Influence of Process Oils on the Mechanical Properties of Elastomers

Plasticisers (also called softener, extender or process oils) are additives for polymers with a low molecular weight. It is well known that by using a plasticiser, the properties of a polymeric melt or of an uncured rubber mixture and therefore also the properties of the resulting polymeric and elastomeric materials respectively can be strongly influenced. Usually, an increasing content of a plasticiser leads to a decrease in the viscosity of the rubber mixture, and therefore, its processability will be improved. In some cases, such as very high amounts of active fillers, processing is impossible without a plasticiser due to the high viscosity of the mixture. With the addition of a plasticiser to a polymeric matrix, the cohesive forces between the polymer chains are lowered and the chain mobility is increased. Therefore, the properties of the vulcanizate, for example hardness, deformability, strength and flexibility at low temperatures can be enhanced. Plasticisers for EPDM and TPE exhibit a low content of aromatic structures and a low or medium content of sulphur [3-9].

Within the literature, some publications exist [10-14] dealing with results of systematic investigations regarding the influence of plasticiser on the rheological and/or the mechanical properties of elastomers or thermoplastic elastomers (TPE). Ibarra et al. [10] investigated ethylene-propylene-diene (EPDM) elastomers, which contained different process oils. The carbon distribution was varied and for example also the density of the oils and their kinematic viscosity were different. It was found that the Mooney viscosity of the rubber was lowered by adding the process oil, but there was not always a connection between the oil viscosity and the Mooney viscosity. Dikland et al.

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[11] performed comprehensive experiments to describe the influence of process oils on the effectiveness of the crosslinking behaviour of EPDM. The crosslinking agent was peroxide. As a result it was found that the crosslinking reaction was disturbed when certain process oils are used. Here, the content of aromatic carbon plays an important role, because the radicals of the peroxide react not only with the EPDM chains, but also with components of the process oil due to their structural similarity. As a result, the crosslink density is reduced. Because there is a direct connection with the crosslink density, also the level of the mechanical properties is strongly influenced by the content of aromatic carbon of the used process oil. A linear decrease in the crosslink density with an increasing content of the aromatic components of the oil could be observed. Furthermore, the authors found that the kinematic viscosity of the oil at 100 °C correlates with the Mooney viscosity of the rubber mixture. However, no functional connections between oils properties and rheological or mechanical properties of the rubber mixture and the vulcanizate respectively could be found.

The dispersion of the filler particles or aggregates, respectively, in a rubber matrix depends on the interactions between both components and determines the resulting properties of the vulcanizate. When process oil is used together with filler, as it is the case for most of the technical rubber mixtures, additional interactions take place having also an influence on the resulting material properties. Here, the characteristics of the filler such as particle size, particle size distribution, size and volume of pores or the particle surface are decisive factors for the adsorption of the plasticiser’s molecules at the filler [5,12]. Furthermore, physical and chemical interactions between filler and plasticisers influence the wetting of the particle surface by the plasticiser.

For the production of compounds on the basis of thermoplastic elastomers (TPE), usually widely refined paraffinic process oils are used as plasticisers. Here, a higher content of aromatic structures of the process oil could influence the crystalline phase and therefore, the mechanical stability of the compounds can be reduced. TPE materials on the basis of SBS with different process oils were investigated by El Sheemy [14]. Here, naphthenic and paraffinic process oils with different density and kinematic viscosity were used. The naphthenic oil was found to be more compatible to the TPE matrix. This resulted in a higher level of the mechanical properties. TPE materials on the basis of SEBS block copolymers and polyolefins have a good compatibility to paraffinic process oils. Due to the low polarity, the oil may be located in such materials in both phases (crystalline and rubber-phase) [15,16]. However, in [16] it was stated that the process oil was concentrated within the soft phase of the material, this means the elastomeric phase.

### Experimental

**Materials**

Two series of ethylene-propylene-diene (EPDM) vulcanizates and one series of thermoplastic elastomers (TPE) on the basis of styrene-ethylene-butylene-styrene copolymer (SEBS) were investigated. The EPDM materials were provided by Lanxess Deutschland GmbH (EPDM) and the TPE materials by KRAIBURG TPE GmbH & Co. KG. One of the EPDM series “black” was reinforced with carbon black N 550 and crosslinked with a sulphur-accelerator system. The second EPDM series “bright” was filled with a combination of titanium dioxide and kaolin and crosslinked with peroxide. Each of the mixture was extended with 50 phr of 6 different process oils. Further details on the composition of the materials and the process oils can be found in the Tables 1-4. The production of the EPDM materials was realized by a two-step mixing process. During the first step, the basic mixture was produced, in a second step, the crosslinking agents were added. The vulcanization time was 12 min at 180 °C for the series EPDM “bright” as well as 15 min at 160 °C for the carbon-black filled EPDM. The processing of the TPE materials was carried out by using a synchronous double screw extruder with a temperature profile between 150 and 180 °C.

All of the used process oils are commercially available products of the company Shell Deutschland Oil GmbH, Hamburg and can be divided into paraffinic hydrocracked (Catenex T, Ondina), paraffinic solvent-extracted (Catenex S), and naphthenic types (Edex). The oils of the Ondina group are medicinal white oils and meet rigorous pharmaceutical demands [17, 18]. All these process oils are on the same viscosity level to eliminate viscosity effects.

### Composition of the series EPDM “bright”

<table>
<thead>
<tr>
<th>Composition of the series EPDM “bright”</th>
<th>Content (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene-propylene-diene polymer BUNA EP G 5450®</td>
<td>100</td>
</tr>
<tr>
<td>Titanium dioxide TRONOX R-U-5®</td>
<td>10</td>
</tr>
<tr>
<td>Kaolin POLESTAR 200 R®</td>
<td>100</td>
</tr>
<tr>
<td>Processing aid</td>
<td>2</td>
</tr>
<tr>
<td>Process oil</td>
<td>50</td>
</tr>
<tr>
<td>Peroxide DPD® (Trigonox 101-45®)</td>
<td>7</td>
</tr>
<tr>
<td>Co-agent TAIC**</td>
<td>2</td>
</tr>
<tr>
<td>Silane</td>
<td>2</td>
</tr>
</tbody>
</table>

* 2,5-Dimethyl-2,5-bis(tert-butylperoxy)hexane
** 1,3,5-Triprop-2-Enyl-1,3,5-Triazinan-2,4,6-Trien

### Composition of the series EPDM “black”

<table>
<thead>
<tr>
<th>Composition of the series EPDM “black”</th>
<th>Content (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene-propylene-diene polymer BUNA EP G 6850®</td>
<td>100</td>
</tr>
<tr>
<td>Carbon black CORAX N 550/30®</td>
<td>80</td>
</tr>
<tr>
<td>Processing aid</td>
<td>1</td>
</tr>
<tr>
<td>Process oil</td>
<td>50</td>
</tr>
<tr>
<td>Mercapto accelerator</td>
<td>0.50</td>
</tr>
<tr>
<td>Thiuram accelerator</td>
<td>1</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1.50</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5</td>
</tr>
</tbody>
</table>

### Composition of the TPE materials

<table>
<thead>
<tr>
<th>Composition of the TPE materials</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEBS</td>
<td>23</td>
</tr>
<tr>
<td>CaCO₃ (calcium carbonate)</td>
<td>28</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>6</td>
</tr>
<tr>
<td>Process oil</td>
<td>41</td>
</tr>
<tr>
<td>Stabilizer</td>
<td>2</td>
</tr>
</tbody>
</table>
**Methods**

The characterization of the processing properties was done by measurements of the Mooney viscosity by using a shearing-disc viscosimeter according to DIN 53523 [19]. As the result of the experiments, the value Mooney viscosity ML (1+4) 100 was determined. This value corresponds to the viscosity of the compound at 100 °C after 1 min preheating and 4 min testing time.

The vulcanization behaviour was investigated by vulcametry according to DIN 53529 [20]. For these experiments, a moving-misch rheometer (MDR) was used. The temperature for the characterization of the crosslinking behaviour of the series EPDM „bright” was set to 180 °C, for EPDM „black” it was 160 °C. The measuring time was 20 min and 30 min, respectively. The values of the vulcanization time t_m and t_p as well as the difference of maximum and minimum torque M_max - M_min, as a quantitative measure of the relative degree of crosslinking were determined.

The resulting vulcanize properties were quantitatively characterized by using different tests, for which following some details will be given. For the characterization of the time-dependent material behaviour, the vulcanizates were investigated by dynamic-mechanical analysis (DMA) in tensile mode according to DIN EN ISO 6721 [21] by using the testing machine Qualimeter Eplexor 500N (Company Gabo GmbH). The dimensions of the strip specimens were length L = 50 mm, width W = 10 mm and thickness B = 2 mm. The measurements were performed in a temperature range between -100 °C and 150 °C with a heating rate of 1 K/min and a frequency of 10 Hz.

The determination of the hardness values Shore A and IRHD-micro (short IRHD-m) of the materials was performed according to DIN 53505 [22] and DIN ISO 48 [23], respectively. IRHD means “International Rubber Hardness Degree”. For the Shore-A measurements, the Zwick Shore tester 3150 was used and for the IRHD-m tests the Zwick 3105 digital test. Ten single measurements were the basis of each reported hardness value. For the Shore-A tests, 6 mm thick samples were used, while the IRHD-micro values were determined by using 2 mm thick samples.

The tensile tests were performed according DIN 53504 [24] by using the universal testing machine Z020 (company Zwick). For each material, 3 dumbbell specimens of the 5.2 type were used. The test speed was 200 mm/min, the initial gauge length was 48 mm. As a result of the tests, the tensile strength and strain at break (σ_b and ε_b), respectively were determined from the recorded stress-strain curves.

A further quasi-static test method, which was applied, is the tear test. Generally, with such tests, the tear resistance of an elastomeric material can be characterized, which is a measure of the sensitivity of an elastomeric material to the tearing of cuts. The reported experimental results were obtained during tests with the universal testing machine Zwicki (Zwick Company) according to DIN ISO 34-1 [25], respectively. For each material, 5 specimens were used. The specimen geometry corresponded to the trouser geometry with a thickness of 2 mm. The test speed was 100 mm/min. As a result of the tests the tear resistance T_s was determined.

A simple technological method for the assessment of the viscoelastic behaviour of an elastomeric material, especially for gaskets, is the determination of the compression set. In principle, the compression set is the remaining deformation of a sample after unloading from the compressed state. According to the present standard DIN ISO 815 [26], the degree of compression must be selected in dependence on the hardness of the materials. Furthermore, the loading time and temperature can be specified in a wide range. For the tests reported here, the deformation of the samples was 25 % of their thickness. The deformed samples were stored for a time of 24 h at 23 °C (room temperature) as well as at 40, 50, 60 and 70 °C.

The elastic and the damping behaviour of the materials, respectively, was assessed in a simple and fast way by determining the technological parameter rebound resilience R according to the DIN 53512 [27]. The rebound resilience defined as the ratio between the recovered and the raised energy and can be calculated on the basis of the rebound and falling angle, respectively which can be experimentally determined by using a so-called Schob pendulum device. The circular samples had a thickness of 12 mm and the experiments were performed at room temperature. Per material 3 individual measurements were done and the mean value was determined.

Complementary, fracture mechanics investigations were performed. The aim was the
characterization of the fracture behaviour of the materials depending on the oil type. For this purpose, the materials’ resistance against unstable crack propagation \( J_d \) was determined on the basis of load-extension diagrams (F-I diagrams) from instrumented tensile-impact tests. These tests were performed according to the now certified testing procedure “Testing of Plastics – Instrumented Tensile-Impact Test” [28] with double-edge notched tensile specimens (DENT). The dimensions of these specimens were \( W = 10 \text{ mm}, L = 64 \text{ mm} B = 2 \text{ mm} \). Further details on this method of experimental fracture mechanics can be found in [29, 30]. The tests were performed by using the pendulum device Resil Impactor Junior 25 from the company Ceast. A pendulum hammer with a maximum working capacity of 7.5 J was used and the falling angle was 150° corresponding to a test speed of 3.7 m/s. The initial gauge length was 30 mm. For each material, 10 specimens were tested. As a result of the tests, the crack toughness \( J_d \) was calculated. Beside these mechanical tests, two simple aging tests were performed to get a first idea of the ageing behaviour in dependence on the oil characteristics. At first, the EPDM and TPE materials with Ondina 941 and Edelex 946 were selected and exposed to a UV irradiation with an Osram Ultra-Vitalux bulb over a period of 40 days. The climate conditions were kept constantly at 23 °C and 50% air humidity. For the tests, the climatic test cabinet VC 7018 (company Vötsch) was used. Furthermore, a heat-ageing test with the EPDM materials was performed. Specimens of all EPDM materials were stored in a heating cabinet for 7 days. Here, two temperatures (125° and 150 °C) were realized. After the irradiation and the heat ageing, tensile tests and Shore-A hardness measurements were performed. The test conditions were described above.

Results and discussion

The results of selected experiments are summarized within the tables 5 - 7. As can be seen, the Mooney viscosity \( ML(1+4) \) 100 of the two EPDM series is influenced by the oil type. With increasing aromatic content, an increase in the viscosity could be found. Similar results were reported in [13]. The reason for the different viscosity level of two EPDM series is the different character-istics of the fillers. While the used carbon black N 550 is a medium-active filler that influences the structure-viscous properties of the rubber mixture, the fillers of the series EPDM “bright” are of a non-active type and do not have a noteworthy influence on the viscosity [2, 31]. The values of the vulcanization time \( t_{50} \) and \( t_{90} \) (see Table 5 and 6) show that there is only a little influence of the oil type in the case of the sulphur-crosslinked carbon-black filled materials. An exception is the mixture with the paraffinic oil Catenex 5946, which possesses a shorter vulcanization time. In contrast, the crosslinking process of the series EPDM “bright” takes longer, if the content of the aromatic carbon of the oil increases. The different kinetics of the crosslinking re-action results in different crosslink densities depending on the oil type, especially for the series EPDM “bright”. As can be seen in Figure 1, an increasing aromatic content of the used process oil leads to a strongly decreasing difference of the maximum and minimum torque as a quantitative measure of the crosslink density of the bright EPDM materials. This effect is due to the reaction of the peroxide radicals with the aromatic components of the oil and was described
also in [11]. As a consequence, the content of a peroxide crosslink agent must be increased, when process oil with aromatic components is used and a constant crosslink density should be realized. For the carbon-black filled series, the crosslink density seems to increases slightly with the aromatic content.

Because the crosslink density is one of the most important parameters determining the macroscopic properties of the vulcanizates, partly large differences of the material parameters depending on the oil type were found. In the Tables 5 and 6, the tensile strength at break \( \sigma_T \), tensile strain at break \( \varepsilon_T \), the hardness values Shore A and IRHD-micro, the rebound resilience \( R \) as well as the tear strength \( T_S \) of the EPDM materials are given. Furthermore, the glass-transition temperatures determined from the DMA experiments are shown, which are mainly independent of the used process oil type.

Due to the reduced crosslink density of series EPDM “bright”, that results when the aromatic content of the oil is enlarged, the tensile strength at break \( \sigma_T \) is lowered by ca. 1 MPa that means more than 20%. At the same time, the deformability of these materials is increased. This connection between strength and crosslink density is well-known and can be traced back to the well-known and can be traced back to the aromatic-carbon content.

In general, the storage modulus \( E' \) for the TPE materials as a function of the content of aromatic carbon the compression set increases. This means, the ability to recover the original form after a long-term mechanical and/or thermal loading is deteriorated. This is an important aspect for the use of a material as a gasket for example. For EPDM “bright”, the compression set from the 70 °C storage is somewhat higher up to a value of 4% aromatic carbon compared to the room-temperature measurement. The oil Edelex 946 with the highest aromatic carbon leads to a much larger compression set at 70 °C compared to room temperature. For the series EPDM “black” (Fig: 2b), the absolute values of the compression set are relatively low and nearly independent of the used oil type, also after the storage at 70 °C. This means, these materials own relatively good elastic properties. However, the use of the peroxide leads to crosslinks, which are thermally more resistant than the sulphur-based crosslinks [2]. For this reason, the increasing storage temperature influences the compression set much more in the case of the series EPDM “black”. Due to their thermoplastic nature, the compression set of the TPE materials is strongly influenced by an increasing storage temperature as it is shown in Figure 3, where the values of the compression set are shown as a function of the temperature for the different oil types. The compression set increases, if the storage takes place at higher temperatures. Especially the elastic recovery behaviour of the material with the oil Edelex 946 with the highest content of aromatic carbon is deteriorated in comparison to the other oil types. Apart from that, no large influence of the carbon distribution of the oil on the compression set could be found at temperatures up to 60 °C. The Figure 4 shows results of the dynamic–mechanical analysis. In general, the storage modulus \( E' \) for the two EPDM series shows a typical behaviour.
When the glass transition area is reached, $E'$ decreases strongly and the entropy-elastic area is reached. Here, the storage modulus is small in comparison to the energy-elastic range. For the series EPDM "bright" (Fig. 4a), an influence of the used process oil could be detected above a temperature of ca. 40 °C. Additionally, in contrast to the results of EPDM "black" (Fig. 4b), a constant decrease in $E'$ above the glass-transition area was found, which is larger with increasing content of aromatic carbon. This means, the material behaviour is completely different, when a sharp notch exists. Furthermore, it can be stated that the carbon distribution of the oil has a different influence on the strength and crack toughness behaviour. In contrast to the series EPDM "bright", the toughness values of the series EPDM "black" are influenced by the oil type only a little. One can assume a small maximum value of the materials with a medium content of aromatic carbon.

It should be mentioned that the deformation behaviour of the two EPDM series is different, although the crack toughness values are on a comparable level. While EPDM "bright" materials show a relatively large deformation until an unstable crack occurs together with a small load, the EPDM "black" materials are characterized by larger maximum loads together with small deformation. Such a reinforcement effect in an elastomer filled with an active carbon black arises from the interactions between polymer chains and filler particles [2,32]. From the maximum of the $J_d$ values, it can be derived that within the series EPDM "black" an influence of the process oil must exist resulting from the different effect of the oil on the filler-filler and polymer-filler interactions. However, only further experiments may deliver further details. For example, DMA investigations with variation of the strain amplitude were found to be very sensitive to changes of the filler network [13]. The toughness of the TPE materials (Fig. 5b) increases with the content of aromatic carbon of the used process oil. An exception is the material with the oil Catenex T 145, which does not contain aromatic carbon, but has a much higher toughness than the material with Ondina 941. The highest resistance against unstable crack propagation was found for the TPE with the process oil Edelex 946 with the highest content of aromatic and naphthenic carbon. As one reason for this finding, the better compatibility of the oil with the matrix can be assumed, as it was reported in [14] for naphthenic oils.

At last, the results of the ageing tests are presented. The Tables 8 and 9 summarize the percentage changes of some selected material parameters after the UV radiation and the heat ageing, respectively. It was found that the UV irradiation leads to a discolouration of the bright materials. If the oil Edelex 946 is used, this effect is much more pronounced in both bright materials (TPE and EPDM) compared to the materials with Ondina 941. However, only in the case of the bright EPDM materials, also the material properties are strongly influenced by the UV irradiation (see Table 8). In [33], the assumption was made that the existence of oxidation products of the peroxidic crosslinking reaction is the reason for the small UV resistance. In comparison to EPDM "bright", the property changes of the series
The heat ageing also led to partly drastic changes of the material properties. The effect of the different process oils was partly different in both EPDM series. In general, the hardness of the elastomers was increased due to the heat influence, but only for the materials EPDM “bright” larger differences of the Shore A values were found depending on the oil type, especially at 150 °C ageing temperature. Furthermore, the deformability of the materials was decreased, especially for the series EPDM “black”. However, only for the series EPDM “bright”, an influence of the oil type could be detected. Here, the aromatic oil Edilex 946 led to the strongest decrease in $\Delta \sigma_2$ and the white oils Catenex T 145 and Ondina 941 without any aromatic parts showed a comparably small decrease in tensile strain at break. Together with the decreased deformability, an increase in the tensile strength at break $\sigma_2$, occurred for the series EPDM “bright” depending also on the oil type. Again, the addition of the oil Edilex 946 resulted in the strongest change. In contrast to this behaviour of EPDM “bright”, the tensile strength at break of the materials series EPDM “black” was reduced with the exception of the materials with Catenex S 541 and Edilex 946 having the highest contents of aromatic carbon. According to [34] the thermal-oxidative ageing is a very complex, multi-stage process, where different, partly competing chemical reactions can take place leading to a further crosslinking or to the opposite: chain degradation. It is assumed that during the ageing of the EPDM materials both effects, crosslinking and chain degradation may have an opposite influence on the macroscopic material behaviour and must be considered for the discussion of the test results. Furthermore, the volatility of the used process oil shall also not be neglected in this context, as naphthenic oils show higher evaporation losses compared to paraffinic oils of the same viscosity.

## Conclusion

In conclusion it should be stated that polymer/filler/process oil compounds are very complex systems, which have to be quantitatively described with well-selected material parameters. The results show the different sensitivity of the various material parameters concerning the oil influence.

The vulcanize properties are partly influenced by the content of aromatic carbon of the used process oil, especially for the series EPDM “bright” (peroxide linking). However, it is assumed that in some cases different effects interfere, which are due to the interaction of filler and oil or polymer and oil. Because of the large number of influencing variables, a detailed discussion is nearly impossible, but main effects are compensated in reality by formulation adoption. Some material parameters are sensitive to structural changes through the used process oil and some are not. It was found that the influence of the process oil depends on the polymer type, crosslinking system and the filler type. Additionally, the interactions of the single components of the rubber mixture are a further aspect, which has to be taken into account.

## Acknowledgements

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## References