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Sustainability in the rubber industry through bio-refinery plasticizers

The use of bio-sourced plasticizers in rubber industry to ensure the environmental sustainability of the entire production cycle was described. A new generation of plasticizers obtained from vegetable oils, commercialized under the name Matrilox®, is reported in the present paper. According to results of various tests (DSC, TGA, physical properties, aging), novel bio-sourced plasticizers, obtained through a bio-refinery approach and compounded in typical rubber formulations (NBR, SBR, BR, NR) can be successfully used as partial or total substitutes of traditional plasticizers.

Keywords: bio-sourced plasticizers, bio-oils, sustainability, environmental protection, rubber plasticizers.

Zrównoważony rozwój w przemyśle gumowym dzięki plastyfikatorom pochodzenia biologicznego

Opisano zastosowanie plastyfikatorów pochodzenia biologicznego w przemyśle gumowym w celu zapewnienia zrównoważonego rozwoju w zakresie bezpieczeństwa dla środowiska całego cyklu produkcyjnego. W niniejszym artykule przedstawiono nową generację plastyfikatorów otrzymanych z olejów roślinnych, skomercjalizowanych pod nazwą Matrilox®. Zgodnie z wynikami różnych testów (DSC, TGA, właściwości fizycznych, starzenia) nowe bio-plastyfikatory, uzyskane metodą bio-rafinacji i zastosowane w typowych mieszankach kauczukowych (NBR, SBR, BR, NR), mogą z powodzeniem służyć jako częściowe lub całkowite zamienniki tradycyjnych plastyfikatorów.

Słowa kluczowe: plastyfikatory biologiczne, oleje biologiczne, zrównoważony rozwój, ochrona środowiska, plastyfikatory do gumy.

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1. Introduction

Many companies are following a “go green” strategy looking for new sources of materials derived from agricultural or sustainable feedstock. The use of these biomaterials may offer several benefits, including reduced dependence on foreign oil, competitive pricing, improved environmental footprint and performance. Versalis is also following a long term route in the forefront of chemistry from renewable sources. This business model, based on the environmental sustainability of the entire production cycle, accounts for bio-sourced monomers and additives for rubber compounding.

Since the primary goal of adding plasticizers into polymers is to facilitate the processing and to improve the flexibility of the finished products, several efforts for increasing the sustainability of these ingredients are reported in the literature. Researchers have studied a wide variety of natural oils, including soy, sunflower, corn, canola, castor oil and others for compatibility and performance in rubber compounds [1]. With diverse options of natural sources available, sustainable oils may vary in degree of polarity, molecular weight, transition temperatures and unsaturation sites. For example Nandan [2] tested various vegetable oils in carbon black filled compounds based on different elastomeric matrices (SBR, NR, NBR), while da Costa et al. [3] described the effect of castor oil in silica filled natural rubber compounds. Dasgupta et al. [4, 5] investigated the influence of several locally available (India) vegetable oils in carbon black filled NR compounds, in comparison to petroleum-based mineral oils. However, further research is necessary to develop compound formulations and oil-rubber compatibility for widespread usage in high performance rubber applications.

Plasticizers such as phthalate and adipate esters are employed successfully in the chemicals, plastics and construction industries, as well as in packaging, adhesives, resins, paper and printing. The use of phthalates, for example has received special attention for many years due to health assessment studies indicating potential risks for humans. The restrictions and limitations imposed in Europe, and more recently in North America, promoted the development of cost-effective alternatives to phthalates. Alternative products to phthalate/adipate plasticizers are then required in the rubber industry for the manufacturing of technical rubber goods. In the last few years, considerable attention has been paid to the replacement of phthalates in NBR through synthetic and bio-sourced materials. Well known plasticizers based on alkyl-sulphonic esters (ASE) were developed according to these trends. Among bio-sourced plasticizers, cottonseed oil and soybean oil derivatives are proposed as replacements for DOP and DOA. More recently, a new plasticizer for NBR compounds obtained from sunflower oil has been reported by Bergmann et al. [1].

Focusing on the tyre industry, rubber plasticizers can be generally classified as mineral oils (petroleum based), synthetic plasticizers, or vegetable oils and other natural products. Mineral oils are further classified by their content of aromatic, paraffinic, and naphthenic hydrocarbons. All mineral oils are nonpolar and relatively cheap, so they are widely used in nonpolar general-purpose elastomers. Mineral oils are used to improve flow and processing and even more to extend the rubber and reduce its cost.

A major challenge for rubber and tyre makers is the replacement of process oils following the groundbreaking European legislation to ban Polycyclic Aromatic Hydrocarbons (PAH). Since 2010, tyres which have oils containing more than 3% PAH can no longer be made or sold in the EU. Replacing mineral oils with vegetable oils may be advantageous as a solution to these problems. However, although vegetable oils have been previously used in rubbers to improve different properties, there has been no systematic study of the effect of the concentration and molecular weight of natural oils on overall rubber properties.

Referring to the tyre business, it has been reported that sustainable oils in SBR tread compounds show promising results for both physical and dynamic mechanical properties, in comparison with petroleum oils [6, 7]. Petrovic et al. [8] investigated polymerized soybean oils of different molecular weights as plasticizers in NR/SBR compositions. Sahakaro et al. [9] reported the properties of tyre tread compounds filled with high abrasion furnace black (HAF) when epoxidized palm oil (EPO) and epoxidized soybean oil (ESBO) are used as the processing oils. Li [10, 11] used a soybean oil modified through the reaction with dicyclopentadiene to convert carbon double bonds of the soybean oil molecules into norbornyl groups of different ratios. Among tyre producers, the use of vegetable oil in tread compound was recently pointed out for example by Michelin (sunflower), Goodyear (soybean), Nokian (canola), Yokohama (orange peel).

2. Experimental

A new generation of plasticizers obtained from vegetable feed-stock, commercialized under the name Matrilox®, is reported in the present paper. Bio-sourced oils are produced through a bio-refining process by Matrìca, a joint venture between Versalis and Novamont, a major player in the bio-plastics market. In particular Matrilox PD family has been engineered to be highly compatible with specialty elastomers such as nitrile rubbers (NBR), polychloroprene (CR) and poly(vinyl chloride) (PVC). It offers a high performance, non-toxic, eco-sustainable alternative to traditional plasticizers like phthalates. These plasticizers have high molecular weight and low release level to achieve excellent plasticization

and thermal stability. Other Matrilox® plasticizers (PF grades) have been specifically designed for the tyre and rubber industry with the aim of partially or totally replacing oil of fossil origin. They can be used, when properly formulated, as free oils in the production of rubber compounds, including the formulation for the tyre industry.

Matrilox vegetable oil derivatives are based on complex mixture of triglycerides and esters of polyols, comprising oligomeric structure of the type $R_4-[O-C(O)-R_1-C(O)-O-CH_2-CH(OR_2)-CH_2]_n-O-R_3$, where R substituents are C_2-C_{22} alkylenes, C_6-C_{24} carboxylic acid residues and alkyl groups. Part of the residual carboxylic acid component is esterified with monoalcohols according to the final application [12].

Matrilox PF801D, specifically designed for SBR/BR application and Matrilox PD204P adapted to the more polar NBR matrix were investigated in the present paper. Widely used commercial NBR plasticizers like DINP, DOA, ASE and petroleum-based process oils (TDAE, naphthenic) were used as reference.

Polymers used in this work are Versalis commercial SSB, ESB and high-*cis*-BR. Natural rubber is of the CV60 type. Polymer/oil swelling measurements were performed at 70 °C on a peroxide cured SSB, characterized by 25% styrene and high vinyl. Rubber compounds were prepared using a laboratory internal mixer (tangential) according to ASTM D3185 for carbon black and to Flanigan et al. [6, 7] for silica. Wet grip and rolling resistance predictors were determined

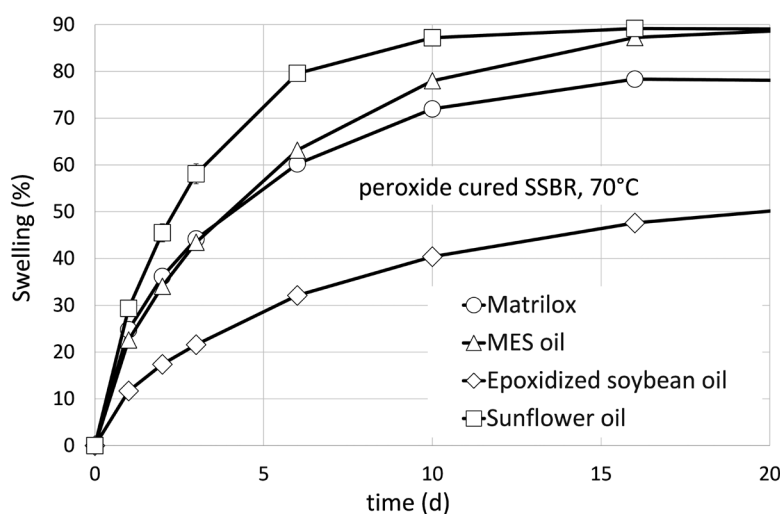


Fig. 1. Effect of various plasticizers on SSB equilibrium swelling at 70 °C. Matrilox PF801D is reported in the picture vs MES process oil and commercially available vegetable oils

Rys. 1. Wpływ różnych plastyfikatorów na pęcznienie równowagowe SSB w 70 °C. Matrilox PF801D przedstawiono na wykresie w porównaniu z olejem procesowym MES i dostępnymi w handlu olejami roślinnymi

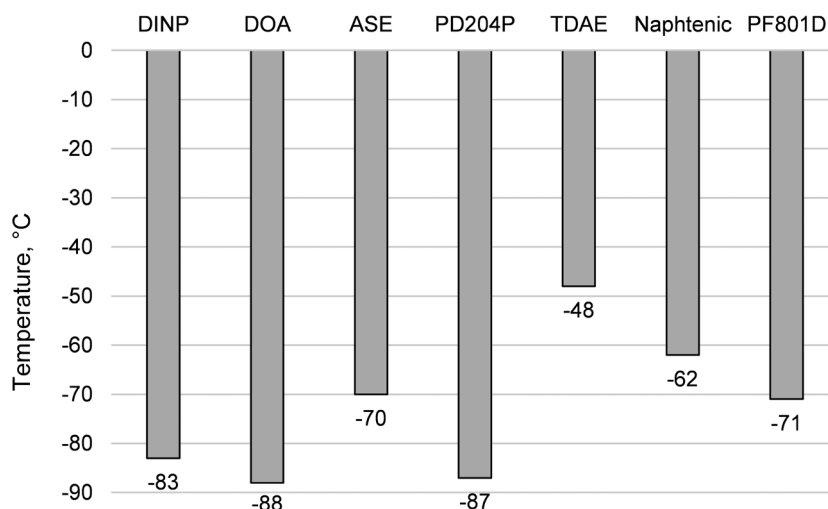


Fig. 2. Glass transition temperature of various plasticizers measured by DSC

Rys. 2. Temperatura zeszklenia różnych plastyfikatorów wyznaczona metodą DSC

by dynamic-mechanic analysis at 0 °C and 60 °C respectively, using a torsional bar geometry. Testing was performed according to ASTM or DIN standards. Aging was carried out using an air hoven for 72 h at 100 °C.

Due to differences in functional groups and polarity, the thermodynamic compatibility of vegetable oils and related derivatives with a rubber matrix is usually lower than that of petroleum oils. The chemical modification operated on Matrilox at the bio-refinery stage partially overcomes this peculiar behavior, making the bio-sourced plasticizer compatible enough to be easily compounded in a wide concentration range. Figure 1 reports the results of the equilibrium swelling experiment with the SSBR polymer matrix, showing a thermodynamic affinity of Matrilox PF801D not too far from that of MES oil [13]. The thermal analysis of the pure plasticizer was performed through DSC and TGA techniques. Results are

reported in Figures 2 and 3. A very low glass transition temperature (T_g) is observed for Matrilox grades. The Matrilox PD204P shows a T_g value lower than DINP and ASE, very close to that of DOA. The transition of Matrilox PF801D value is also occurring at much lower temperature than that of reference process oils (TDAE, naphthenic).

3. Results and discussion

Table 1 shows a model formulation used for testing plasticizers in NBR compound, providing a total replacement of phthalates, adipates and ASE with Matrilox. The compounding cycle (two steps) is not significantly affected by the addition of the bio-sourced

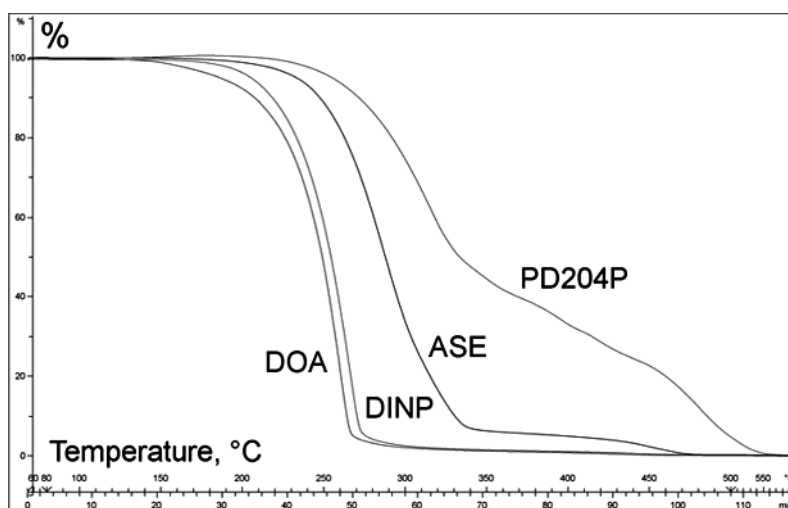


Fig. 3. Thermo-gravimetric analysis of various plasticizers for NBR, including Matrilox PD204P
Rys. 3. Analiza termogravimetryczna różnych plastyfikatorów do NBR, w tym Matriloxu PD204P

Table 1. NBR compound formulation

Tabela 1. Skład mieszanki NBR

Material	phr
Europrene N 3380	100
Plasticizer	15
SRF 772	70
ZnO	3
Stearic acid	1
MMBI	2
TMQ	2
Sulfur	0.2
TMTDS	2.5
MBTS	2.5

ingredient, even during the initial stage of filler wetting, as reported in Figure 4, accounting for a good capability of replacing traditional plasticizers without requiring a complex tuning of mixing parameters.

Figure 5 reports the overall performance of Matrilox in NBR compound. The bio-grade PD204P shows a good combination of properties in the vulcanized state together with one of the lowest compound viscosities, accounting for a good processability. For investigating the temperature-retraction and for comparing viscoelastic properties of compounds at low temperatures, a TR-test was performed (Figure 6). The response of the Matrilox based compound in the range -10/10 °C is in line with that of DOA and not much different from DINP and

ASE. Aging measurements were performed in air oven at 100 °C for 72 h, results are reported in Figure 7. Also in this case Matrilox PD is performing well, in particular versus DOA. Moreover, no oil exudation was observed on aged or stored specimens. Even in the presence of reduced compatibility with the rubber matrix, the bio-plasticizer migration toward the surface is prevented, due to the large size of the molecules obtained through the bio-refinery approach.

Matrilox PF801D (glass transition temperature of -71 °C) was used as process oil for SBR based compounds. This grade is specifically designed for the replacement of traditional petroleum-based plasticizers like TDAE, RAE, MES or naphthenic oil. Figure 8 represents a formulation

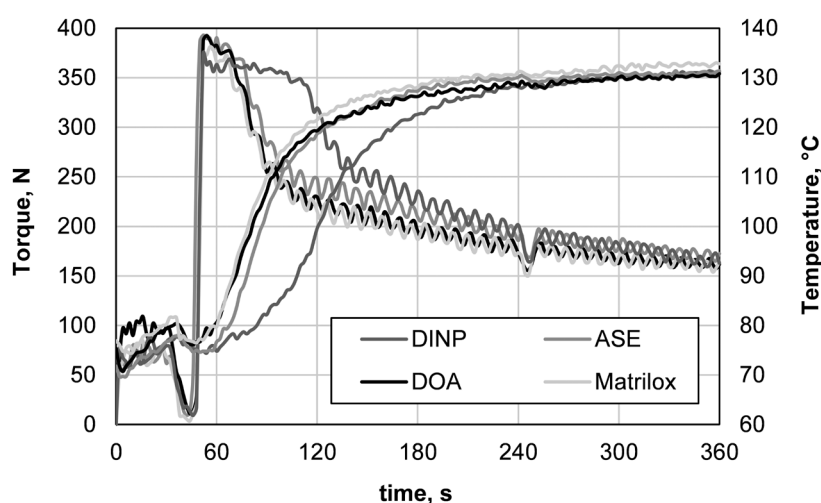


Fig. 4. Torque/temperature plot of the first non-productive mixing step of NBR. Compounds with various plasticizers, including Matrilox PD204P, are reported in the picture

Rys. 4. Wykres momentu obrotowego w stosunku do temperatury dla pierwszego nieprodukcyjnego etapu mieszania NBR. Na rysunku pokazano mieszanki zawierające różne plastyfikatory, w tym Matrilox PD204P

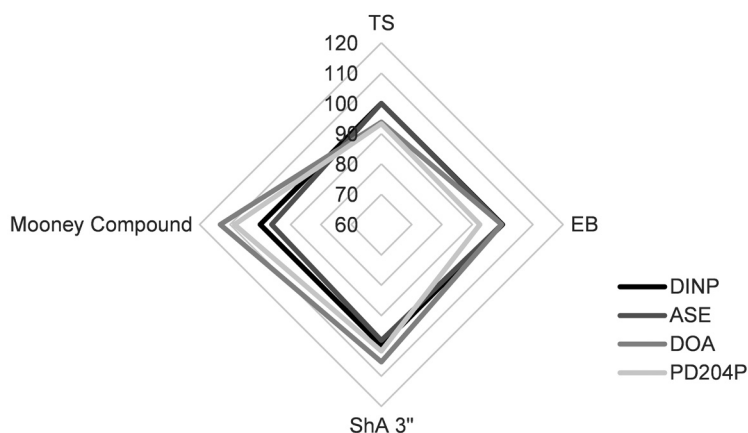


Fig. 5. Main properties of NBR compounds containing various plasticizers, including Matrilox PD204P. Indexed results are reported. Higher value means better performance

Rys. 5. Główne właściwości mieszanek NBR zawierających różne plastyfikatory, w tym Matrilox PD204P. Przedstawiono wyniki indeksowane. Wyższe wartości oznaczają lepsze parametry

for conveyor belts in which 5 phr of TDAE oil were totally replaced by Matrilox. The overall property balance is in line with that of the reference plasticizer. The lower glass transition temperature of the bio-sourced grade positively affects the rolling resistance index, measured

by dynamic-mechanical response in terms of loss tangent at 30 °C. The lower value of tensile strength, not supported by other data, is most probably due to the higher plastifying effect of bio-oil, together with experimental uncertainty.

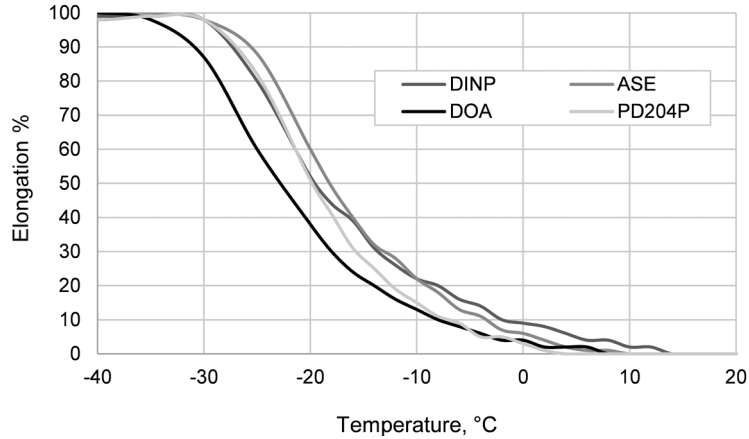


Fig. 6. TR-test performed on NBR compounds with various plasticizers, including Matrilox PD204P

Rys. 6. Test TR przeprowadzony na mieszankach NBR zawierających różne plastyfikatory, w tym Matrilox PD204P

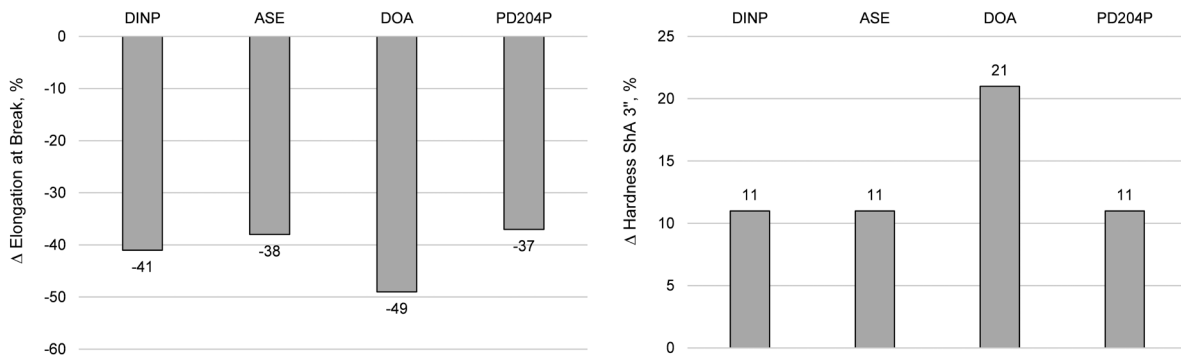


Fig. 7. Aging behavior of NBR compounds with various plasticizers, including Matrilox PD204P. Aging was performed in air oven for 72 h at 100 °C

Rys. 7. Starzenie mieszanek NBR zawierających różne plastyfikatory, w tym Matrilox PD204P. Starzenie prowadzono w suszarnie powietrznej przez 72 h w temperaturze 100 °C

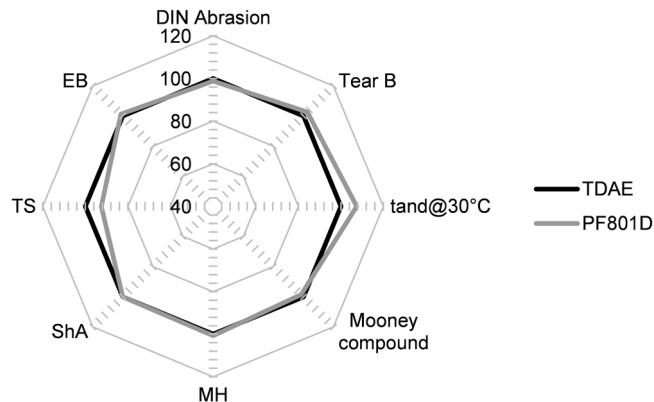


Fig. 8. Process oil comparison in conveyor belt formulation (NR/SBR1500 70/30, 55 phr N330, 5 phr oil). Indexed results are reported. Higher value means better performance

Rys. 8. Porównanie olejów procesowych w mieszance na taśmę przenośnikową (NR/SBR1500 70/30, 55 phr N330, olej 5 phr). Przedstawiono wyniki indeksowane. Wyższe wartości oznaczają lepsze parametry

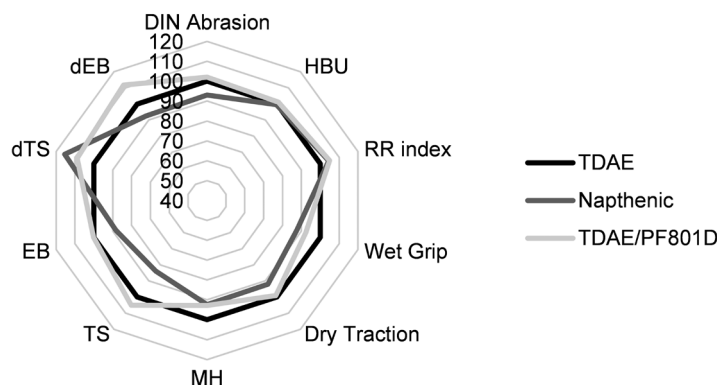


Fig. 9. Process oil comparison in tyre tread formulation (SSBR/BR 75/25, 60 phr silica, 33 phr oil). 10 phr of reference oil were replaced by Matrilox PF801D in the green compound. Indexed results are reported. Higher value means better performance

Rys. 9. Porównanie olejów procesowych w mieszance na bieżnik opony (SSBR / BR 75/25, krzemionka 60 phr, olej 33 phr). W „zielonej” mieszance 10 phr oleju referencyjnego zastąpiono olejem Matrilox PF801D. Przedstawiono wyniki indeksowane. Wyższe wartości oznaczają lepsze parametry

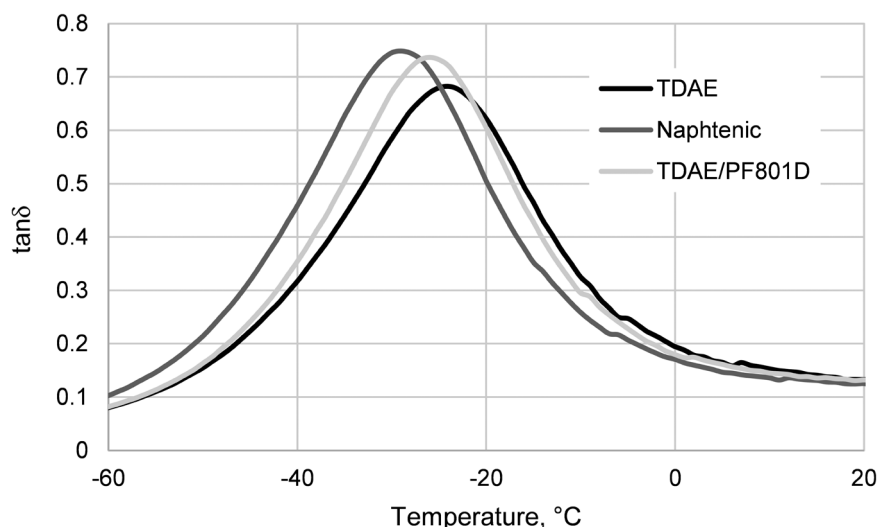


Fig. 10. Loss modulus coefficient ($\tan \delta$) as a function of temperature of tyre tread compounds (SSBR/BR 75/25, 60 phr silica, 33 phr oil). 10 phr of reference oil were replaced by Matrilox in the green compound

Rys. 10. Zależność współczynnika stratności mechanicznej ($\tan \delta$) w funkcji temperatury dla mieszank na bieżnik opony (SSBR / BR 75/25, krzemionka 60 phr, olej 33 phr). W „zielonej” mieszance 10 phr oleju referencyjnego zastąpiono olejem Matrilox PF801D

Primary plasticizers solubilize the rubber and assist in Brownian motion of the polymer chains. Secondary plasticizers do not completely solubilize the elastomer, but can act as lubricants between the polymer chains to improve flow. As already discussed (Figure 1), polar vegetable oils usually show lower compatibility with common elastomers. In the present paper, the investigated Matrilox grade (PF801D) was used as coplasticizer, for a partial replacement of petroleum oil, according to a previously suggested strategy [6, 7]. In the reported silica compound evaluation, roughly 30% of TDAE was replaced with Matrilox PF. Naphtenic oil was also included in the benchmark for comparison.

The overall behaviour of the Matrilox based compound reveals to be very close to the one containing only petroleum-based process oil in terms of mechanical properties, aging and tyre traction predictors (Figure 9). Vulcanization properties are not strongly affected by the introduction of the Matrilox, according to the low iodine number and the chemical modification of the bio-refinery plasticizer (from a kinetic point of view, t_{90} of the bio-based compound is just 10% shorter than reference). Other commercially available pure vegetable oils require a more important tuning of the vulcanization package [13]. The dynamic-mechanical response of tyre tread

compounds is shown in Figure 10. Using process oils with a different glass transition temperature, a different shift of the compound glass transition is expected, according to the position of the maximum in the loss tangent plot vs temperature. For the Matrilox containing compound the T_g shift seems to be smaller than expected, due to a different compatibility with the rubber matrix. It may be concluded that the dosing of a bio-plasticizer in a tread compound requires a careful formulation design to match the desired traction properties. In principle, drop-in replacement of petroleum-based oil in tread compound through vegetable oil derivatives is possible, but with a tuning step which results to be easier in the case of more neutral bio-refinery products.

According to the NBR compound, also in this benchmark no oil migration or exudation was observed after air aging or specimens' storage, accounting for high thermal stability and negligible mass loss. This important improvement in aging resistance needs further investigation and is most probably related to a decrease of the plasticizer diffusion coefficient, due to the average larger size of Matrilox molecules, as a result of the bio-refinery process technology. Moreover, as reported by Li et al. [11] there is also a potential chemical interaction of bio-oils residual double bonds and functional groups with compounding ingredients, leading to a reduced migration in the rubber matrix.

4. Conclusions

Bio-sourced plasticizers offer a high-performance, non-toxic, eco-sustainable alternative to traditional plasticizers. However, replacing a petroleum derivative with a bio-based one involves key technical issues including compatibility with the rubber matrix, interaction with compounding ingredients and tuning of cure packages. Novel bio-sourced plasticizers (Matrilox grades), obtained through a bio-refinery approach and compounded in typical rubber formulations, are successfully described

as partial or total substitutes of traditional plasticizers. The proposed bio-sourced oils provide opportunities to further expand the idea of green rubber compounds.

Acknowledgements

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