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RESEARCH ARTICLE

Compatibility Study of Viton, NBR 70 and EPDM O-rings with Selected Solvents

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Abstract
The major part of O-rings is caoutchouc, which is not resistant to several solvents, acids, oils, or bases, and this can cause structural deviations in sealing. The present work shows a compatibility study of O-rings to solvents at laboratory scale. The tested O-rings are the following ones: Viton, NBR 70 and EPDM, and the applied solvents are levulinic acid (LA), formic acid (FA), dimethyl sulfoxide (DMSO), lactic acid (LAA), gamma-valerolactone (GVL) and acetonitrile (AC). Based on the measured geometric parameters of O-rings and the weight increments obtained in different solvents, we set up a compatibility table from which we can suggest the proper O-ring for a given solvent or vice versa: which type of O-ring is compatible with which solvent. This work offers a supplementary table to the O-ring handbook, which can contribute to proper selection of O-ring and solvent pairs in the future.

Keywords
O-ring, Viton, NBR, EPDM, compatibility, solvent resistance

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1 Introduction

1.1 O-rings' importance in industries

Although O-rings are cheap accessories, we need to take care about their proper states and behaviours, otherwise they could often cause serious problems in machines and processes. In many cases information is available on O-rings-solvent compatibility, however sometimes we cannot find anything on the applied solvents. O-rings basically consist of rubber, but producers give additives during die-cast to improve their qualities, whose concentrations are often unknown for users, affecting their applicability at given conditions. Gaskets are used in various apparatus: valves, taps, pipes and O-rings can be used as extra sealing on the top of the joining pipes or at interfaces, to avoid leaking. Resilient elastomeric type sealings are usually placed in grooves or in flanges, where they can sit in tightly. O-rings have a crucial role in valves, especially in high-pressure equipments, like membrane filters [1].

1.2 The importance of solvents in the industry

Nowadays solvent recovery is attaining more importance in the industry. The main goal is to recover solvents that can be utilized in the production again, which is crucial both economically and environmentally. Distillation, filtration and extraction can be applied to recover solvents from effluents. The units operating in these technologies are usually equipped with O-rings. O-rings in filters have special importance, since they separate two liquids: the effluent to be treated (feed) and the purified stream (permeate). In addition, O-rings have to be insensitive to intrinsic properties of solvents, temperature, and pressure without any sign of degradation, as well.

Beside the conventional solvents applied in large quantities (e.g. dimethyl sulfoxide in pharmaceutical industry or acetonitrile in HPLC methods), bio-based solvents gather greater attention. Levulinic acid (LA) is one of the newly proposed bio-based solvents. There is a highly selective method to produce LA from cellulose in SO_3H-functionalized ionic liquids, where microwave assisted heating is applied. Ionic liquids were found to be good reaction media due to their good thermal stability [1, 2]. LA can be used as a platform molecule, and can be modified into a wide range of compounds with several possible applications, such as polymer precursors, pharmaceutical intermediates and fuel additives. Diphenolic acid (DPA) (4,4-bis-(4-hydroxyphenyl) pentanoic acid) is prepared in a condensation reaction of LA with two phenol molecules. DPA is expected to be a possible alternative to bisphenol A, a building block of epoxy resins and polycarbonates. From LA GVL can be produced selectively with high yield via catalytic hydrogenation, thus we rightly declare LA as one of the most important molecules of the future [3, 4].

Gamma-valerolactone (GVL) was also proposed as a platform molecule, and gained great importance as a solvent [5, 6]. It can be produced from renewable resources (mainly from carbohydrates), stored and transported in large quantities easily and safely. Due to the outstanding physical chemical properties of GVL [5], it could be used for the production of energy and carbon-based chemicals. Another possible use is applying as a lighter fluid [7]. GVL can be prepared from levulinic acid (4-oxopentanoic acid) by homogeneous catalytic reaction [8].

Lactic acid (LAA) is also a commonly used molecule in the industry, particularly in the food and beverage industry. L-lactic acid is added to foods and beverages (E270), where a sour flavour is desired, and it is used as a non-volatile acidifier. LAA is also important in fermentation processes, such as fermentation in beer brewing, or in yoghurt- and cheese production. It can be used to control bacterial contamination, to ensure good storage of beverages [9]. LAA is gaining attention in the polymer industry as a monomer for a biodegradable polymer. Poly(lactic acid) (PLA) is a though polymer, that decomposes faster than conventional polymers [10]. Lactic acid can be produced either by fermentation methods [11] from renewable resources or by hydrothermal conversion of glycerol with high selectivity [12]. The intensive biodiesel generation produced about 3 million tons of crude glycerol in 2011, as a by-product.

Formic acid (FA) is a commonly used solvent in organic chemistry, mainly used as an agent in esterification reactions. Formic acid is synthetized from carbon monoxide and water [13], moreover it is formed as a by-product of biomass conversion reactions. When carbohydrates are catalytically converted to LA, equimolar amount of FA is formed. Consequently the investigation of the compatibility of O-rings with FA is highly desired.

Acetonitrile (AC) represents a typical mobile phase in uHPLC, and also an entrainer in extractive distillation. It can be used as an extractive agent in separation of olefin-diolefin mixtures. Although it is a polar aprotic solvent, it is soluble in water and organic medium, too. This amphoteric character makes it preferable in organic chemistry [14-16].

Dimethyl-sulfoxide (DMSO), a polar aprotic solvent, is a frequently applied medium for SN_2-type reactions. In addition DMSO was applied successfully as a reaction medium in the formation of centimetre-sized mesoporous silica-aerogels [17]. Its importance was emphasized worldwide in medical and clinical implications.

1.3 Composition of O-rings and expected behaviour in selected solvents

Viton O-rings are fluorocarbon elastomers, composed of copolymers of hexafluoro-propylene and vinylidene-fluoride, and trace amounts of other compounds added to improve their qualities. The types and concentrations of additives are unknown, and differ by each supplier. Viton has large importance in industrial life: it is compatible with a wide variety of chemicals, in wide range of temperature and has excellent aging characteristics. Fluorocarbon elastomers are recently used in processes where they have to resist to harsh chemicals and ozone attack as well [18]. Viton was tested with 10% hot LAA and showed excellent resistance [19]. NBR-70 (hereafter NBR) is composed from a copolymer of butadiene and acrylonitrile. NBR type O-rings are less resistant to concentrated acids than Viton types however they withstand the intensive hydraulic and pneumatic effects at low temperature [20]. NBR was tested to 10% hot LAA and showed excellent resistance similarly to Viton [19]. Formic acid seems to be harmful for NBR [19].

EPDM is a terpolymer composed of ethylene, propylene and diene monomers. Typically used dienes are dicyclopentadiene (DCPD), ethylidene norbornene (ENB) and vinyl norbornene (VNB). EPDM has excellent resistance to heat, alkali, mild acidic media and oxygenated solvents. EPDM compounds are not recommended for gasoline or petroleum [21]. Formic acid slightly affects EPDM, but no significant deviation could be observed [19]. Hot LAA having a concentration of 10% seems to have no effect on EPDM O-rings.

1.4 Tensions of selected solvents

For safety reasons we calculated the vapour pressures of solvents using the Antoine equation before starting the experiments. Here we present the different equations used for vapour pressure calculations.

$$\log_{10}\left(p^0\left[bar\right]\right) = A - \frac{B}{C + T\left[K\right]} \quad (1)$$

$$\ln\left(p^0\left[Pa\right]\right) = A + \frac{B}{T\left[K\right]} + C \cdot \ln\left(T\left[K\right]\right) + D \cdot T^E\left[K\right] \quad (2)$$

$$\log_{10}\left(p^0\left[mmHg\right]\right) = A - \frac{B}{C + T\left[°\mathrm{C}\right]} \quad (3)$$

$$\log_{10}\left(\mathrm{p}^0\left[kPa\right]\right) = A - \frac{B}{C + T\left[K\right]} \quad (4)$$

where p^0 is the vapour pressure, T is temperature and A, B, C, D, E are the Antoine constants. When different sources were available for the same solvent, we used both equations. Table 1 shows the Antoine constants of solvents, calculated vapour pressures at 50°C (highlighted with italics and bold) according to Eqs. (1)-(4) and transformed vapour pressures into other measurement units for easy comparison.

Table 1 Antoine constants, applicable temperature ranges and calculated vapour pressures of selected solvents

Solvent	A	B	C	D	E	T_{min} [K]	T_{max} [K]	p^0 (Pa)	p^0 (kPa)	p^0 (mmHg)	p^0 (bar)	Eq. Nr.	Ref.
LA	6.63219	3152.908	-43.564			375	519	2	0.00	0.00	***2.234E-05***	(1)	[22]
LA	158.19	-15257	-19.116	7.2330E-06	2	308.15	738	***4***	0.00	0.00	3.539E-05	(2)	[23]
FA	7.3779	1563.28	247.07			271	409	99171	99.17	***130.49***	9.917E-01	(3)	[24]
FA	50.323	-5378.2	-4.203	3.4697E-06	2	281.45	588	***17167***	17.17	22.59	1.717E-01	(2)	[23]
DMSO	109.58	-9311.4	-13.21	1.4770E-05	2	291.67	462.15	***392***	0.39	0.52	3.916E-03	(2)	[23]
LAA	225.19	-18757	-28.816	1.2998E-05	2	289	675	***7***	0.01	0.01	7.287E-05	(2)	[23]
GVL	5.43786	1182.70387	-134.6076			347.1	477.1	145	***0.14***	0.19	1.445E-03	(4)	[25]
AC	7.0735	1279.2	224.01			260	390	193139	193.14	***254.13***	1.931E+00	(3)	[24]
AC	58.302	-5385.6	-5.4954	5.3634E-06	2	229.32	545.5	***34111***	34.11	44.88	3.411E-01	(2)	[23]

Our future goal is to use membrane filtration for the recovery of LA, FA, DMSO, LAA, GVL and AC solvents. Therefore, we tested 3 different types of O-rings (Viton, NBR and EPDM) whether they can withstand the contact with these solvents. Based on literature data we expect that Viton and EPDM shall be resistant to most of our selected solvents.

2 Experimental methods

Above 30 kPa vapour pressure a reflux condenser was attached to our experimental apparatus. Below this value flasks were tightly closed. O-ring producers recommend different operating temperature ranges for each type of O-rings, therefore soaking experiments were performed at constant 50°C. The experimental apparatus consisted of flasks equipped with heating jacket, which were connected to a thermostat, and a reflux condenser if required.

Three pieces of a given type O-ring (all of them were manufactured by DICHTOMATIK Corp.) were placed into the flasks filled with 50 mL of solvent. To gather comparable results, identical conditions were applied for all solvent and O-ring pairs.

One can follow the behaviours of O-rings in solvents easily by measuring the changes in their geometry. O-rings have two characteristic attributions: outer diameter, and thickness. During our experiments we measured not only these two typical traits, but also their weights. To measure all these, we used a calliper and an analytical balance. At first, we measured the original size of the selected O-rings and the dry weight as well. Then we placed them into a flask filled with one of the investigated solvents. We measured the sizes and masses after 10, 30, 60 minutes, then after every hour until their traits didn't change further. During the repeated experiments the properties were determined more frequently in the first hour. When no more change was observed in weight or outer diameter compared to previous values, soaking experiments were stopped.

We determined the possible errors during measurements. The weight of solvent can cause error in the measurement: if solvent remains on the surface, but does not swell the O-ring, it gives a positive false result. The complete removal of solvent from the surface is highly recommended before weighing. Another possible error could originate from the use of callipers. As O-ring materials are elastics, the calliper can easily compress them resulting a negative error in size. For precise experiments we made three parallel measurements for each solvent and O-ring pairs, thereby reducing standard deviation.

The rate of change determines whether an O-ring and a solvent pair is recommended to be used together or not. Taking the measurement error into account, we set the level of significance at a relative change (R_M) of 5%. When R_M is higher, than 5%, we do not recommend the solvent and O-ring pair use together. We consider the swelling change significant by the following equations:

$$R_M = \frac{M_{\max} - M_{\min}}{M_{\max}} \cdot 100\% \tag{5}$$

where R_M the relative mass change (%),
M_{max} means the maximal weight what the O-ring achieved during the measurement (g),
M_{min} represents the original weight of O-rings (g).

$$R_D = \frac{D_{\max} - D_{\min}}{D_{\max}} \cdot 100\% \tag{6}$$

where R_D the relative change in outer diameter (%),
D_{max} means the maximal diameter what O-ring achieved during measurement (mm),
D_{min} represents the original diameter O-rings (mm).

3 Results

The mass and outer diameter measurements revealed that some of the O-rings became heavier and bigger than initial ones but others kept their original values during experiments.

The measured data are categorized according to the types of O-rings, while the figures based on measured parameters:

Figs. 1, 3 and 5 show the trends in outer diameter and Figs. 2, 4, and 6 show the changes in mass versus soaking time. When swelling occurred, significant increase could be observed in the first half hour and was optically visible in all cases. If there were not any changes during two or three hours, the experiment was stopped. Swelling can be explained by the diffusion of solvent molecules into the polymer chains therefore resulting in increased mass and size, as well. Another explanation could be that the solvent segregate bonds between the polymer chains. Segregated segments of polymer chains could be extracted by the solvents. The latter would explain the weight fluctuations that were experienced during the experiments.

3.1 Soaking results of Viton O-rings

Outer diameter changes of Viton O-rings in several solvents are shown Fig. 1. No changes were observed in the case of LA, LAA and FA. In general, it can be stated that Viton type O-rings are compatible with these solvents since acids do not attack Viton. Significant change could be observed however, with AC, DMSO and GVL. Oxygenated solvents such as GVL and DMSO, and organic nitrile containing solvents can diffuse into Viton, resulting an increase in diameter. The swelling can be described by functions tending to saturation. Compared to literature data, soaking in pure LAA did not affect the O-ring's structure, keeping its original size, as expected. Considering mass increment (Fig. 2), we can come to the same conclusions. In the case of AC, fluctuation can be seen on figures. The growing trend of functions is visible in spite of the measuring error. The greatest effect was observed in GVL, and the descending order of the effect of solvents is as follow: DMSO > AC > FA > LAA ≈ LA.

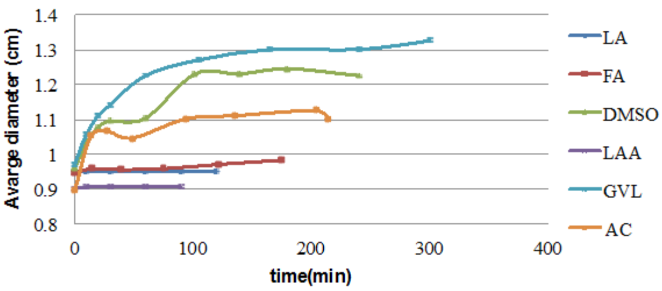

Fig. 1 Viton O-ring: diameter changes in solvents at 50°C

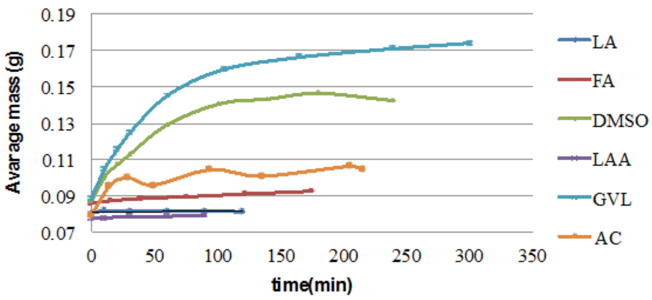

Fig. 2 Viton O-ring: mass changes in solvents at 50°C

3.2 Soaking results of NBR O-rings

The changes of NBR 70 type O-ring in different solvents can be seen in Figs. 3 and 4. The results show that NBR is resistant to LAA and LA (we obtained a straight line) however, it is not proven to be resistant to the other solvents.

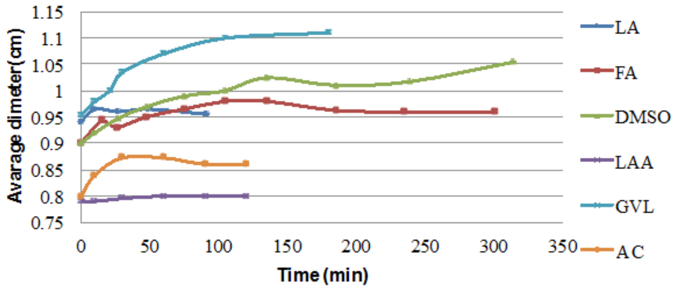

Fig. 3 NBR 70 O-ring: diameter changes in solvents at 50°C

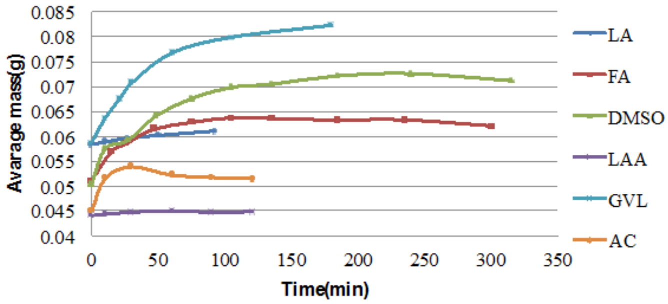

Fig. 4 NBR O-ring: mass changes in solvents at 50°C

The greatest effect was observed in GVL and the descending order of the solvent effects is: GVL > DMSO > AC > FA > LA > LAA.

The same tendency was observed in the case of mass measurements, as expected.

3.3 Soaking results of EPDM O-rings

According to Figs. 5 and 6, minimal changes can be observed for all tested solvents. It seems that EPDM withstands all of the solvents used in this work thus EPDM fulfilled our expectations. We used two different sized O-rings, similarly to those used Section 3.2. While a slight change (mainly in mass) could be observed for other types of O-rings, EPDM shows constant values. It can be stated that there was not any change, and the accuracy of our measurements was also proven.

Considering the relative changes in diameter (R_D) and mass (R_M) we obtained higher deviations for R_M than for R_D due to the higher accuracy of mass measurement. Although we observed deviations in diameter, we draw our conclusions based on the more accurate measurements of R_M values and set up a reliable ranking for stability of O-rings. The calculated R_M and R_D values are summarized in Table 2. In general, EPDM seems to withstand all the tested solvents, as expected. Viton is known to be resistant to a wide variety of solvents. The aprotic and dipolar solvents (DMSO, GVL) however, showed significant effect on the polymer chains of Viton, which can be explained by increased secondary interactions. Viton soaked in FA resulted in a slight change (7.56%), which is just above the limit of 5%. Viton was resistant to pure LAA similarly to 10% LA [19]. In case of solvents having hydroxyl group besides oxo-group, we obtained moderate swelling. Nitrile group also showed noticeable interaction with Viton. NBR showed similar behaviour to that of Viton, but FA caused more significant mass increment.

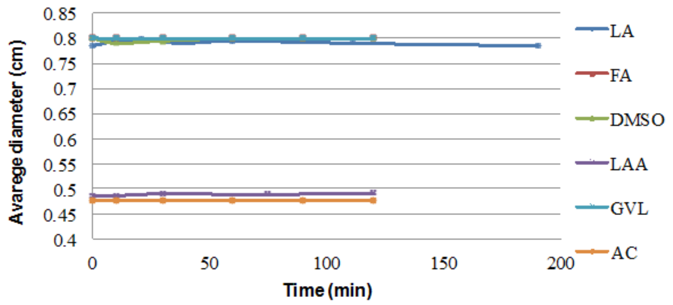

Fig. 5 EPDM O-ring: diameter changes in solvents at 50°C

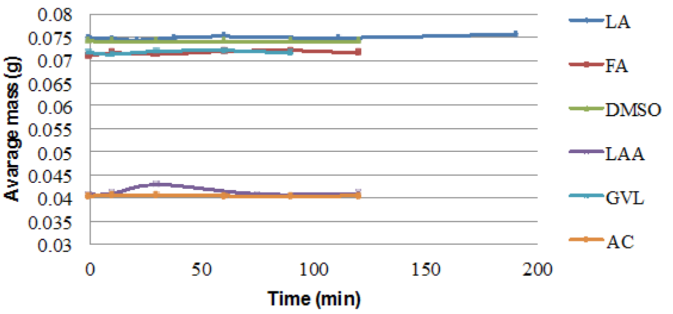

Fig. 6 EPDM O-ring: mass changes in solvents at 50°C

Table 2 Relative changes in diameter(R_D) and mass (R_M)

	R_D			R_M		
	Viton	NBR	EPDM	Viton	NBR	EPDM
LA	0	2.66	1.27	1.87	4.62	0.94
FA	3.96	8.89	0	7.56	24.51	1.69
DMSO	30.21	17.22	0	75.23	40.99	0.07
LAA	0.56	1.27	1.29	2.5	2.05	5.65
GVL	36.59	25.19	0	96.94	82.23	1.41
AC	22.91	9.06	0	32.19	19.78	0.62

Based on our experiments herein we present a summarized table that suggests the possible pairs of O-rings and solvents that can be used. The plus sign (+) is used for recommended O-ring -solvent pairs, minus sign (-) shows the pairs that are not compatible. In case of zero sign (0) a slight deviation was observed in both diameter and mass, therefore we suggest further experiments.

Table 3 Compatibility table of O-rings: recommended solvent (+), slight effect (0), not recommended (−)

	Viton	NBR	EPDM
LA	+	+	+
FA	**0**	−	+
DMSO	−	−	+
LAA	+	+	0
GVL	−	−	+
AC	−	−	+

We recommend Viton O-ring for equipment that treats LA and LAA, but do not recommend it for DMSO, GVL and AC. Long-term study of FA compatibility is suggested before application.

In the case of NBR LA and LAA can be applied and the other solvents are not recommended for use, due to the significant swelling effect.

EPDM showed the highest resistance to the selected solvents, but in the case of LAA we suggest further long-term experiments.

4 Conclusions

For efficient solvent recovery a properly operating equipment is essential. Leaking of solvents can have negative influence on the recovery moreover it can cause environmental issues. Accordingly, sealing plays a significant role in industrial units. The compatibility of O-rings applied for sealing is commonly available, however not always given for many solvents. Since compatibility is a crucial point in solvent recovery, we selected levulinic acid, formic acid, dimethyl-sulfoxide, lactic acid, gamma-valerolactone and acetonitrile as test solvents. Based on our soaking experiments we set up a compatibility table for Viton, NBR and EPDM O-rings for the selected solvents. We recommend the following O-ring-solvent pairs to be applied: Viton with LA and LAA, NBR with LA and LAA, and EPDM with LA, FA, DMSO, GVL and AC, but we do not recommend Viton with DMSO, GVL and AC, NBR with FA, DMSO, GVL and AC. EPDM showed the highest resistance to the selected solvent, however in the case of LAA we suggest further long-term experiments.

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