

# Oil from tyre pyrolysis as a plasticizer in rubber compounds

Cezary Dębek<sup>1)</sup>

DOI: [dx.doi.org/10.14314/polimery.2019.7.10](https://doi.org/10.14314/polimery.2019.7.10)

**Abstract:** The paper presents the results of research on the possibility of using as plasticizers of rubber compounds the heavy fractions of pyrolytic oil obtained in the industrial process of pyrolysis of car tyres. The content of carcinogenic polycyclic aromatic hydrocarbons (PAHs) in the obtained pyrolytic plasticizers was determined. Compounds and vulcanizates of styrene-butadiene rubber (SBR) containing the above plasticizers as well as commercial petroleum derivatives' plasticizers were prepared for comparative purposes. The basic properties of compounds and vulcanizates containing pyrolytic plasticizers were investigated. The research showed that one fraction of pyrolysis oil meet the requirements of the permitted content of PAHs. SBR blends and vulcanizates have similar properties as in the case of commercial plasticizers.

**Keywords:** tyre pyrolysis, pyrolytic oil, plasticizer, rubber compound, vulcanizate, rubber.

## Olej z pirolizy opon jako plastyfikator w mieszankach kauczukowych

**Streszczenie:** Oceniono możliwość zastosowania jako plastyfikatory mieszanek kauczukowych frakcji ciężkich oleju popirolitycznego uzyskanego w przemysłowym procesie pirolizy opon samochodowych. W badanych plastyfikatorach oznaczano zawartość rakotwórczych wielopierścienowych węglowodorów aromatycznych WWA. Sporządzono mieszanki, a następnie wulkanizaty kauczuku styrenowo-butadienowego (SBR) zawierające wspomniane plastyfikatory oraz dla porównania – handlowe plastyfikatory ropopochodne. Stwierdzono, że mieszanki kauczukowe i wulkanizaty SBR z udziałem badanych plastyfikatorów wykazują podobne właściwości mechaniczne jak analogiczne materiały z plastyfikatorami handlowymi. Z dwóch badanych frakcji oleju popirolitycznego tylko jedna spełniała określone normami wymagania dotyczące dozwolonego poziomu zawartości WWA.

**Słowa kluczowe:** piroliza opon, olej popirolityczny, plastyfikator, mieszanka kauczukowa, wulkanizat, guma.

Rubber is obtained by an irreversible process of vulcanization of a rubber compound, which transforms the plastic material into a highly flexible one. Rubber products are durable and not easily decomposable, so their recycling is not easy. In the management of waste and used rubber products, tyres are the biggest problem. A tyre is a multicomponent material rubber product which accounts for the majority of rubber production by mass. Apart from many types of rubbers, tyres also contain steel (cord and bead wire) and textile reinforcements (usually polyamide cords). Mass production of tyres accounts for about 60–70 wt % of rubber industry production, and the share of tyres in rubber waste is even higher and amounts to about 80 wt % [1–10].

Crushing tyres into granulate in order to use in the production of new elastomeric products is one of the

methods of tyre material management. However, products containing rubber granulate usually show much worse properties than primary rubber products. So the use of whole tyres is limited to a small number of applications. Therefore, still the main and cost-effective way of utilization of rubber waste, especially used tyres, is combustion, most often in cement plants [1–10]. However, incineration is, for environmental reasons, limited by the Waste Incineration Directive [11].

Another method of managing used tyres or other rubber waste is their pyrolysis. Pyrolysis is the process of thermal decomposition of organic substances – in the case of rubber of macromolecules of crosslinked rubber – without oxygen or oxidizing substances access. The pyrolysis of tyres produces four products: gas and pyrolytic oil formed by cracking macromolecules and other organic substances, steel from cord and bead wire, and pyrolytic carbon black [1–10, 12, 13].

If tyres are subjected to pyrolysis, the pyrolytic carbon black is produced in amount of about 35 wt %, depending on the parameters of the process. Pyrolytic carbon black

<sup>1)</sup> Institute of Engineering of Polymer Materials and Dyes, Department of Elastomers and Rubber Technology, Harcerska 30, 05-820 Piastów, Poland.  
e-mail: [c.debek@ipgum.pl](mailto:c.debek@ipgum.pl)

is basically a recovered technical carbon black (technical carbon black mixtures), contaminated with minerals (ash, about 15–25 wt %), oil (usually less than 5 wt %), resinous substances and steel particles. The heating value of pyrolytic carbon black is 25–30 MJ/kg, therefore its frequent application is to obtain solid fuel – briquettes or direct combustion in dust furnaces. Pyrolytic carbon black after magnetic refining, grinding, sieving, reduction of volatile and optionally solid impurities as well as normalization of properties can be used in rubber industry as a filler of technical carbon black type, especially for bulk products with lower mechanical requirements. It can also be used as a pigment for dyeing of plastics, concrete or undercoat, as well as a raw material for obtaining sorbents [5, 7–10].

Pyrolytic oil is usually, for economic reasons, considered to be the most important or at least the most easily sellable product on the market. Depending on the type of tyres used for pyrolysis and the parameters of the oil process, it is usually obtained in quantities of about 35–50 wt % [3–6].

Pyrolytic oil obtained, *e.g.*, as a result of periodic, low-temperature pyrolysis of whole car and van tyres is a dark, unclear, thick liquid with a rather intense smell. It consists of 3 wt % of saturated alkanes, 7 wt % of dienes (causing oil instability), 5 wt % of cycloalkanes, 4 wt % of cycloalkenes, 6 wt % of cycloaliphatic-aromatic compounds, 47 wt % of aromatic compounds, 2 wt % of polymeric substances, polluted with carbon black and mineral deposits, and contains significant amounts of total sulfur – over 1 wt %. This disqualifies its direct use as, *e.g.*, motor fuel or heating fuel, both in terms of light and heavy oils [3, 8].

Despite its high sulfur content, limited stability and other unfavorable features, in Poland pyrolytic oil is sometimes used to compose heating fuels due to its significantly lower price. For example, mixing of pyrolytic oil with crude rapeseed oil in the ratio of 1 : 1 reduces the sulfur content to the level which meets the requirements for heavy fuel oils according to the Polish Standard [14], which allows sulfur content up to 1 wt %. Additionally, mixing with rapeseed oil weakens the aromatic character of pyrolytic oil. The advantageous feature is the lack of vanadium, which eliminates the corrosive effect of oil on heating installations. Thus, obtaining standardized heating fuel is simple, however, limited to heavy oil, the combustion of which is possible only in appropriate heating installations [6].

The biggest problem hindering the wider use of pyrolytic oil, *e.g.*, for the composition of light heating oils, is the high total sulfur content of over 1 wt %. By hydrorefination, it is possible to reduce the sulfur content even below 0.1 wt %, *i.e.*, the level permitted by the above mentioned standard [14] for L1 light oil. Hydrorefinate fraction devoid of lighter hydrocarbons lowering the flash point can be used as a component of light heating oils [4].

In addition to the energy application, the possibilities of using pyrolytic oil as plasticizer in rubber materials are also being investigated. It is still a poorly researched direction of pyrolytic oil use, only a few publications contain scarce information about this.

The paper [9] discusses the results of studies on the use of pyrolytic carbon black and pyrolytic oil as recyclable materials for the rubber industry. Compounds based on SBR rubber containing 6 or 12 phr of pyrolytic oil and control P3 type DAE (distillate aromatic extract) oil produced in Poland were prepared. It was found that pyrolytic oil practically does not change the kinetics of vulcanization of compounds in comparison to the control oil, minimally shortens the time of optimal vulcanization, while maintaining the scorch time. It is advantageous because the compounds are equally safe in processing and shortening the time of vulcanization improves the economy of production. Mechanical properties of vulcanizates have been investigated. The results showed that pyrolytic oil has a similar effect to control oil and even slightly better, *e.g.*, the tear strength of a vulcanizate containing pyrolytic oil is significantly better than in the case of P3 oil.

The publication [10] shows the results of the analysis of pyrolytic oil obtained by continuous pyrolysis of tyres on a semi-technical scale, carried out under reduced pressure 10 kPa at 480–520 °C. The oil was divided into four fractions, each of which was characterized and tested in different applications. The light fraction with initial boiling point *ibp* < 204 °C was used as an energetic raw material, the fractions 204/240–450 °C were analyzed as a plasticizers for rubber compound, the fraction with an initial boiling point *ibp* > 350 °C was coked and the residue was used as a road bitumen modifier.

A number of rubber compounds and vulcanizates were prepared. The fraction of pyrolytic oil 204–450 °C was compared with commercial plasticizer Sundex 790. The obtained results showed that the compounds with pyrolytic oil had slightly lower Mooney viscosity, and the time of optimum vulcanization was shorter. Mechanical properties of vulcanizates turned out to be no worse than those of Sundex 790, whereas the fraction of pyrolytic oil boiling in the range 240–450 °C was compared with Dutrex 729. In this system it turned out that the fraction of pyrolytic oil, compared to Sundex 729, prolongs the scorch time and optimum time of vulcanization. Mechanical properties, especially the modulus at 100 % of elongation, indicate that the investigated fraction of pyrolytic oil is a better plasticizer than Dutrex 729. However, the strength properties change in different ways. At a lower content of plasticizer – below 10 phr – the fraction of pyrolytic oil causes a greater decrease in breaking strength than in the case of Dutrex 729. In the case of the addition of 10 phr of plasticizers the effect is similar. On the other hand, in compounds containing more than 10 phr of plasticizer, Dutrex 729 gives a greater increase in elongation at break, which the authors bind to a different hydrocarbon composition of the compared plasticizers. The obtained results indicate that the 240–450 °C fraction of pyrolytic oil is a good plasticizer of rubber compounds, similar to Dutrex 729 oil.

However, these publications do not discuss the problem of polycyclic aromatic hydrocarbons (PAHs) content in pyrolytic oils.

In June 2005 the European Parliament through 27th amendment to Directive 76/769/EEC [15] prohibits from 1 January 2010 the placing on the market and use in the production of new and retreaded tyres certain plasticizers containing PAHs; as long as their content classified as carcinogenic, exceeds a certain level [15, 16].

There are eight carcinogenic PAHs that must meet the new requirements: benzo(a)pyrene (BaP), benzo(e)pyrene (BeP), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(j)fluoranthene (BjF), benzo(k)fluoranthene (BkF), dibenzo(a,h)anthracene (DBahA).

Permitted content of listed PAHs in plasticizers:

- BaP not more than 1 mg/kg of oil,
- the total content of eight PAHs does not exceed 10 mg/kg.

Oils for which dimethyl sulfoxide (DMSO) extract does not exceed 3 % of mass are also considered to meet this condition, provided that the manufacturer or importer confirms with separate tests (every six months, or at changes in the production process) that the limits of BaP and eight PAHs have not been exceeded.

These requirements are met by new petroleum-based plasticizers: TDAE (treated distillate aromatic extract) – modified aromatic extract from a vacuum petroleum distillate (in Poland produced by Lotos Oil: Quantilus T50 and Quantilus 60) and MES (mild extraction solvates) – refine from mild solvent extraction of vacuum petroleum distillate [9, 15–20].

Old type plasticizers – DAE (distillate aromatic extract) – extract obtained from vacuum distillate of crude oil, do not meet current requirements and are no longer available on the market of plasticizers [19].

In recent years the technology of pyrolysis of tyres and other used rubber products has been implemented in Poland in a dozen or so plants. These are small companies, processing 10 to 40 Mg of rubber waste per day. There are also known companies processing polyolefin wastes or other plastics. Most of them produce crude pyrolytic oil, without refining processes. This oil is mainly sold to companies dealing with the blending of heating fuels. After mixing, *e.g.*, with heavy oils, it is burnt in appropriate installations [4, 6, 21].

The material application of heavy fractions of pyrolytic oil may be an alternative path of use of liquid product from pyrolysis of tyres and other rubber scrap, being economically competitive, as the expected prices of oil as a plasticizer are significantly higher than in the case of energy use. Moreover, material recycling is more desirable than energy recovery. The separated light and medium fractions can be used for the composition of industrial solvents and, due to the high sulfur content, in a limited extent to light heating oils [3, 4].

Therefore, the paper presents the results of research on the possibility of using as plasticizers of rubber compounds the fractions of heavy pyrolytic oil obtained in the industrial process of pyrolysis of car tyres. The content of carcinogenic

PAHs in the obtained pyrolytic plasticizers was determined. Compounds and vulcanizates of styrene-butadiene rubber containing the above plasticizers as well as commercial petroleum derivatives' plasticizers were prepared for comparative purposes. The basic properties of compounds and vulcanizates containing pyrolytic plasticizers were investigated and compared to those containing commercial plasticizers.

## EXPERIMENTAL PART

### Materials

The following rubbers and auxiliary raw materials were used: styrene-butadiene rubber (SBR) – KER 1500 (Synthos Rubbers), N330 Orion technical carbon black, *N*-cyclohexyl-1,3-benzothiazolo-2-sulfenamide (CBS), in the form of a granulate containing 80 wt % of accelerator (Konimpex), ground sulfur, oiled 2.5 wt % (Siarkopol), technical stearic acid (Brenntag), zinc oxide grade I (Huta Oława, ZM Silesia S.A.), L-AN 68 (LA68) machine oil, obtained from selectively refined oil distillates from the processing of crude oil (Orlen), TDAE-class Quantilus T50 (QT50) aromatic type plasticizer (Orlen). OS1C plasticizer was obtained from a wide fraction of pyrolytic oil from pyrolysis of a tyre mix carried out on an industrial scale by periodical method as a result of distillation of the fraction with boiling point up to 255 °C (48 wt %), OM1C plasticizer was obtained from heavy fraction of pyrolytic oil from pyrolysis of tyre mix conducted on an industrial scale by periodic method, collected on the first condenser after the reactor, as a result of distillation of fraction with boiling point up to 255 °C (about 1 wt %).

### Rubber compounds

In order to investigate the influence of pyrolytic plasticizers as compared to petroleum-based plasticizers on the properties of rubber compounds and vulcanizates, SBR was selected as a rubber base, whose properties of

**Table 1. Composition of SBR compounds containing plasticizers from tyre pyrolysis and commercial plasticizers derived from crude oil**

Component, phr	Sample			
	SOS1C	SOM1C	SLA68	SQT50
KER 1500	100			
ZnO	3			
Sulfur	1.75			
Stearic acid	1			
CBS 80 %	1.25			
Carbon Black N330	50			
OS1C	8			
OM1C		8		
LA68			8	
QT50				8

compounds and vulcanizates strongly depend on the composition. The formula was based on the one proposed in the standard [22] for testing the carbon black activity in the SBR matrix. Table 1 presents the composition of SBR compounds containing plasticizers from pyrolysis of tyres and commercial plasticizers from crude oil processing.

SBR compounds were made according to ASTM D3191–02 by the Internal Mixer method, using a Banbury type mixer with chamber capacity of 1.2 dm<sup>3</sup> and a rubber mixing mill with cylinder diameter of 300 mm and length of 600 mm.

### Samples of vulcanizates for testing

Samples were vulcanized in laboratory press at 145 °C. Strength test plates of 2 mm thickness were vulcanized during optimum vulcanization time ( $t_{90}$ ) multiplied by a factor of 1.1. Type II dumbbell specimens were cut out of the plates in accordance with ISO 37:98 standard. Corks for determination of abrasion resistance were vulcanized during the time  $t_{90} \cdot 1.3$ .

### Methods of testing

– The content of polycyclic aromatic hydrocarbons was determined according to the own procedure of the “Labgum” Laboratory of the Polymer Materials and Dyes Engineering Institute, based on the ISO/DIS 21461:2005; PN-EN ISO 17993:2005 standard. Determination of PAHs was carried out using high-performance liquid chromatography with fluorescence detection (HPLC-FLD) Agilent 1260 Infinity by Perlan Technologies [20].

– The vulcanization kinetics were surveyed according to PN-ISO 3417:2015-12, by the Monsanto MDR 2000 rheometer. The following parameters were determined:  $t_{s1}$ ,  $t_{s2}$  – times after which the torque increased by 1 and 2 dNm,  $t_{10}$ ,  $t_{50}$  – times after which the torque increased by 10 and 50 %,  $t_{90}$  (optimum vulcanization time) – time after which the torque reaches the following value: minimum + 0.9 · (maximum – minimum);  $ML$  minimum and  $MH$  maximum torque,  $S''ML$ ,  $S''MH$  – viscous components of the minimum and maximum torque,  $\tan \delta ML$ ,  $\tan \delta MH$  – tangent of the shift angle between the viscous component and the elastic modulus of the minimum and maximum torque.

– Mooney viscosity, including relaxation ( $\alpha$ ), was made according to PN-ISO 289-1, determinations were carried out using the Mooney apparatus Monsanto MV 2000.

– The strength properties were tested using a Zwick 1445 tensile tester. Tensile strength ( $TS_b$ ),  $S_{e100}$ ,  $S_{e200}$ ,  $S_{e300}$  modules at 100, 200, 300 % of elongation, elongation at break ( $E_b$ ) were determined according to PN-ISO 37:98. The elongation set after break ( $E_i$ ) was determined by our own method, Zwick 1445. Shore hardness A (ISO 7619-1: 2010), Zwick 7201.

– Abrasion resistance according to Schopper-Scholbach (PN-ISO 4649:2007, met. A) (VEB Thüringer Industriewerk Raunstein).

– The morphology of vulcanizates was studied using SEM (scanning electron microscope) technique, with the following equipment: HITACHI SU8010 equipped with a Cressington Sputter Coater sprayer with a gold layer thickness measurement module. The current accelerating the electron beam was 10 kV. Samples of vulcanizates for measurement were broken after freezing in liquid nitrogen, next they were sprayed with gold.

## RESULTS AND DISCUSSION

### Investigations of PAHs content in pyrolytic plasticizers

Table 2 shows the content of eight carcinogenic PAHs, which in total must not exceed 10 mg/kg and the BaP content must not exceed 1 mg/kg of plasticizer.

OS1C plasticizer obtained from pyrolytic oil meets the requirements of Directive [15] on PAHs content. From a set of eight PAHs, a sample of OS1C was found to contain 0.67 mg/kg BaP, *i.e.*, below the permitted limit of 1 mg/kg. The total PAHs content of the group is 5.34 mg/kg, which is much lower than the permitted 10 mg/kg. The PAHs content in OS1C is similar to the TDAE oil tested at work [18]. This plasticizer can be used in tyres and other rubber products, especially in recycling products (retreading of tyres, anti-vibration liners for the road industry).

OMIC plasticizer obtained from heavy fraction of pyrolytic oil, collected from the first condenser after the exit of gases from the pyrolysis reactor, as shown in the Table 2 contains very large amounts of carcinogenic hydrocarbons, *e.g.*, as much as 880 mg/kg of chrysene. The content of PAHs is many times higher – over nine times higher than in oils of the old type (P0, P3, PG-12), which have already been withdrawn from production.

In its raw form OMIC is therefore not suitable for use as a plasticizer or in other material applications. In the industrial pyrolysis, this fraction is recycled to the process.

### Characteristics of rubber compounds and vulcanizates

Compounds based on SBR rubber with the composition given in Table 1 have been prepared. The results of Mooney viscosity tests with relaxation of rubber compounds containing pyrolytic and petroleum-based plasticizers are presented in Table 3.

The initial Mooney viscosity [ $M(1+0)$ ] of compounds differs by nine Mooney units (MU). The highest viscosity at the moment of switching on the rotor of the measuring device shows the compound plasticized with QT50 aromatic oil and the OS1C fraction of pyrolytic oil. The Mooney viscosity value after 4 minutes [ $M(1+4)$ ] is also the highest for QT50 and the lowest for a compound containing LA68 oil. Compounds containing pyrolytic plasticizers have only a slightly higher value of Mooney viscosity

**Table 2.** PAHs content in OS1C and OM1C pyrolytic plasticizers and commercial plasticizers of the old and new type

PAH content mg/kg	Plasticizer type								
	pyrolytic		naphthenic		aromatic		high aromatic		
	OS1C	OM1C	Nyflex 221 [19]	Nytex 820 [19]	TDAE [18]	Nytex 461 [19]	P0 [19]	P3 [19]	PG-12 [19]
CHR	n.f.	879.60	0.30	0.10	1.20	0.00	31.20	31.20	27.80
BaP	0.67	41.27	0.30	0.00	0.70	0.02	14.10	21.38	9.00
BeP	n.f.	21.35	n.d.	n.d.	0.90	n.d.	n.d.	n.d.	n.d.
BaA	n.f.	n.f.	0.30	0.10	0.40	0.00	3.50	0.00	0.90
BbF	4.67	145.41	0.90	0.20	n.f.	0.00	27.05	68.67	32.60
BkF	n.f.	n.f.	0.90	0.20	n.f.	0.00	27.05	68.67	32.60
BjF	n.f.	87.43	n.d.	n.d.	1.20	n.d.	n.d.	n.d.	n.d.
DBahA	n.f.	n.f.	0.60	0.00	0.10	0.00	4.70	2.70	2.87
Total PAH content	5.34	1175.06	2.40	0.40	4.50	0.02	80.55	123.95	73.17

n.f. – not found, n.d. – not determined.

**Table 3.** Results of Mooney viscosity tests at 100 °C

Parameter	Sample			
	SOS1C	SOMIC	SLA68	SQT50
$M(1+0)$ , MU	88.1	83.4	83.4	92.4
$M(1+4)$ , MU	51.5	52.4	50.5	55.1
$\alpha$ , lgM/lgK	-0.3689	-0.4224	-0.4053	-0.3792
$K$ , MU	21.5	21.0	21.3	22.9

**Table 4.** Results of studies on vulcanization of rubber compounds (145 °C)

Parameter	Sample			
	SOS1C	SOMIC	SLA68	SQT50
$t_{S_1}$ , min	10.42	9.90	12.53	12.45
$t_{S_2}$ , min	11.92	11.80	15.20	15.13
$t_{10'}$ , min	11.37	11.44	14.36	14.53
$t_{50'}$ , min	16.41	16.52	20.55	20.76
$t_{90'}$ , min	27.23	28.13	33.62	33.39
$ML$ , dNm	2.03	1.95	1.89	2.03
$MH$ , dNm	16.97	18.89	17.44	18.63
$\Delta M$ , dNm	14.94	16.94	15.55	16.60
$S''ML$ , dNm	1.43	1.41	1.32	1.43
$S''MH$ , dNm	1.81	1.46	1.19	1.44
$\tan \delta ML$	0.705	0.724	0.699	0.705
$\tan \delta MH$	0.107	0.077	0.068	0.077

$M(1+4)$  than the compound containing LA68 plasticizer. The absolute value of the relaxation rate  $\alpha$  of the compound for SQT50, like SOS1C, is lower than the others, which means that these compounds relax the stress more slowly after stopping the rotor than the others, so they are more flexible. SOMIC and SLA68 compounds show a little more plasticity. It should be assumed that the plasticizers better plasticize the rubber matrix. When comparing the Mooney viscosity parameter of the initial and final viscosity and relaxation rate, QT50 oil at least plasticizes the SBR compound, then OS1C. OM1C, on the other hand, most plasticizes the tested compound. However, the differences are not particularly high, especially for the final Mooney viscosity.

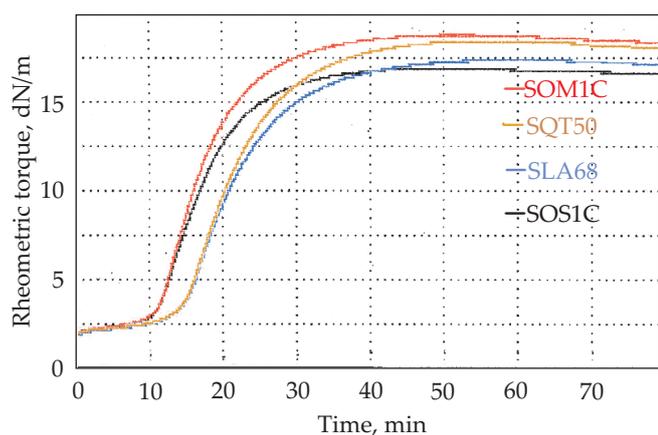
The results of studies on the kinetics of vulcanization of rubber compounds containing pyrolytic and petroleum-based plasticizers are presented in Table 4.

The addition of pyrolytic plasticizers shorten  $t_{90}$  time. It results from the presence of sulfur compounds in these oils, which can act as catalyst for vulcanization of rubber compounds, hence it is possible to reduce the addition of expensive accelerators used in rubber compound vulcanization systems. At the same time, pyrolytic plasticizers do not cause any significant changes to increase in the rheometric torque ( $\Delta M$ ) indicating on the degree of crosslinking of compounds. Only the compound with plasticizer OS1C slightly deviates from this value,  $\Delta M$  is lower. It correlates with the value of  $\Delta M$  with the highest value of the tangent of loss angle  $\delta$  at the moment of reaching the maximum moment ( $\tan \delta MH$ ). Both parameters indicate a slightly smaller degree of crosslinking of the SOS1C compound.

Figure 1 shows the vulcanization curves of rubber mixtures containing pyrolytic and petroleum plasticizers.

**Table 5.** Hardness and strength properties of compounds containing pyrolytic and petroleum-based plasticizers

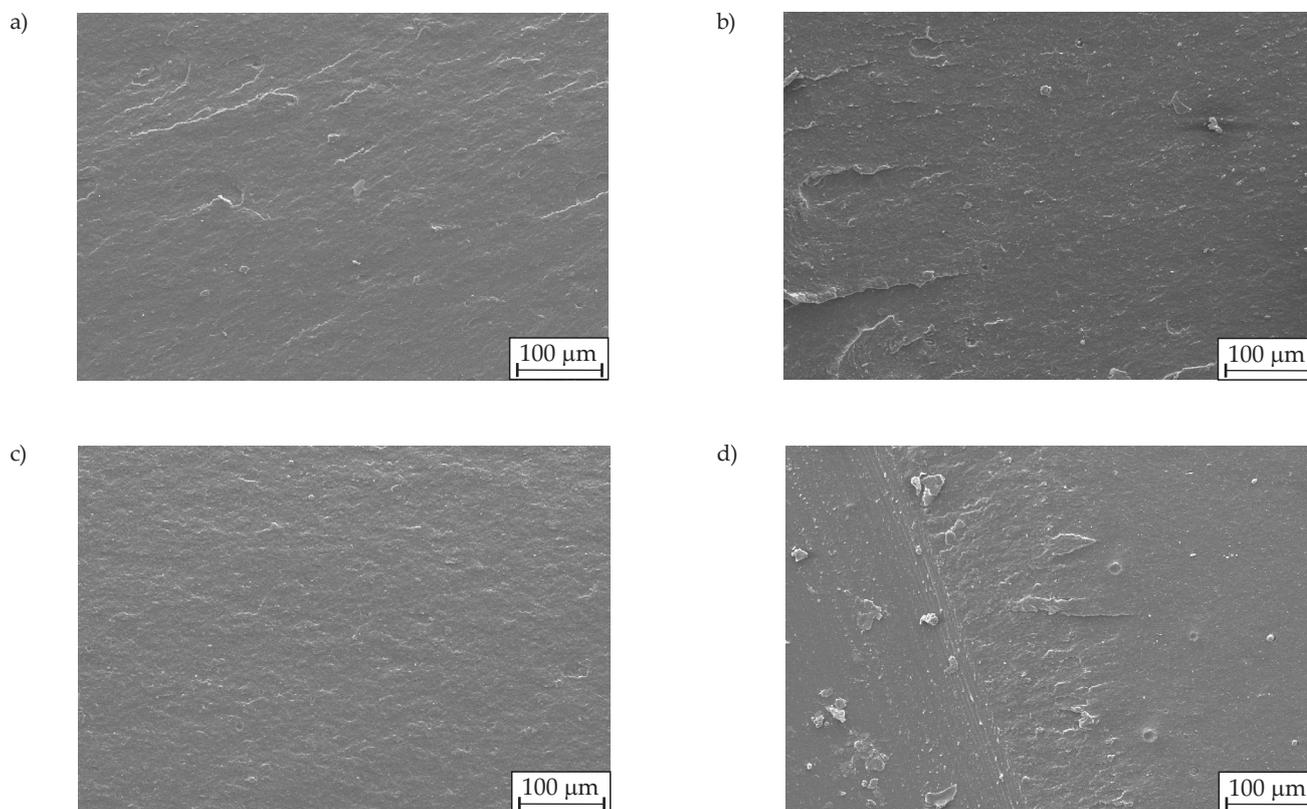
Parameter	Sample			
	SOS1C	SOMIC	SLA68	SQT50
Hardness A, °ShA	59	61	61	60
$TS_b$ , MPa	26.1	24.7	26.2	17.0
$E_b$ , %	457	461	408	300
$S_{e100}$ , MPa	2.4	2.4	2.8	2.8
$S_{e200}$ , MPa	7.3	7.3	9.2	8.9
$S_{e300}$ , MPa	13.8	14.2	17.9	16.2
$E_b$ , %	10	10	10	10
Abrasion resistance, mm <sup>3</sup>	133.1	128.5	129.0	130.4

**Fig. 1.** Curing curves of rubber compounds containing pyrolytic and petroleum-based plasticizers

Compounds containing pyrolytic plasticizers, as mentioned, show an optimum vulcanization time shorter by about 16 % than compounds with commercial plasticizers. The shape of the curves is almost identical, characteristic for the group of sulfenamide vulcanization accelerators.

The results of investigations of mechanical properties of vulcanizates containing pyrolytic and petroleum derived plasticizers are presented in Table 5.

Pyrolytic plasticizers have very good mechanical properties to SBR vulcanizates, significantly better than QT50 aromatic oil. The tensile strength of a SOS1C sample with pyrolytic plasticizer is 26 MPa and is equal to the SLA68 sample and much higher than that of a vulcanizate containing QT50 plasticizer, which is only 17 MPa.  $TS_b$  of SOM1C vulcanizate is also very good at 25 MPa. Both pyrolytic plasticizers increase the elonga-

**Fig. 2.** SEM photos of cracked cross-sections of vulcanizates containing pyrolytic and petroleum-based plasticizers: a) SOS1C, b) SOM1C, c) SLA68, d) SQT50

tion at break, which correlates with a lower  $S_{e100}$  value, *i.e.*, a higher degree of softening of the vulcanizate than is observed for vulcanizates containing petroleum-based plasticizers (higher value of the  $S_{e100}$  modulus).

The abrasion resistance of all vulcanizates is good and practically equal, about 130 mm<sup>3</sup>.

One of the problems with the use of crude pyrolytic oil is its intense smell. In the case of both heavy fractions OS1C and OM1C the smell did not turn out to be a significant problem. In compounds and vulcanizates it did not differ from the smell of petroleum plasticizers, *e.g.*, QT50.

The morphology of obtained vulcanizates containing pyrolytic and petroleum derived plasticizers is presented in Fig. 2.

Pyrolytic plasticizers do not change the morphology of vulcanizates. In all cracked cross-sections of the samples a uniform dispersion and size of N330 technical carbon black particles is observed.

## CONCLUSIONS

OS1C plasticizer obtained from pyrolytic oil by distilling out from crude oil the fraction with boiling point up to 255 °C meets the PAHs limit values set by the Directive [15]. The BaP content is 0.67 mg/kg, so it does not exceed the limit of 1 mg/kg and the sum of eight hydrocarbons is 5.34 mg/kg, well below the limit of 10 mg/kg.

Pyrolytic plasticizer – OM1C obtained from the heavy fraction of pyrolysis oil collected on the first condenser after the gas outlet from the pyrolysis reactor, contains very high amounts of carcinogenic hydrocarbons. In its raw form, it is therefore not suitable for use as a plasticizer or in other material applications. In pyrolysis this oil fraction is normally returned to the process, which is basically a good solution. However, it is possible to selectively extract PAHs and obtain a valuable plasticizer for material applications.

According to Mooney viscosity tests, pyrolytic plasticizers better plasticize the SBR compound than reference plasticizers of petroleum origin. The studied group of plasticizers shows that OM1C plastifies best and the least is QT50 aromatic petroleum-based plasticizer.

Pyrolytic plasticizers shortened the optimal vulcanization time of SBR compounds. It results from the presence of sulfur compounds in these oils, which can act as catalyst in rubber compounds, so it is possible to reduce the addition of expensive accelerators of vulcanization introduced into rubber compounds.

Pyrolytic plasticizers of SBR vulcanizates have very good mechanical properties, significantly better than QT50 plasticizer. The tensile strength of samples containing pyrolytic plasticizers is 25–26 MPa and is much higher than that of vulcanizate containing QT50 plasticizer, which is only 17 MPa. Pyrolytic plasticizers increase the elongation at break, which correlates with a lower modulus of 100 % elongation, *i.e.*, a higher degree of softening of the vulcanizate than is observed in the case of vulcani-

zates containing petroleum-based plasticizers. The abrasion resistance of all vulcanizates is good and practically equal about 130 mm<sup>3</sup>.

One of the common problems with the use of crude pyrolytic oil is its intense smell. But in the case of OS1C and OM1C the smell did not turn out to be a problem. In compounds and vulcanizates it did not differ from the smell of petroleum plasticizers, *e.g.*, QT50.

As shown by SEM studies, pyrolytic plasticizers do not change the morphology of vulcanizates. In all cracked cross-sections of the samples a uniform dispersion and particle size of N330 carbon black is observed.

To sum up, it should be noted that according to the conducted studies and few revealed literature data [9, 10], it is possible to use some heavy fractions of oil from pyrolysis of tyres as recyclable materials – plasticizers of rubber compounds.

*Scientific work financed from funds for the statutory activity of the Department of Elastomers and Rubber Technology of the Institute for Engineering of Polymer Materials and Dyes.*

## REFERENCES

- [1] Williams P.T.: *Waste Management* **2013**, 33, 1714. <http://dx.doi.org/10.1016/j.wasman.2013.05.003>
- [2] Martinez J.D., Puy N., Murillo R. *et al.*: *Renewable and Sustainable Energy Review* **2013**, 23, 179. <http://dx.doi.org/10.1016/j.rser.2013.02.038>
- [3] Dębek C., Walendziewski J.: *Fuel* **2015**, 159, 659. <http://dx.doi.org/10.1016/j.fuel.2015.07.024>
- [4] Dębek C.: *Materials* **2019**, 12 (6), 880. <https://doi.org/10.3390/ma12060880>
- [5] Ostaszewska U., Dębek C., Magryta J.: “Pyrolysis of used rubber products as a source of carbon secondary raw material” (in Polish), Institute for Engineering of Polymer Materials and Dyes, Toruń 2014, pp. 7–29.
- [6] Dębek C., Magryta J., Sobczak M. *et al.*: *Przemysł Chemiczny* **2010**, 89, 242.
- [7] Dębek C.: *Elastomery* **2018**, 22, 281.
- [8] Dębek C., Stępkowski R., Magryta J. *et al.*: *Elastomery* **2009**, 13, 24.
- [9] Magryta J., Dębek C., Stępkowski R. *et al.*: *Elastomery* **2009**, 13, 21.
- [10] Roy C., Chaala A., Darmstadt H.: *Journal of Analytical and Applied Pyrolysis* **1999**, 51, 201. [http://doi.org/10.1016/S0165-2370\(99\)00017-0](http://doi.org/10.1016/S0165-2370(99)00017-0)
- [11] Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste, Official Journal L 332, 28/12/2000, pp. 0091–0111.
- [12] Quek A., Balasubramanian R.: *Journal of Analytical and Applied Pyrolysis* **2013**, 101, 1. <http://dx.doi.org/10.1016/j.jaap.2013.02.016>
- [13] Aydın H., İlkılıç C.: *Fuel* **2012**, 102, 605. <https://doi.org/10.1016/j.fuel.2012.06.067>
- [14] PN-C-96024:2011 “Petroleum products – Fuel oils”.

- [15] Directive 2005/69/EC of the European Parliament and of the Council of 16 November 2005 amending for the twenty-seventh time Council Directive 76/769/EEC of 27 July 1976.
- [16] Parasiewicz W., Pyskło L.: *Elastomery* **2005**, 9, 25.
- [17] Ptak S.: *Nafta-Gaz* **2017**, 73, 675. <http://doi.org/10.18668/NG.2017.09.07>
- [18] Ptak S., Antosz A., Jakóbiec J.: *Nafta-Gaz* **2018**, 74, 49. <http://doi.org/10.18668/NG.2018.01.06>
- [19] Dębek C., Stępkowski R.: “Ingredients of rubber compounds (vulcanizates), vulcanization, unpublished training materials” (in Polish), Department of Elastomers and Rubber Technology in Piastów Institute of Engineering of Polymer Materials and Dyes, Toruń 21.07.2010.
- [20] Stępkowska A., Parys T., Kleps T.: *Elastomery* **2013**, 17, 19.
- [21] Łuksa A., Sobczak M., Goś M.: *Przemysł Chemiczny* **2008**, 87, 715.
- [22] ASTM D3191-02 “Standard Test Methods for Carbon Black in SBR (Styrene-Butadiene-Rubber)-Recipe and Evaluation Procedures”.

Received 5 II 2019.