrystalline wax predominates, the microcrystalline being present at 30% or less. These waxes are formulated so that specific results are achieved, namely tailoring the specific influence on the properties of the elastomeric composites that contain them. The main reason for using wax blends can be stated as follows: To protect the rubber, there must be a wax film present on the surface of the rubber regardless of the ambient temperature. On the other hand, depending on molecular weight and structure, each wax has an optimum temperature at which it will migrate on the surface and form a film [4, 5]. These two requirements (to migrate and to form a film) are met easier, if wax blends are used rather than individual waxes. 2,2,4-Trimethyl-1,2-dihydroquinoline (TMQ) is a very important category of rubber antioxidants (Fig. 1). It has a good

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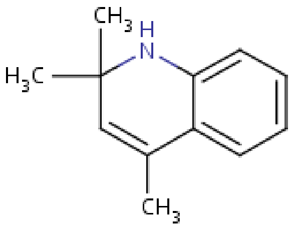


Fig. 1. Structural formula of TMQ

protective effect against heat and oxygen and a stronger inhibitory effect against metal catalytic oxidation, used widely in the manufacture of tyres, different technical rubber goods, adhesive tape, cables, etc. TMQ has limited to medium-strength activity as an antiozonant, medium effectiveness as an anti-fatigue agent, and low effectiveness against crack growth [6].

In this regard, the thesis of the present study is that changing the composition of waxes, respectively wax blends (the ratio between the microcrystalline and macrocrystalline part) we can control the impact of those blends onto the properties of rubber mixtures and vulcanizates containing TMQ as antioxidant, and thus enhance their effectiveness as antiaging agents.

The aim of the present work is to study how the composition of various wax blends, evaluated by the amount of normal and branched iso-hydrocarbons in them, affects a significant number of properties of natural rubber-based composites containing TMQ as an antioxidant. The evaluation can also be made by the number of carbon atoms in the normal and iso-hydrocarbons present in the largest quantities in the wax blends, according to data from their gas chromatographic characterization.

Other authors [4, 7] have also investigated the influence of waxes on a very large number of properties of natural rubber-based composites (rheological, vulcanization, physicomechanical (stress at 100 and 300% deformation, tensile strength, elongation, Shore hardness, tear resistance, fatigue during cyclic deformations, etc.). In [4] the authors came to the conclusion that the optimal properties are achieved by combining paraffin and microcrystalline waxes. In [7], only the individual influence of paraffinic hydrocarbons on the properties listed above was studied. It was compared with the influence of an antioxidant from the group of p-phenylenediamines. In [8] the individual influence of an antioxidant from the group of p-phenylenediamines on a very large number of composite properties was compared to that of TMQ. The effect was demonstrated to be dependent on the concentration of the antioxidants and on the time of their mixing with the elastomeric matrix.

We did not find anything like our study in the literature.

EXPERIMENTAL

Materials

Natural rubber TSR-10, made in Thailand, was used as an elastomeric matrix. Its strictly standardized content of non-rubber substances is given in Table 1.

Table 1. Characteristics of natural rubber TSR-10 used.

Parameters	Value
Mechanical impurities, % by mass	not more than 0.10
Ash content, % by mass	not more than 0.75
Nitrogen, % by mass	not more than 0.6
Volatile substances, % by mass	not more than 0.8
Plasticity retention index (PR)	not less than 50
Wallace plasticity	not less than 30

Furnace carbon black N 220, produced in Russia, was used as a filler of the rubber composites. The other ingredients were stearic acid, zinc oxide, N-tert-butyl-2-benzothiazolylsulfenamide (TBBS) with a density of 1.29 g/cm^3 and a melting point of 105°C; diphenylguanidine - DPG (medium active vulcanization accelerator with a density of 1.19 g/cm^3 and a melting point of 145 ºC); sulfur, processing oil, 1,2-dihydro-2,2,4-trimethylquinoline (TMQ). Blends of different individual brands of paraffin and microcrystalline waxes, manufactured by Evricom Ltd., Bulgaria, with the compositions and characteristics shown in Tables 2 and 3, were used as additives.

Table 2. Characteristics of the individual wax brands used.

Product	Type of the wax	Melting point, °C	Oil content, %	Penetration, 0.1 mm
E4	paraffin	53-55	0.5-0.8	18-20
E57	paraffin	55-57	1.0-1.5	30-36
E58	paraffin	58-60	0.3-0.5	17-19
E62	paraffin	60-64	0.5-0.7	14-16
EC35	microcrystalline	76-78	2.0-3.0	30-35

Table 3. Compositions of the wax blends used.

Sample	E4 %	E57 %	E58 %	E62 %	EC35 %
1	-	20	30	30	20
2	-	-	-	70	30
3	-	-	80	-	20
4	-	80	-	-	20
5	80	-	-	-	20

Table 4. Compositions of natural rubber-based compounds - TSR-10 (all ingredients are in parts by weight per 100 parts by weight of rubber).

Compounds Ingredients	NR-0	NR-1	NR-2	NR-3	NR-4	NR-5
NR (TSR-10)	100	100	100	100	100	100
Carbon black N 220	50	50	50	50	50	50
Wax blend 1	-	1	-	-	-	-
Wax blend 2	-	-	1	-	-	-
Wax blend 3	-	-	-	1	-	-
Wax blend 4	-	-	-	-	1	-
Wax blend 5	-	-	-	-	-	1
Processing oil	3	3	3	3	3	3
TMQ	1	1	1	1	1	1
Stearic acid	2	2	2	2	2	2
ZnO	5	5	5	5	5	5
Sulfur	1.2	1.2	1.2	1.2	1.2	1.2
TBBS	0.95	0.95	0.95	0.95	0.95	0.95
DPG	0.35	0.35	0.35	0.35	0.35	0.35

NR-0 denotes the rubber of the compound and the vulcanizate, which do not contain a wax mixture, but only TMQ antioxidant.

Production of rubber compounds

The rubber compounds were made on an open laboratory rubber mixer (two-roll mill) with dimensions: L/D 320×160 mm and friction 1.27 (non-dimensional). The speed of the slower rotating roll was 25 min^{-1}. The finished compound was removed from the rollers in the form of a sheet and left to stay for 24 hours before being vulcanized.

Basic compositions

Table 4 shows the compositions of the tested natural rubber based compounds.

Vulcanization procedure

The test specimens were vulcanized on a hydraulic press with electric heating at a temperature of 150 °C. Vulcanization was performed in the vulcanization optimums for each compound determined using an MDR 2000 oscillating disk vulcameter (Alpha Technology) by applying a pressure of 10.0 MPa. The obtained sheets of vulcanizates had dimensions of 150×150×2 mm.

Test methods

Determination of the quantitative composition of hydrocarbons in the used wax mixtures according to ASTM D 5442. The quantitative method was used to determine the content of hydrocarbons with a chain length from C17 to C44 included in the composition of the macro- and microcrystalline waxes and their mixtures. The method is based on gas chromatographic determination using an internal standard and a flame ionization detector. A gas chromatograph with Agilent 6850 flame ionization detector and specialized Clarity software for electronic data processing was implemented.

Determination of vulcanization characteristics. The vulcanization characteristics of the investigated rubber compounds were determined on an oscillating disk vulcameter MDR 2000 (Alpha Technologies Inc.), according to the standard of ISO 3417: 2010.

Determination of the physicomechanical parameters of the studied vulcanizates

Determination of Shore A hardness. The Shore A hardness of the test bodies was determined 24 hours after vulcanization using a portable Mitotoyo hardness tester of the company according to ISO 7619-1: 2012. The forced penetration into the material of a special nozzle under certain conditions was measured.

Determination of strength-elastic properties in the course of tensile deformation. 24 hours after vulcanization, double-sided blades (dumbbells) were cut from the test specimens on a punch press with a standard-shaped knife. A micrometer with an accuracy of 0.01 mm was used to set the dimensions of the blades. The stresses at 100 and 300% elongation, tensile strength and elongation at break was determined on a dynamometer at a movable jaw speed of 500 mm/min, according to ISO 37: 2008.

Determination of the residual elongation at tensile deformation. The measurement of the residual elongation in the working area of the samples was performed 1 min after rupture. The two parts of the torn dumbbells were joined and the length of the working section was measured. The residual elongation is calculated from the experimental results by the equation:

$$E_{res.} = \{(\ell_2 - \ell_0) / \ell_0\}.100, \% \qquad (1)$$

where: ε_{res}. - residual elongation, %; ℓ_0 - length of the working section before deformation, cm; ℓ_2 - length of the working section one min after the rupture, cm.

Determination of tear resistance according to ISO 34-1:2012

Determination of resistance to accelerated thermal aging. The resistance to thermal aging was determined in a thermal cabinet with forced air circulation according to ISO 188: 2009. The samples were heated at 70 °C for 72 hours. The "minus" sign in front of the aging coefficient (%) indicated the decrease of the respective mechanical parameters in percent.

The aging coefficients are calculated by the formula:

$$K = [(B-A) / A] .100, \% \qquad (2)$$

where: B - value of the studied indicator after aging; A - value of the studied indicator before aging.

Determination of resistance to light aging

Artificial aging was performed in an ILKA Feutron 3001 climate chamber (Germany) with illumination of ultraviolet light for 320 h at 30 °C.

Determination of the abrasion of the studied vulcanizates

Determination of abrasion was performed by means of a device with a rotating cylindrical drum. The method consists in determining the reduction of the volume of a test vulcanizate body under the influence of friction with a certain type of sandpaper (abrasive).

A cylindrical vulcanizate test body with a diameter of 16 mm and a height of 8 mm was exposed to abrasive fabric (sandpaper) with a certain degree of abrasiveness (sandpaper coefficient) at a certain contact pressure on a certain area. The mass loss of the test piece was determined and the reduction in volume was calculated by the density of the material using the equation:

$$\Delta V = \frac{m_0 - m}{\rho.b}.1000\text{, mm}^3 \qquad (3)$$

where: ΔV - reduction of the volume (erasability) of the working body, mm^3; m - mass of the working body after erasing, g; m_0 - mass of the working body before erasing, g; b - coefficient of sandpaper; ρ- density of the test specimen.

The density of the test specimens was determined by the formula:

$$\rho = \frac{G}{G-(G_1 - G_2)}.\rho_0\text{, g/cm}^3 \qquad (4)$$

where: G - mass of the test body, g; G_1 - mass of the test piece attached to a needle in water, g; G_2 - the mass of the needle immersed in water; ρ_0 - density of the liquid in which the test body is immersed (in this case water), g/cm^3.

RESULTS AND DISCUSSION

Gas chromatographic determination of the composition of hydrocarbons in the studied wax blends

The composition of hydrocarbons in the tested wax blends is presented in Table 5.

Table 5. Quantitative composition of hydrocarbons in the used wax blends according to data from gas chromatographic analysis.

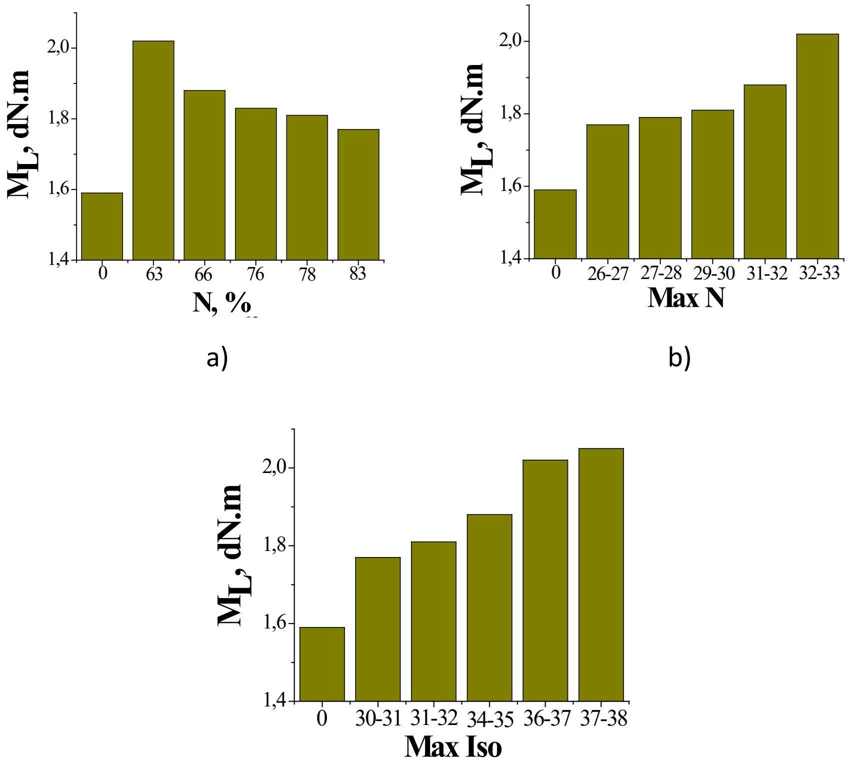
Sample	N[1] %	ISO[2] %	Max N[3]	Max ISO[4]
1	76	24	27-28	37-38
2	66	34	31-32	34-35
3	63	37	32-33	36-37
4	83	17	26-27	30-31
5	78	22	29-30	31-32

Notes: [1] Quantity of normal hydrocarbons, %; [2] Quantity of iso-hydrocarbons, %; [3] Number of atoms in normal hydrocarbons contained in the largest quantities; [4] Number of atoms in iso-hydrocarbons contained in the largest quantities.

Vulcanization characteristics of elastomeric composites containing wax blends

As seen from Fig. 2, as the amount of normal hydrocarbons in the wax blend increases, the minimum torque gradually decreases. The minimum torque is related to the effective viscosity of the mixtures. It is obvious that the greater the amount of normal hydrocarbons, the fewer are the branched iso-structures that can cause an increase in viscosity because they hinder the flow of mixtures. As the number of atoms in the normal and iso-hydrocarbons present at maximum amounts in the wax blends increases, the viscosity gradually increases, what can be explained by the increase in the molecular weight of the wax blends, also causing a slower flow. In the case of iso-hydrocarbons, the effects are somewhat more pronounced because the number of atoms in the chains, their molecular weights, respectively, are higher than normal hydrocarbon chains (30-38 *vs.* 26-33). Rubber viscosity is influenced by various factors such as mixing time [9], mixing temperature [10], filler type, filler loading [11, 12] and chemical curatives [13]. This study showed that the addition of small amounts (1 phr) of wax blends into the natural rubber composites has also a noticeable effect on the viscosity depending on their composition, in particular on the ratio between normal and iso-hydrocarbons, and the number of carbon atoms present in them in the largest quantities.

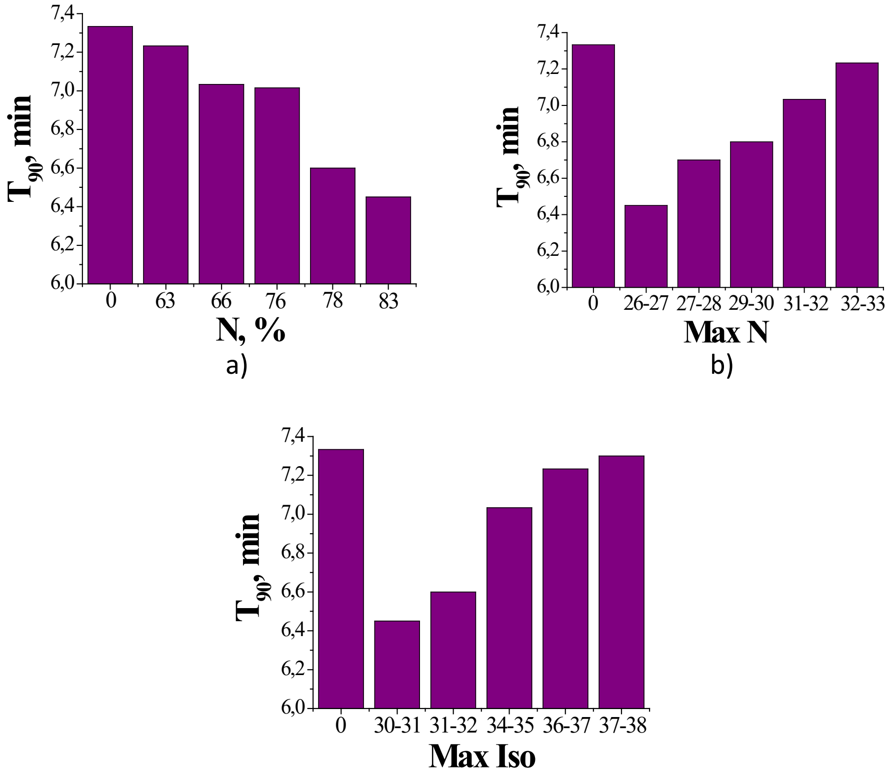
As Fig. 3 shows, the higher amounts of normal hydrocarbons lead to a shorter optimal vulcanization time, i. e. vulcanization is accelerated and proceeds at a higher rate. As the number of atoms in the hydrocarbon chains of both normal and iso-carbons present at maximum amounts increases, the optimal vulcanization time is prolonged. The observed effects may be related to the effect that wax blends have on the access of vulcanizing agents and accelerators to the elastomeric macromolecules. Increasing the number of branched structures and the number of carbon atoms, obviously makes this access difficult, and hampers the migration, which in turn slows down vulcanization. The effect of waxes on the optimal time of vulcanization has been confirmed also by other authors [7].



a) b)

c)

Fig. 2. Dependence of the minimum torque of the tested rubber compounds on: a) the amount of normal hydrocarbons in the composition of the wax blends (N); b) the number of atoms in the normal hydrocarbons contained at maximum amounts in the wax blends; c) the number of atoms in the iso-hydrocarbons contained at maximum amounts in the wax blends.



a) b)

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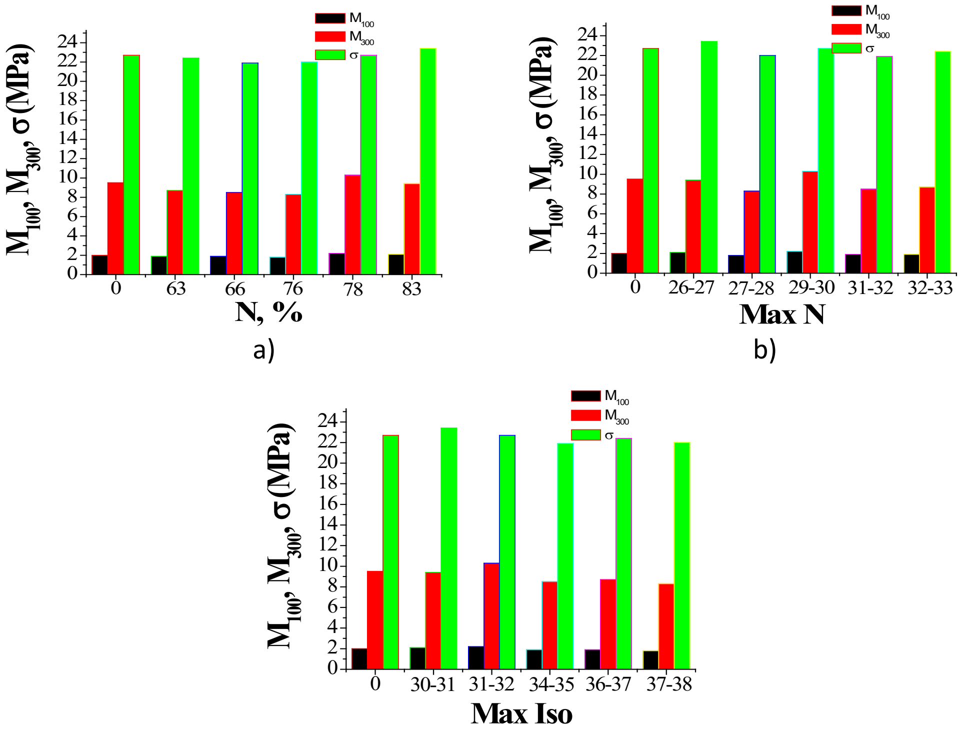
Fig. 3. Dependence of the optimal time of vulcanization of the studied rubber mixtures on: a) the amount of normal hydrocarbons in the composition of the wax blends (N); b) the number of atoms in the normal hydrocarbons contained at maximum amounts in the wax blends; c) the number of atoms in the iso-hydrocarbons contained in maximum amounts in the wax blends.

Physicomechanical parameters of the studied composites

The results presented in Fig. 4 demonstrate that, as expected, the wax blends at the amounts of 1 phr used do not have a noticeable effect on the studied physicomechanical parameters. The values are comparable, the differences being less than 10%.

Tear resistance of the studied composites containing various wax blends

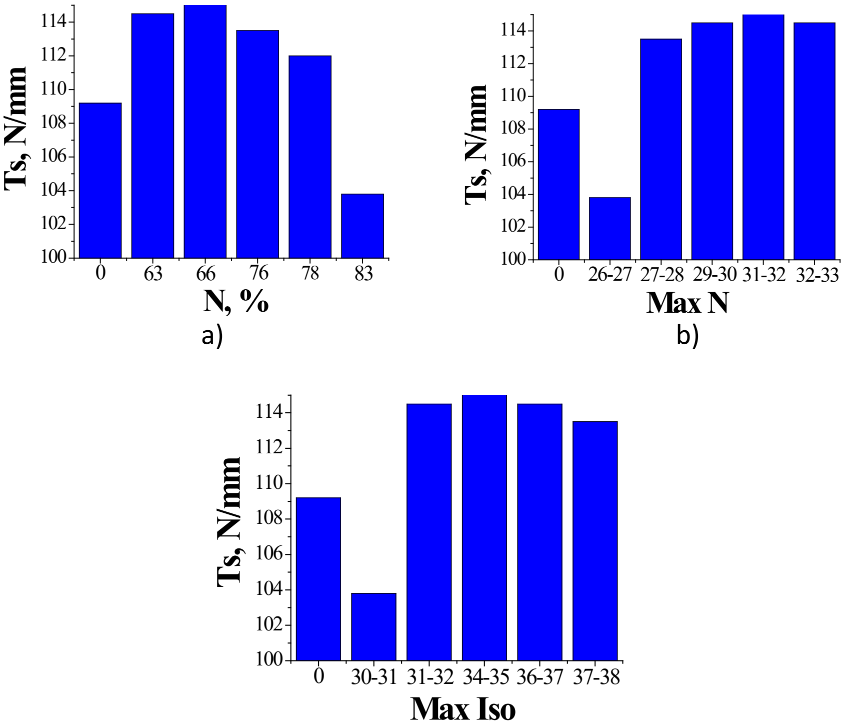
The influence of the wax blends on the tear resistance of the studied composites is shown in Fig. 5. As seen from the figure, with increasing the amount of normal hydrocarbons, the tear resistance decreases, and with increasing the number of atoms in the carbon chains, both normal and iso-, there is a tendency to increase. A crossing through a slightly pronounced optimum is observed in the latter cases. In our opinion, this is due to the different ability of different wax blends to migrate. In general, the presence of wax blends in the elastomeric matrix probably has a certain plasticizing effect, which provides some possibility for mobility of the elastomeric macromolecules relative to each other under the conditions of applied external tear force. The faster migration of normal hydrocarbons to the surface complicates the manifestation of this effect and therefore, with increasing their amount the tear resistance decreases, as the composite depletes the plasticizing agent. As the number of atoms in the hydrocarbon chains present at the maximum amount in the wax blends increases, the migration is hampered due to the increase in their molecular weight, which creates greater opportunities for manifestation of their plasticizing effect. That leads to an increase in the resistance of tearing.



a) b)

c)

Fig. 4. Dependence of physicomechanical parameters (M100-module at 100% deformation, MPa; M300-module at 300% deformation, MPa; σ-tensile strength, MPa) of the studied vulcanizates on: a) the amount of normal hydrocarbons in the composition of the wax blends (N); b) the number of atoms in the normal hydrocarbons contained at maximum amounts in the wax blends; c) the number of atoms in the iso-hydrocarbons contained at maximum amounts in the wax blends.



a) b)

c)

Fig. 5. Dependence of the tear resistance of the studied vulcanizates on: a) the amount of normal hydrocarbons in the composition of the wax blends (N); b) the number of atoms in the normal hydrocarbons contained in maximum amounts in the wax blends; c) the number of atoms in the iso-hydrocarbons contained in maximum amounts in the wax blends.

Abrasion resistance of the studied composites containing different wax blends

The influence of the wax blends on the abrasion resistance of the studied composites is shown in Fig. 6. Here again, the observed effects can be explained by the migration of the wax blends, though in the opposite way to the tear resistance described. The rapid release of waxes to the surface has a lubricating effect, which reduces abrasion and it becomes much lower for normal hydrocarbons, especially with increasing their amounts. The slower migration process and the release of the wax mixtures on the surface with the increase of the molecular weight, and the amount of branched hydrocarbons reduces the lubrication effect during abrasion, hence the abrasion is greater. This statement is proved by the fact that the highest abrasion in all cases undergo composites in which there are no wax blends.

It is well known that the heterocyclic nitrogen-containing stabilizer TMQ is a classical antioxidant of high efficiency. In all the vulcanizates studied, it is present at the same amount, being combined with different wax mixtures, except for the control sample. Therefore, we believe that the different results for the parameters studied are mainly due to the synergetic effect of TMQ and the combination of waxes of different composition and structure, and not to the antioxidant itself.

Aging resistance of the studied composites containing different wax blends

Tables 6 and 7 summarize the results of thermal and light aging of the studied elastomeric composites.

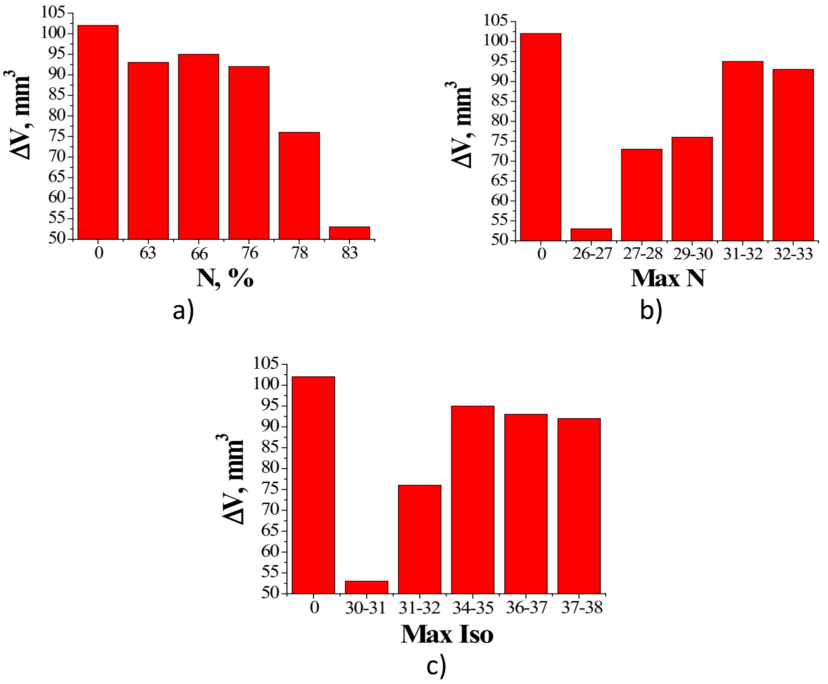


Fig. 6. Dependence of the abrasion resistance of the studied composites on: a) the amount of normal hydrocarbons in the composition of the wax blends (N); b) the number of atoms in the normal hydrocarbons contained at maximum amounts in the wax blends; c) the number of atoms in the iso-hydrocarbons contained at maximum amounts in the wax blends.

Table 6. Change in thermal aging coefficients (K_ε, %) with respect to elongation (70 °C, 72 h) depending on the amount of normal hydrocarbons in the composition of the wax blends N (a); depending on the number of atoms in the normal hydrocarbons present at maximum amounts in the wax blends (b); and depending on the number of atoms in the iso-hydrocarbons present at maximum amounts in the wax blends (c).

a) N	Kε, %	b) Max N	Kε, %	c) Max Iso	Kε, %
0	-15.6	0	-15.6	0	-15.6
63	-4.8	26-27	-9.1	30-31	-9.1
66	-5.4	27-28	-6.5	31-32	-6.5
76	-6.3	29-30	-6.3	34-35	-4.8
78	-6.5	31-32	-5.4	36-37	-5.4
83	-9.1	32-33	-4.8	37-38	-6.3

Table 7. Change in light aging coefficients with respect to elongation (320 hours) depending on the amount of normal hydrocarbons in the composition of the wax blends N (a); depending on the number of atoms in the normal hydrocarbons present at maximum amounts in the wax blends (b); and depending on the number of atoms in the iso-hydrocarbons present at maximum amounts in the wax blends (c).

a) N	Kε, %	b) Max N	Kε, %	c) Max Iso	Kε, %
0	-3.5	0	-3.5	0	-3.5
63	3.7	26-27	-2.2	30-31	-2.2
66	6.0	27-28	-2.9	31-32	3.2
76	3.2	29-30	3.2	34-35	6.0
78	-2.2	31-32	3.7	36-37	3.7
83	-2.9	32-33	6.0	37-38	-2.9

Table 6a shows that with increasing the amount of normal hydrocarbons in the wax mixtures, aging accelerates. That may be due to an increase in the migration of waxes to the surface, which is also accelerated, but the resulting protective film is increasingly ineffective due to the declining amount of iso-hydrocarbons in it. With increasing the molecular weight of normal hydrocarbons as a result of the increasing the number of atoms, their migration to the surface is lessened, the presence of waxes in the volume of the composite hinders oxygen access to the elastomeric macromolecules and aging processes take longer (Table 6b). It is also obvious that there is an optimum in the molecular weight and the number of atoms in the carbon chains of the iso-hydrocarbons, as well as an optimal ratio between normal and iso-hydrocarbons, respectively, between their molecular masses and the number of atoms in them. That ensures maximum protective effectiveness of the film formed as a result of their migration to the surface of the vulcanizate (Table 6c).

The explanation of the observed effects is analogous to that of the effects of thermal aging with the peculiarity that here the effects of aging are much less pronounced, mainly due to the presence of furnace carbon black in the composites. The filler is known to be an effective absorber of ultraviolet light and to increase the resistance to light aging. Another feature that makes a strong impression is that the highest protective efficiency in light aging was observed at the same ratio between normal and iso-hydrocarbons, respectively, the number of atoms in their chains, which is also observed in thermal aging.

The interpretation of the obtained results can be summarized as follows:

- The greater the number of atoms in the hydrocarbon chain, the higher the molecular weight, the higher is the melting point and the higher is the ambient temperature required for the migration and so called blooming of the wax blends on the surface of the rubber product. It should be kept in mind that while paraffin waxes can be said to have a relatively clearly defined melting point, microcrystalline waxes do not have such a clearly defined melting point due to their wider molecular weight distribution. That is why the so-called drop point temperature is often used for their characterization [3].

- The movement (migration) of the waxes to the surface of the rubber product depends on the following factors:

• Molecular weight or the number of carbon atoms in the wax, respectively. The higher they are, the higher is the ambient temperature needed to ensure sufficient mobility for migration [3].

• Branched waxes migrate and bloom slower [3].

•The concentration of wax in the rubber product. After crossing the solubility threshold, the more wax present in the composite, the greater is the concentration gradient to the surface, which will stimulate migration to a higher degree [7].

•Higher ambient temperatures increase the solubility of waxes and increase migration, especially of higher molecular weight waxes.

The waxes that migrate and bloom the most are paraffin waxes. Microcrystalline waxes are too bulky to bloom and to create an effective protective film. However, studies have shown [3, 7] that microcrystalline waxes play another extremely important role in wax mixtures: when paraffin waxes reach the surface, they create a highly crystalline and inelastic film with poor adhesion. In this large-crystal structure, "holes" are formed, which allow air to penetrate freely through them and reach the rubber products. Adding a small but optimal amount of branched (microcrystalline) waxes to the paraffins creates a more amorphous, much finer crystalline protective film on the surface, which is already impermeable to air. The reduction of the film crystallinity due to the presence of microcrystalline waxes in it also makes it more elastic. This more elastic film is no longer so fragile and does not break down so easily, i.e. it is more durable. In addition, the microcrystalline wax has a higher adhesion to the elastomeric surface than the paraffin wax, which also contributes to the creation of a longer lasting wax film on it. Therefore, the most commonly used wax blends should contain several paraffin waxes of different molecular weight in combination with a small amount of microcrystalline wax. In order to achieve maximum efficiency and optimal properties, the ratio between paraffin and microcrystalline waxes, as well as the number of carbon atoms in the normal and iso-hydrocarbons present in maximum amounts in them must be optimized.

CONCLUSION

The composition of wax blends containing paraffin and microcrystalline waxes, as well as the number of carbon atoms in the hydrocarbons present in maximum quantities in the blends, affect a number of properties of elastomeric composites, as follows:

1. As the amount of normal hydrocarbons in wax mixtures increases, vulcanization is accelerated, and as the number of atoms in the hydrocarbon chains of both normal and iso-carbons present at maximum amounts increases, vulcanization is retarded.
2. The wax blends at the used amounts of 1 phr do not have a noticeable effect on the studied physicomechanical parameters and the values are comparable, the differences being less than 10%.
3. With increasing the amount of normal hydrocarbons in the wax blends, the tear resistance decreases, and with increasing the number of atoms in the hydrocarbon chains, both normal and iso-, there is a tendency of increasing the values of this parameter.
4. All tested vulcanizates containing waxes and TMQ exhibit better resistance to thermal aging compared to the control sample which contains only TMQ as an antioxidant. As the amount of normal hydrocarbons in wax blends increases, aging accelerates. With the inclusion in molecular weight of normal and iso-hydrocarbons the aging process is prolonged.
5. The observed effects of light aging are similar to the effects of thermal aging, but here they are much less pronounced.

By varying the composition of the wax blends with respect to the amount of paraffin waxes with normal hydrocarbons and microcrystalline waxes with iso-hydrocarbons and the number of atoms in the two types of chains present in maximum amounts, a number of properties of the composites containing them can be controlled in the desired direction, including rheological, vulcanizing, mechanical (such as abrasion and tear resistance), resistance to heat and light aging, etc.

The combination of TMQ and an optimized mixture of paraffin and microcrystalline waxes has a synergetic impact and can be successfully used in the production of rubber products for various purposes, as it guarantees good performance and better protection compared to the use of TMQ solely.

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