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The O-Ring as Standardized Rubber Component

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With the new ISO 3601 Part 5 Standard (O-Ring Materials) the O-ring finally becomes a standardized rubber component. While, until now, only dimensions (in Part 1) and the permissible variation of the surface (in Part 3) were specified, the new edition of the Standard contains also requirements for the different material classes and the degree of vulcanization of O-rings (hardness and compression set). This review explains the individual parts of the new O-ring Standard in general and the reasons why the new Part 5 is very important for users in particular.

How has the ISO 3601 covered the function of O-rings until now?

The sealing effect of O-rings results from two essential effects (see Figure 1 [1]):

1. The O-ring establishes the contact with sealing surfaces and at the same time seals off the surface roughness by its adaptive behavior.
2. The O-ring produces a contact force (sealing surface compression), which increases with the action of high pressures (the O-ring becomes “activated”). This allows the O-ring to be able to seal up at almost any high pressure. The actual limits are given by the extrusion resistance of the rubber material (at one-sided pressure application). The usual nominal hardness values are between 70 and 80 IRHD, which allow pressures up to about 150 bar with typical installation spaces of O-rings (according to ISO 3601-2) without the use of back-up rings.

The contact area of the O-ring is dependent on its degree of deformation. If this degree of deformation (expressed as the percentage of deformation, also referred to as compression or squeeze) is very small, a higher susceptibility for sealing defects of the sealing area and O-rings results. In addition, with small deformations, the O-rings can only utilize the elastic restoring potential to a limited degree. When the relative deformations are too small, a considerable part of the restoring force produced by the compression alone is lost due to physical relaxation processes, thus even without aging of the material the O-ring may lose its functionality. If the compression is too high, the risk of formation of stress cracks in the O-ring core increases, particularly with the effect of high temperatures, moreover an increased risk of assembly errors results in rod and piston housings. Therefore, it is important during the design of an O-ring to ensure that O-rings in installed state are within a certain deformation range. The guidelines for that can be found in ISO 3601, Part 2 or DIN ISO 3601-2 as well as in the German Preceding Standard DIN 3771, Part 5.

Part 1 of ISO 3601 Standard defines the dimensions; for O-rings the functional dimension is the cross section (see above). Part 3 of this Standard then describes where there is the limit for the surface imperfections of the O-rings. With that it is also possible to ensure essential sealing conditions for O-rings by means of Parts 1, 2 and 3 of this standard. However, the requirements for the properties of materials for O-rings were not specified until the approval of the latest version of ISO 3601-art 5 in the year 2015. The previous version was of little help as it only included a rough compatibility guideline in order to be able to select a suitable elastomer for a given fluid. For further guidelines it was recommended to contact the supplier of the seals.

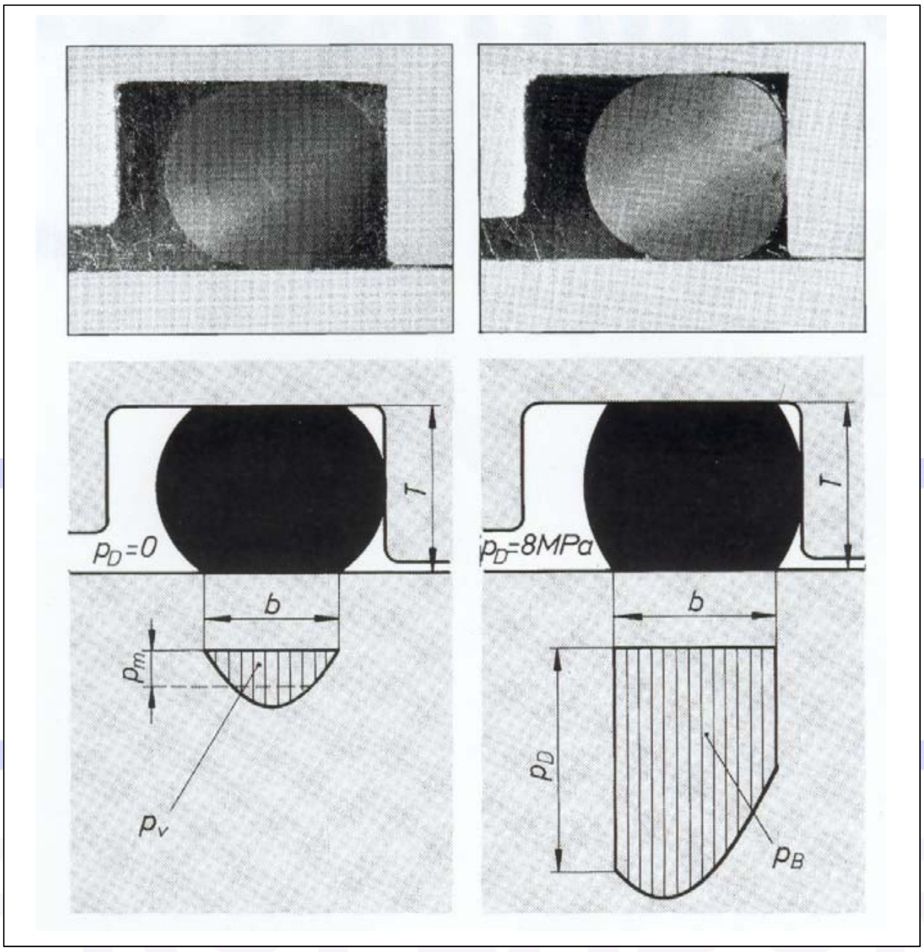

Figure 1 [1]: The O-ring as an active sealing element

What is necessary to specify the material properties for O-rings?

In order to understand which effects can play an important role, it is necessary to first show by charting what determines the material grade of an O-ring or of an elastomeric seal; for that see Figure 2.

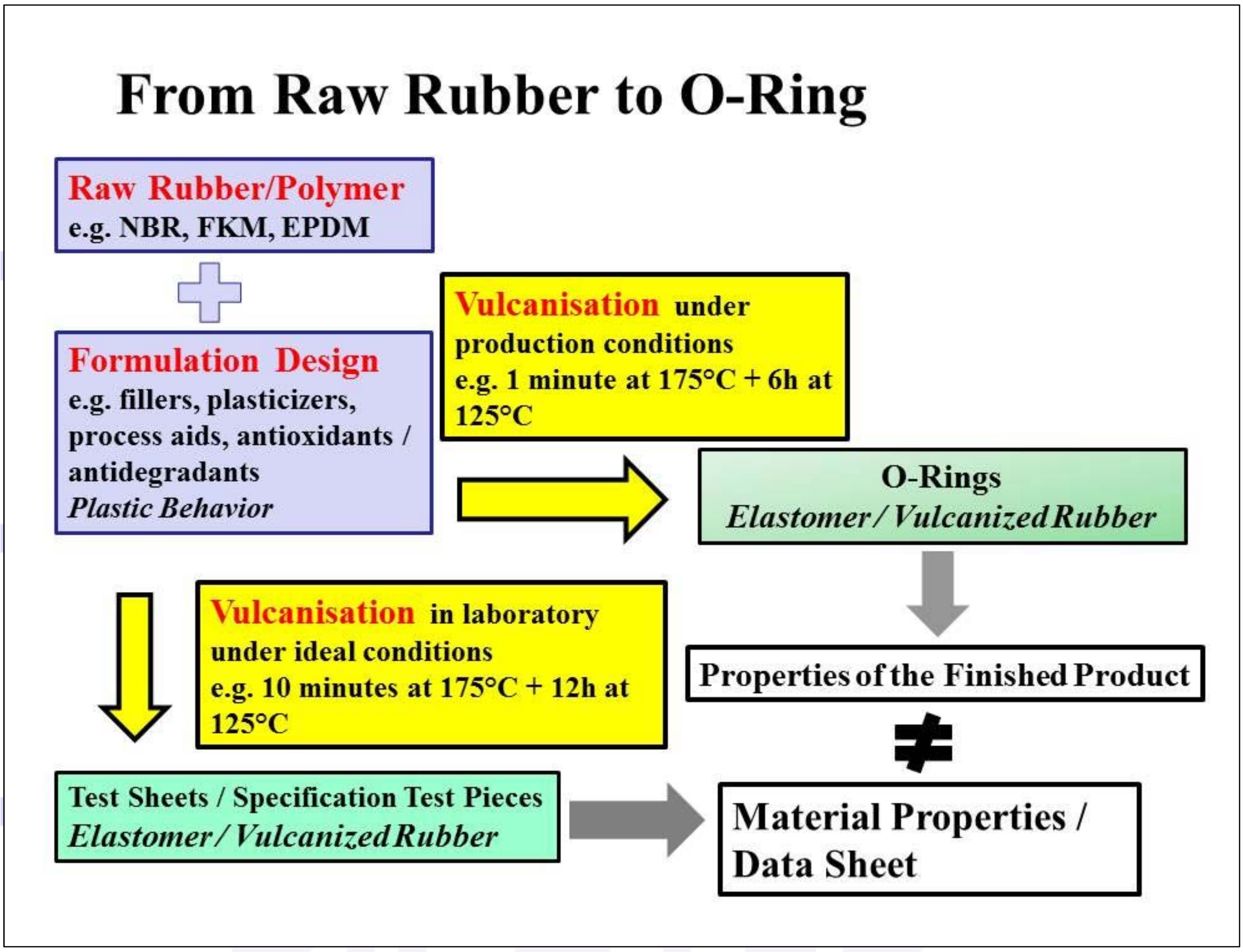

Figure 2: The three major influencing factors, polymer, formulation design, and vulcanization

The large material diversity of O-rings results ultimately from the following three influencing factors:

1. The Diversity of Polymers

A large variety of properties within the same family of polymers is hiding behind the abbreviations (e.g. FKM, NBR, EPDM). This can be explained by the fact that the abbreviated designations describe only the kind of possible monomers, but leave their mass proportions open. Moreover, the average chain length, or average molecular weight and molecular weight distribution of the polymers are not at all settled by the abbreviated designations. Thus there exist NBR polymers with different contents of acrylonitrile, which can lead to big differences in their flexibility at low temperatures (-20 to -50°C). The EPDM polymers contain typically 40% ethylene (polymers with low compression set up down to -40°C) up to 90% ethylene (polymers with higher compression set already at -10°C). EPDM grades containing less than 1% diene exhibit a very good heat aging resistance at 150°C, while those with 6% and more diene have poor heat aging resistance at 150°C. FKM materials are divided into five basic types of polymers [2] with different flexibilities at low temperatures and different resistances to swelling.

2. A Great Degree of Freedom in Formulation Design

There is a great deal of space in formulation design because of the choice of quality and quantity of fillers, plasticizers, cross-linking agents and additional chemicals for the improvement of certain properties, such as antidegradants or waxes for ozone protection. Specifically, that means that with an EPDM material it is determined only by formulation design if the polymer content is 30 or 60% or if the cross-linking agent used is sulfur (permissible continuous service temperature being 100°C) or peroxide (permissible continuous service temperature being 150°C). Thus even when two formulations contain the same base polymer, the properties of the materials may be very different.

3. Strong Influence of the Process Parameters in Vulcanization

Since rubber materials, at the same time they are being molded are also subjected to chemical conversion, the process parameters during vulcanization in compression molds (particularly the mold temperature and the curing time) and subsequent post-cure in an oven (temperature/time) have a significant effect on the degree of cross-linking and with it on the elastic properties of the finished part. If two batches of the same material, that is, of the same formulation, are vulcanized differently, it can happen that significantly different properties will result, for example in terms of compression set or tensile strength. The values from elastomeric materials in the data sheet refer to ideally cured test pieces and therefore demonstrate nothing but the potential that is set in the formulation. However, the details in the data sheet do not provide binding values for finished parts. Thus if O-rings are ordered without defining limits for the finished part, only by referring to the corresponding data sheet, it is in the suppliers' hands if the O-rings are properly vulcanized or not.

Practical Examples of the Polymer Effects

Table 1 shows DSC data [3] (thermodynamic glass transition points) from 4 different O-rings made from NBR, which were consistently identified by the supplier as materials for low temperature service up to -40°C. While the O-ring positions 1 to 3 have shown glass transition well below the mentioned -40°C, sample 4 exhibits glass transition already at -31 °C; consequently, the latter is no low temperature grade, as stated in the data sheet. These differences in the behavior at low temperatures can be explained by the contents of acrylonitrile in the NBR polymer that can vary from 18 to 50%.

	Hardness IRHD	Density g/cm³	T_g (DSC)
NBR1	**71**	**1,22**	**-62°C**
NBR2	**73**	**1,20**	**-58°C**
NBR3	**66**	**1,28**	**-52/-33 °C**
NBR4	**77**	**1,24**	**-31°C**

Table 1: Glass transition temperatures of 4 different O-rings

Table 2 shows two different peroxide cross-linked EPDM materials that demonstrate differences in the behavior at low temperatures. The material EPDM A has a TR-10 value [4, 5] (a conservative cold temperature guide value for O-rings) worse by 20K than the material EPDM B. These found differences can be explained by the different contents of ethylene in the EPDM polymer that can vary from 40 to about 90%. A high content of ethylene in EPDM O-rings causes a kind of cold rigidity already near room temperature.

	TR2	**TR10**	TR30	TR50	TR70	TR70 to TR10
EPDM A	-45,3°C	**-27,4°C**	-9,0°C	1,1°C	9,5°C	36,9°C
EPDM B	-52,6°C	**-47,1°C**	-40,1°C	-34,0°C	-25,0°C	22,1°C

Table 2: Comparison of two EPDM materials in terms of the TR10 value

The same is demonstrated by Table 3. Two well vulcanized peroxide cross-linked EPDM O-rings would show only minute differences in the compression set test at 100°C (DIN ISO 815-1) when they are released at the testing temperature after being aged for 24 hours at 100°C (Method A). On the other hand, a relaxation only after cooling down to 23°C (Method B) brings about too great differences with the same pre-aging. The differences between Method A and Method B are resulting from reversible freezing effects, in contrast to that, the permanent deformation from procedure A is irreversible since it is exclusively the result of aging. The size of this permanent set is then a good measure of the cross-link density, i.e. of the degree of vulcanization.

EPDM 80 O-Rings, d_2=3,53 mm Compression set	**EPDM A Lower Ethylene Content**	**EPDM B Higher Ethylene Content**
24h/100°C ISO 815-1 Method A	**7%**	**14%**
24h/100°C ISO 815-1 Method B	**14%**	**60%**
24h/0°C ISO 815-2	**14%**	**65%**

Table 3: The compression set behavior of two peroxide cross-linked EPDM materials with different content of ethylene at high and low temperatures

The comparison with the compression set at 0°C, which can be explained by the reversible freezing effect, clearly demonstrates also the effects of the different contents of ethylene in the polymer.

Practical Examples of the Influence of the Formulation Design

A typical example of the effects of formulation is the cross-linking system of EPDM O-rings. Well vulcanized peroxide cross-linked EPDM O-rings have values of compression set measured after 24 hours at 150°C between 10 and 30%, sulfur cross-linked EPDM O-rings tested at the same conditions yield values between 60 and 80%. Another possible difference in EPDM materials may be caused by the amount of plasticizer used in the compound. Here the market offers within the peroxide cross-linked materials formulations without or with small amounts of plasticizers (0-3%) but also with amounts of plasticizers up to 30% with a nominal hardness of 70 Shore (or IRHD). This has enormous effects on the heat resistance, because plasticizers outgas at elevated temperatures and this leads to shrinkage and hardening of O-rings. Thus after exposure for 72 hours at 150°C an EPDM O-ring can exhibit an extremely low increase of hardness (less than 3 IRHD) but also up to over 20 IHRD.

Practical Examples of the Effect of Vulcanization

Good values in a data sheet for compression set are no guarantee for low compression set values from O-rings. In the daily laboratory routine, time and again, it is possible to find alarming deviations. Finding compression set values of 99% from HNBR O-rings for where the data sheet specifies a value of 28% after 24 hours at 150°C [6], happens fortunately rather seldom. However, finding compression set values from O-rings that are by 25 to 50 percentage points above the values shown in the data sheet (for 24 hours at 150°C) happens in cases of HNBR and EPDM O-rings alarmingly often. This can be explained as being process-related: the vulcanization degree of not fully vulcanized peroxide cross-linked EPDM and HNBR O-rings cannot be improved significantly by post-curing (= heating in an oven), as it is possible, for example, in case of NBR (sulfur cured) and FKM O-rings.

How to Specify the Material Properties of O-Rings?

As mentioned above, the quality of the formulation as well as of the processing and vulcanization have a substantial influence on the overall quality of the O-rings. The simplest way to express this relationship is to use a multiplicative correlation:

O-Ring Quality = Formulation Quality x Production Quality

When the factor approaches zero the quality of the overall product approaches zero. No matter how good the data sheets or formulation quality are, they become useless when the materials are poorly processed, that is, in this case, poorly vulcanized. Otherwise even the best quality processes of an O-ring manufacturer are of no use when he uses formulations, which are not close to the state-of-the-art technology and were, for example, only optimized for processability. In order to assure a proper state-of-the-art quality of O-rings, both factors must be clearly defined, that is, the formulation (by material properties), and the vulcanization (by the specific requirements for the compression set of the O-rings). This sounds rather simple, but in reality, it is not, because at best only the aerospace industry has regulations for O-rings and other seals, which clearly implement this. Therefore, until now, users could protect themselves in this respect only by in-house specifications, and then often in order to obtain O-rings conforming to this specification on the market, they do so at considerably higher expenses. The new material standard for O-rings ISO 3601-5 (2015-4) has now implemented this subject matter in a practice-oriented fashion.

What Can the New ISO 3601 Part 5 (2015-04) do?

Table 2 of the Standard defines the requirements for O-rings regarding hardness (IHRD-CM) and compression set, so that the degree of vulcanization of the O-ring is bindingly stipulated. For the compression set the limiting values for 24 hours and 72 hours are specified, which can be used alternatively. Because of the shorter time for testing and of the minor effect of the cross section it can be expected that the 24-hour testing time will prevail. The stipulated limited values for the 24-hour compression set test are approximately 15 to 20% over the possible state-of-the-art values measured at a test button size 13x6 mm (test piece B according to ISO 815-1).

Following materials are specified in the ISO 3601-5

NBR 70, 90, cross-linked with sulfur = standard

NBR 70, 90, cross-linked with peroxide (P)

HNBR 75, 90

FKM 70, 75, 80, 90

VMQ 70

EPDM 70, 80, cross-linked with sulfur (S)

EPDM 70, 80, cross-linked with peroxide (P), and

ACM 70

This is quite a considerable number of materials, although it can be already discussed why materials such as CR 70 and FVMQ 70 are not included. Another possible discussion is, if peroxide cross-linked NBR or sulfur cross-linked EPDM are really needed in the standard, since they actually play practically a subordinate role. However, somebody who knows how difficult it is to arrive at an agreement in international standardization groups will likely be positively surprised by the number of materials. From the point of view of application technology it is often irrelevant if an O-ring has the nominal hardness of 70, 75 or 80 IHRD. Thus the different manufacturers of O-rings can retain their standard materials without causing too great problems for users.

For these above mentioned groups of materials there are corresponding requirements as to their formulation quality in Tables 3 to 10 of the new ISO 3601-5. Also here the competent user will be at first positively surprised, that in the ISO 3601-5 substantially more properties are specified than generally common in data sheets from O-ring suppliers. In particular, the values of compression set are without exception specified over two weeks; this secures the required long-term behavior. It is particularly worth mentioning that for EPDM materials, this is the main headache for users, a TR 10 value below -40°C is prescribed. Many offered EPDM O-rings on the market currently provide the user with substantially less than the state-of-the art is capable of giving. Consequently, this new standard represents thoroughly in an acceptable way a good state-of-the-art technology and reduces thereby the risk of O-ring failure for the user due to insufficient quality of material (see above) markedly. Where the required formulation parameters are insufficient in the opinion of the user, additional agreements with the supplier can be reached. For example, if a user in hydraulic systems is not satisfied with sulfur cross-linked NBR 70 material with regard to swelling in IRM 901 Oil (+5/-15%) and the TR 10 value (less than -20°C), he can in this case negotiate with the supplier narrower limits, such as swelling in IRM 901 Oil of +5/-10% and TR10 value less than -25°C and refer in all other points to this Standard.

In summary, it can be said that the required formulation properties definitely represent a good state-of-the-art technology. However, at the same time, it leaves enough possibilities for the formulations of the premium supplier in order to distinguish themselves through better properties, such as improved long-term performance, low temperature flexibility or resistance to media.

Practical Implementation of the Standard ISO 3601-5 (2015-04)

1. Proof of Conformity of Formulations

The least complicated implementation of the Standard on the part of the O-ring suppliers would be if they provided data sheets with an already compiled target/actual comparison with the standard, which means, that all such data sheets would be modified in accordance with the requirements of the ISO 3601-5. The Standard itself does not state anything about who is authorized to issue such conformity reports. Thus the supplier could substantiate the conformity through his own laboratories. However in accordance with the insurance law the customer or user can protect himself against incorrect delivery and damage suffered from that, when he follows his duty of care and verifies the data from the supplier or have them checked. However, if the supplier can present a conformity report from an accredited laboratory, it is valid as a certificate independent of the supplier, comparable to one, which the customer prepared himself or obtained from a test done on his behalf. ISO 3601-5 does not regulate how the identity certificate of a formulation should look like so that the user can in case of doubt identify if the supplied O-rings actually were made from the formulation that was qualified for it. In this case it is recommended that the verification is done by means of density and thermogravimetric analysis. Finally further discussion is possible regarding the time span of the validity of the conformity report, if necessary. Intervals of repeating tests up to 5 years appear to be reasonable; this is common in current industrial practice in other fields (e.g. DVGW (=German Association for Gas and Water) approvals, approvals for the use in drinking water).

2. Proof of the O-Ring Properties

First of all, it should be pointed out here that ISO 3601-5 clearly defines in its Table 2 requirements for O-rings (not for standard test pieces) regarding their hardness and compression set, regardless of how frequently the conformity must be proven. The frequency of the testing should be mutually agreed upon by the customer and supplier. Table 2 offers nominal values for testing times of 24 and 72 hours to choose from. It is assumed that the 24 hour testing times will prevail because the results are obtained faster. It is recommended to agree on these fast tests at least on initial samples. As mentioned above, good properties of finished O-rings result from the combined effect of formulation and process management. With the results from initial samples the user can assure that the supplier has in principle a good control of the vulcanization process for each individual dimension of O-rings. The quantity of further receiving inspections should then be decided on depending on the process risk in the production (low: NBR-S, FKM, ACM; middle: VMQ, EPDM-S; high: EPDM-P and HNBR) and the sensitivity of the application to quality fluctuations. For hot and warm water applications, where peroxide cross-linked EPDM O-rings are used, testing of each production batch is quite common.

Summary

With the new ISO 3601-5 (2015-04), the O-ring became finally a true standardized component. This standard offers to the user the opportunity to obtain a good state of technology of O-rings independent of the manufacturer. The future will show to what extent users will take advantage of this opportunity.

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