Sealing compatibility of ester base oils

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Introduction

When using ester base oils, the product developers focus initially on application parameters such as viscosity, viscosity index, oxidation stability and pour point. But other parameters are not less important. This also includes the seal compatibility.

In the past, sealing materials like elastomers were optimised for the contact with mineral oils. These days, synthetic esters gain importance and are more often used. As there are fundamental differences between mineral and synthetic based esters the used sealing materials are not always compatible with the new base oils. For example, elastomers – especially those with higher polarity – tend to swell more when exposed to a synthetic ester while mineral oils only lead to slight swelling or even shrinking.

But even if we just keep an eye on synthetic esters, the different ester types show considerable differences in elastomer compatibility. They are mainly caused by differences in structure and physical characteristics as well as chemical parameters of the esters.

Knowledge on how different types of synthetic esters can impact elastomers is crucial for lubricant developers. It makes it possible to assess the potential influence on sealing materials during the first selection of suitable products.

Elastomers and their Characteristics

At the beginning of the last century, leaks and high levels of wear and tear, for example on bearings, were common in machine and vehicle construction. Felt or leather were often used as sealing materials. The next milestone was the shaft seal developed by Prof. Simmer, which initially consisted of leather as a sealing material. A decisive step forward was achieved through the use of synthetic elastomers, Buna (SBR) and later Perbunan (NBR) instead of leather.

Elastomers are amorphous polymers whose glass transition temperature is below the application temperature. They are dimensionally stable but elastic and return to their original state after mechanical deformation. This characteristic is caused by a linear structure of the molecular chains with a wide mesh network of the main valences. They cannot be melted, are non-soluble and swell in solvents.

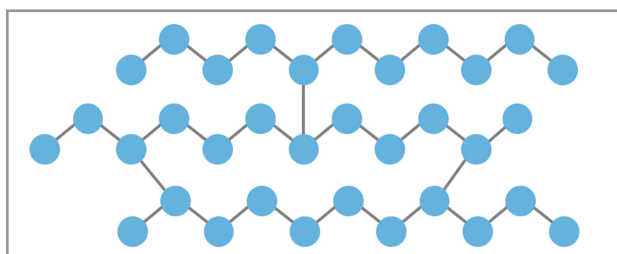Additionally, elastomers are sensitive to light, ozone,

Figure 1: *Simplified elastomer structure*

high temperatures and chemicals. The structure of the elastomers themselves as well as the used additives play an important role on how much they are affected by the aforementioned parameters.

When elastomers have direct contact with an ester, various processes can take place. The elastomer can absorb the lubricant. This leads to swelling of the elastomer as it gains volume and weight. It is also possible that substances from the elastomer are dissolved in the ester. This would cause shrinkage of the elastomer as volume and thickness decrease. In general, chemical reactions of the elastomer and a liquid medium are also possible but not very likely when it comes to esters.

Besides the elastomer itself, the used additives are also involved in these processes. Plasticisers or antioxidants have a high probability of being dissolved in the lubricants. As a result, elasticity, wear resistance and durability are affected. Fillers, on the contrary, tend to lead to a better resistance of the elastomers.

Both processes, adsorption and elution, can overlap. A discoloration of the medium indicates the latter.

Materials and Method
Elastomers
For the swelling tests, mainly elastomers with a good compatibility with lubricants were selected. All test specimens were obtained from Bundesanstalt für Materialforschung und - prüfung (BAM) in Berlin and comply with ISO 6072.

NBR – Nitrile Butadiene Rubber
NBR generally provides good oil resistance. It is widely used for gaskets, seals, diaphragms, gasoline hoses, liners, tubing, O-rings and cable jacketing.

The elastomer is produced by radical polymerisation of acylonitrile and butadiene. Higher proportions of acrylonitrile lead to better stability and mechanical strength. A higher butadiene content results in better low-temperature flexibility.

HNBR – Hydrogenated Nitrile Butadiene Rubber
HNBR is the hydrogenated variant of NBR. The elimination of the double bonds in the butadiene part increases the resistance to oxidation, chemicals and oils. Simultaneously, the resistance to aromatics or polar substances is reduced.

EPDM – Ethylene Propylene Diene Rubber
EPDM elastomers are insensitive to physical influences and have a high resistance to aging. The polymer shows good chemical compatibility, even with more polar solvents, while it is less resistant to low molecular weight hydrocarbons.

EPDM is produced by copolymerising ethylene, propylene and a non-conjugated diene, mostly 1,4 hexadiene or dicyclopentadiene.

FKM – Based on Vinyldenfuorid-Hexafluorpropylen-Copolymer
Fluoro-Elastomer (FKM) rubber is a product group of elastomers based on fluorocarbon polymers. They are characterised by good high temperature properties and excellent chemical resistance.

Base Oils
To assess the seal compatibility, the following ester base oils were used without additivation:

Chemical Name	Abbreviation	ISO VG Class
Trimethylolpropane tri-caprylate-caprate	TMP TCC	22
Trimethylolpropane tri-cocoate	TMP TCO	n.a. (between 32 – 46)
Trimethylolpropane tri-oleate	TMP TO	46
Trimethylolpropane tri-isostearate	TMP TiS	100
Trimethylolpropane tri-stearate	TMP TS	n.a. (solid at 40 °C)
Trimethylolpropane tri-linolate	TMP TLi	n.a. (between 32 – 46)
Neopentylglycol di-oleate	NPG DO	22
Pentaerythritol tetra-oleate	PE TeO	100
Glycerine mono-oleate	GMO	100
Glycerine di-oleate	GDO	46
Glycerine tri-oleate	GTO	n.a. (between 32 – 46)

Table 1: *Ester base oils used without additivation*

Determination of the change in weight and volume of the elastomers

The seal compatibility was determined according to ISO 6072:2011. The elastomer test specimens were all cut to the same size and weighed. Testing glasses of a proper size were filled with the test liquid. The test specimens were attached to a bracket and then completely immersed in the test liquid. After that, the glasses were closed.

In order to achieve a possibly high comparability of the results, every tested combination of elastomer and ester was stored at 80 °C for 168 hours. When the test period was over, weight and dimensions of the test specimens were determined again.

The changes in weight and volume were calculated based on the measurements before and after the test. Both values are given as a change in percent.

Results and Discussion

The following explanations focus on the swelling behaviour of the elastomers once they get in touch with an ester base oil. Of course, this does not allow any conclusions on the suitability of seals under operating conditions. But it enables an assessment of the resistance of the elastomers to different base oils.

In terms of chemical structure, the fundamental difference between mineral oils or polyalphaolefins (PAO) and ester base oils is their polarity. As hydrocarbons, mineral oils and PAOs are non-polar, highly lipophilic substances. With at least one ester group, esters have polar molecular components. This difference in polarity constitutes the different effects on elastomers. Therefore, esters are more likely to dissolve in more polar polymers than in typically non-polar ones.

EPDM has a saturated, non-polar structure. Double bonds may originate from non-crosslinked diene components. As a result of the hydrogenation, HNBR has a lower polarity than NBR, which represents a polymer of medium polarity. FKM polymers also have a low polarity, but are in general very resistant to chemical influences.

Different types of esters also show considerable differences in seal compatibility within the same group of polymers. Therefore, G. van der Waal (Van der Waal, 1985) suggested the use of a non-polarity index (npi). The npi should help to estimate the influence of an ester on the resistance of seals. It is calculated according to the following equation:

$$\frac{total\ number\ of\ carbon\ atoms\ X\ molecular\ weight\ of\ the\ ester}{number\ of\ carboxyl\ groups\ *\ 100}$$

The test results of 4 different polyol esters based on trimethylolpropane (TMP) are given in figure 2. They show that there is a strong correlation between the npi and the swelling behaviour for TMP TCC, TMP TCo and TMP TO. This applies to both, the weight and volume increase of the test specimens. Based on this information a moderate decrease could also be expected for TMP TiS. However, the data show that this assumption is not correct.
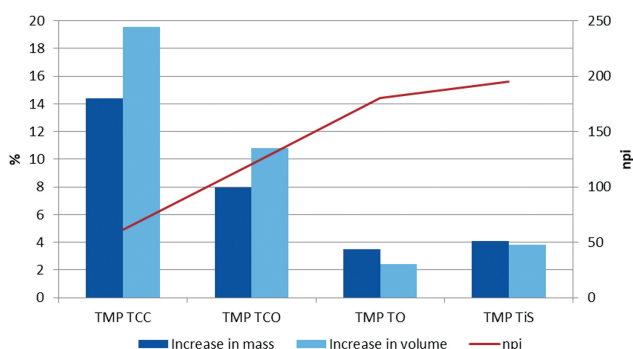

Figure 2: *Swelling of NBR 1 at 80 °C as a function of the fatty acid*

Other molecular components, such as double bonds or free OH valences, also have a considerable influence. The npi of a TMP tri-ester of the pure stearic, oleic or linoleic fatty acid is approximately

the same. Nevertheless, the differences in the mass absorption shown in figure 3 result primarily from the contribution of the double bonds to the overall polarity of the molecules.

Therefore, the proportion of double bonds was also considered in a newly calculated npi which is called npi 2. Npi and npi 2 are both displayed in figure 3. This approach enables a better explanation for the swelling behaviour. However, as expected the double bonds have less influence on the swelling action than the carboxyl groups.
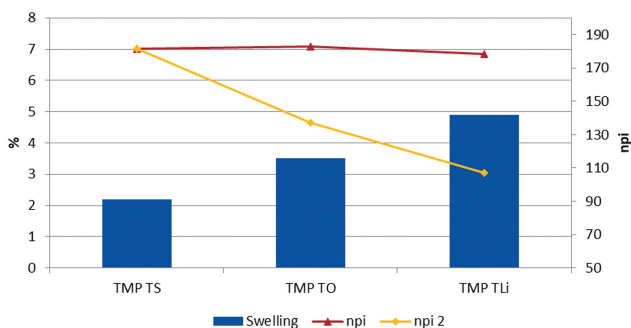

Figure 3: *Mass increase of NBR 1 at 80 °C as a function of the iodine value (IV)*

Figure 4 shows the swelling behaviour of four different polyol esters based on oleic acid. It becomes clear that the different swelling actions cannot only be explained by the npi. The gap between NPG and glycerol esters is somewhat more pronounced than anticipated from the npi. The TMP ester does not behave as expected and shows significantly lower values. The size of the molecules will certainly play a role here, but also the difference in steric arrangement of the acid group. However, all these factors cannot explain the swelling of the PE ester. Less swelling would be expected due to the molecular size, the npi and the steric arrangement of the fatty acid groups. Obviously, in the area of low swelling other factors also need to be considered. Fundamental aspects of thermodynamics, as discussed in the next section, probably play an essential role here.
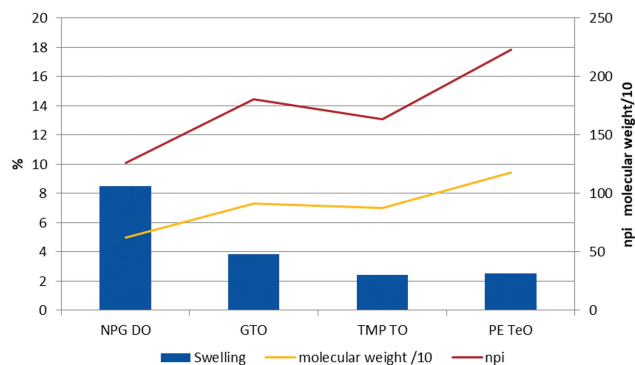

Figure 4: *Volume increase of NBR 1 at 80 °C as a function of the polyol type*

Figure 5 shows the swelling of TMP TO for different elastomers. The data for NBR 1 and HNBR 1 are not surprising. The hydrogenation of the double bonds in the HNBR reduces the polarity. Therefore, HNBR is more stable for polar base oils like esters and there is less swelling. Furthermore, the results show that EPDM 1 is incompatible and FKM 2 is resistant. This swelling cannot be explained by the npi. Due to its more non-polar nature, EPDM, for example, should be significantly more resistant.
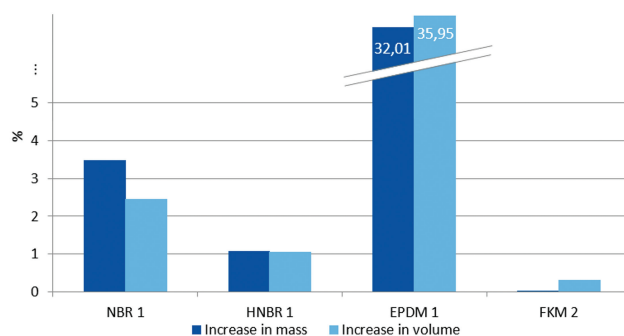

Figure 5: *Swelling of different polymers at 80 °C for 168 h in TMP TO*

In order to explain the unexpected behaviour of EPDM 1 and FKM 2 the following aspect could be considered: According to Starmer (Starmer, 1993), the swelling behavior of elastomers can be described by the Gibbs-Helmholtz equation:

$$\Delta G = \Delta H - T\Delta S$$

The polymers swell when the free energy (ΔG) is negative. Therefore, the change in free enthalpy (ΔH) must be smaller than the change in the product of temperature (T) and entropy (ΔS). This approach explains the temperature dependence of the swelling.

Starmer describes the change in enthalpy as a parameter controlling diffusion of the base oil through the liquid / solid interface. This effect reaches a maximum with the same polarity of liquid and rubber. The change in entropy, on the other hand, is responsible for the enclosure of the base oil in the polymer matrix. Smaller molecules of the liquid lead to a greater change in entropy and thus to greater swelling.

Swelling of the rubber is also counteracted by the retractive force of its network structure which is related to the crosslink density. De Broutelles (de Broutelles, et al., 1975) showed that the swelling of a rubber is inversely proportional to the average molecular weight between the crosslink, which stands for a higher density of the network structure.

At the same time, the molar volume between the crosslinks is lower with a higher degree of crosslinking. This results in a smaller change in entropy, which tends towards zero with the same or greater molar volume of the base oil compared to the volume within the network structure. This is shown in figure 6 where the increase in molar mass leads to lower swelling.
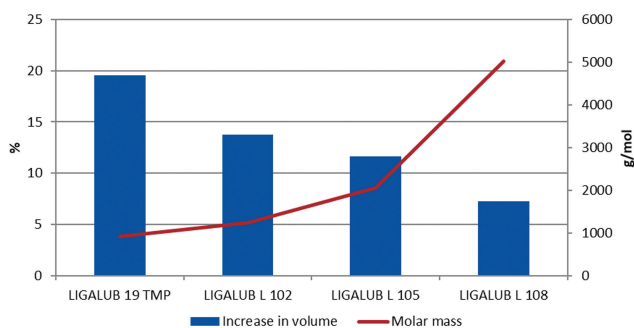

Figure 6: *Volume increase of NBR 1 at 80 °C for 168 h as a function of molecule size*

For the same type of polymer, these parameters can be changed, for example, by the type of crosslinking or usage of additives, such as fillers.

It also becomes clear that the resistance to lubricants is a specific material property. This explains the fundamental differences between EPDM and FKM materials

The results presented so far were determined on production samples that are characterised by a good degree of esterification. However, there are also products on the market that do not have this characteristic. A lower degree of esterification is reflected in a higher acid value (AV) and hydroxyl value (OHV), i.e. ultimately a higher proportion of the starting materials within the product.

In order to study this influence more in detail, TMP TO with different hydroxyl values were synthesised on lab scale. The acid value of the esters was below 0.6 mg KOH / g.
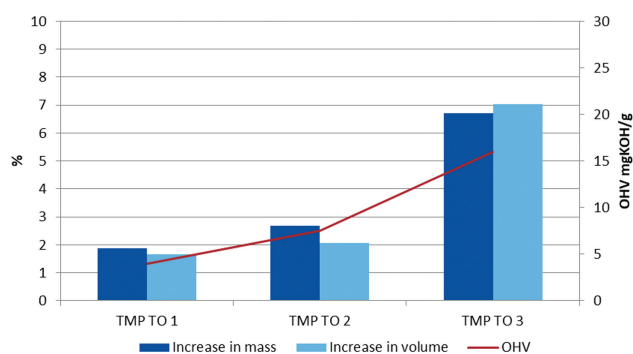

Figure 7: *Swelling of NBR 1 at 80 °C for 168 h in TMP TO with different hydroxyl values*

As displayed in figure 7, there is a significantly higher swelling with increasing hydroxyl value. A doubling of the hydroxyl value almost doubles the swelling, both in terms of mass and volume. It can be assumed that the hydroxyl groups have a similar contribution to polarity as the ester number. At the same time, a higher hydroxyl value means there is a higher content of TMP dioleate (TMP DO) in the product. The fact

that TMP DO has a lower mass with nearly the same polarity will decrease the npi. Furthermore, the smaller molecular size compared to TMP TO also reduces the elastomer compatibility.

Summary
Different ester base oils show a fundamentally different sealing compatibility. For a prediction of the compatibility, three different factors can be considered: polarity, viscosity and double bonds. Polar polymers are more likely to be attacked than non-polar ones. Esters with a higher viscosity show better compatibility due to the higher molar volume. In terms of double bonds, it can be seen that unsaturated esters are less prone to swelling.

Taking a look at different polymer types, FKM polymers generally show very good resistance to ester oils and are therefore the first choice with regard to resistance. Other materials, such as EPDM, have proven to be unsuitable. Polymers like NBR and HNBR show a lower compatibility than FKM polymers but taking the above-mentioned factors into account, it is possible to find a suitable ester base oil.

Elastomer compatibility should also be considered if an existing lubricant formulation is modified as changes of the base oil might have a significant impact. An example are existing systems for Stern Tubes which have to be converted to Environmentally Acceptable Lubricants (EAL). The change to a new, biodegradable ester base oil or sometimes even a mixture of two is common in this application. When selecting a new base oil, particular attention has to be put on the low-viscosity component as it has a decisive influence on the elastomer compatibility of the entire system.

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