VDMA
Fluid Power Association

22nd ISC

International Sealing Conference

Stuttgart, Germany
October 01 - 02, 2024

Sealing Technology –
Challenges accepted!

UNI STUTTGART

ISBN 978-3-8163-0768-6

Fachverband Fluidtechnik im VDMA e. V. Lyoner Str. 18
50628 Frankfurt am Main
Germany

Phone +49 69 6603-1513
E-Mail maximilian.baxmann@vdma.org
Internet www.vdma.org/fluid

Poetry and truth, how does the hydrolysis-resistant structure come into the polyurethane ? - New, soft, chemical-resistant TPU for pneumatics with a proportion of biogenic raw materials

Joachim Möschel, Dipl. Ing (FH), Konzelmann GmbH, Löchgau

Pneumatic cylinders convert the compressed air generated by compressors into mechanical energy. The piston rod in the cylinder is moved using compressed air, which means that power is usually transmitted in a linear direction. The elastic seals on the piston and rod play a central role here when it comes to function, tightness, energy efficiency and service life in the case of pneumatic cylinders and valves.

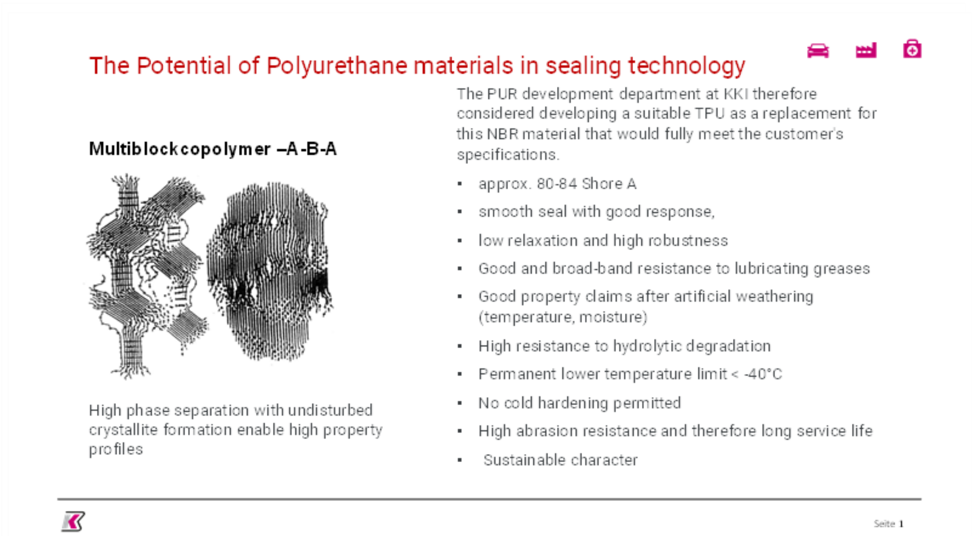
Traditionally, TPUs compete with soft rubber materials, especially when it comes to covering high-quality chemical resistance in this genre. Rubber materials have so far been the first choice when it comes to higher temperature requirements and chemical resistance.

Konzelmann (KKI) is currently working on bringing a platform of high-performance TPU materials for pneumatics, among other things, to market maturity. These should not only have high chemical resistance, but also meet all standard market requirements for cylinders and valves.

In the usual structure of TPU, urethane hard phases are used, which are homogeniously distributed as domains in an ester or ether soft phase. Their characteristics and frequency are the reason for the high-quality physical properties.

The predominantly amorphous soft segment consists of special macrodiols, which are potentially at risk of degradation due to their polar structure. The ester groups present in the soft segment can be attacked by various application-relevant media: e.g.

- Lubricating greases with alkaline soaps
- External cleaners
- Diluted acids, alkalis
- Food media
- CIP media
- Bio-oils
- Tropical humidity in combination with bio-oils or lubricating greases



Objective:

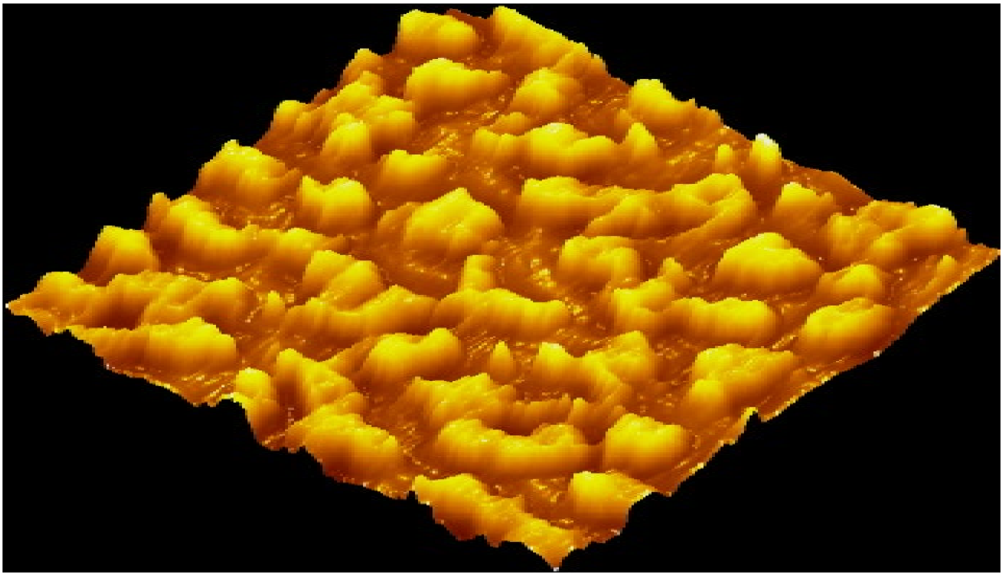
The starting point was the requirement to develop a tailor-made sealing lip material for a pneumatically operated pulse generator piston used in a truck brake. This was to be manufactured as a complete piston using a 2K process, with the hard core made of aliphatic polyketone being overmolded with the new polyurethane material.

In the previous generation, the complete piston was made of aromatic polyamide paired with a soft NBR. The problem arose on the one hand from a certain influence of moisture, which caused the piston based on aromatic polyamide to swell, the sealing lip was pressed too tightly and as a result there was severe abrasion. The NBR, which was trimmed to meet the demanding cold requirement of -40°, was initially able to meet this high requirement. After heat exposure at 85°C, the flexibility in the cold area deteriorated significantly, with the piston allowing very high leaks at low temperatures. The analysis showed cold hardening, which was noticeable due to plasticizer migration and increasing post-crosslinking on the butadiene groups of the NBR. This meant that the cold tightness requirement of -40°C could no longer be met.

The PUR development department at KKI therefore considered developing a suitable TPU as a replacement for this NBR material that would fully meet the customer's specifications:

- approx. 80-84 Shore A
- smooth seal with good response, low relaxation and high robustness
- Good and broad-band resistance to lubricating greases
- Good property claims after artificial weathering
- High resistance to hydrolytic degradation
- Permanent lower temperature limit < -40°C

- No cold hardening permitted
- High abrasion resistance and therefore long service life
- Sustainable character



TPU as a high-performance elastomer with a two-phase structure: Atomical force microscopy / submicrometer structure / Picture: Currenta

The protruding areas visualize the hard segment, the valleys the soft segment

Due to the bivalent structure of the TPU chains, the crystallization-capable areas can separate from the amorphous areas. This means that the phase-separated polymer can form ordered areas in the form of hard and soft segments.

Regularly structured, aromatic urethane hard phases are usually used, which are distributed as clusters in a non-crystalline ester or ether soft phase. They cause physical cross-linking points by means of hydrogen bonds on the negatively charged electron pairs of the carbonyl groups (in the urethane functions) and thus ensure high cohesive forces (tear propagation energies). The predominantly amorphous soft segment consists of special macrodiols, which, as mentioned, are based on ester and ether functions. Due to its polarity, it mainly contributes to the material swelling in polar media and the TPU breaking down over time under the influence of temperature.

Based on new modified biogenic raw materials, innovative TPU materials have been developed. Their soft segments also enable significantly lower glass transition ranges and, due to their more hydrophobic nature, higher chemical stability (1).

The following table shows the physical property profiles of the new TPU materials, VP 020 and VP 026, in comparison to a commodity TPU and a low temperature NBR:

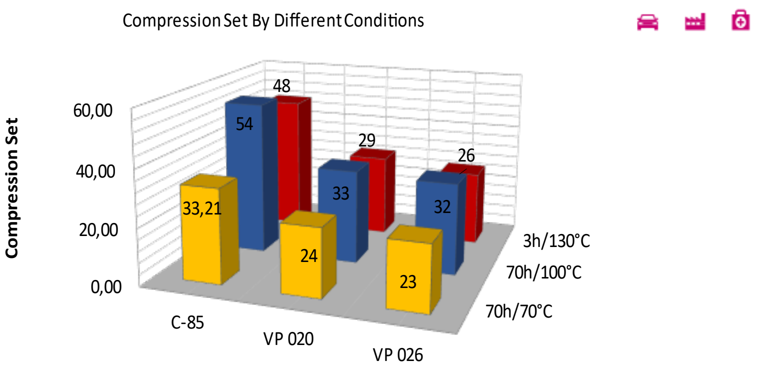
These are consistently at a high level: Compared to the referenced NBR material, 3.6 times the tensile strength and 5.8 times the tear resistance as well as 80% lower abrasion values according to DIN ISO 4649.

Eqo rctkuqp"qh"rtqrgtv{"rtqdgu<"Jkij"rgthqto cpeg"VRW xu0"eqo o qfkv{"xu0"PDT

	Hardness Shore A	Tensile-Modulus (Mpa)	Tensile Strength (Mpa)	Elongation at break (%)	Tear Resistance (N / mm)	Rebound Resilience (%)	Abrasion mm³	Content of biogenic Raw material
Norm	DIN ISO 7619-1	Tangenten -modul	DIN 53504	DIN 53504	DIN ISO 34-1	DIN 53517	DIN ISO 4649	
VP 020	84,9	12	51,2	>500%	47	62,9	21,	**26%**
VP 026	84,5	12	51,5	>500%	53	58,5	21,6	**45%**
C-TPU 85 A AU	87	28	33,1	750	58	49,3	30	---
NBR 75	76	8	14	220	8	20	118	---

For the newly developed materials there could be found a much higher level of physical properties in comparison to the C-TPU and the NBR-material.

The values for permanent deformation at higher temperatures are only slightly higher than for NBR. In contrast, C-TPU 85 A falls significantly in this comparison. At a short-term elevated temperature (3h/130°C), relatively low CS values are determined for VP 020 and VP 026.



	C-85	VP 020	VP 026
70h/70°C	33,21	24	23
70h/100°C	54	33	32
3h/130°C	48	29	26

Seite 1

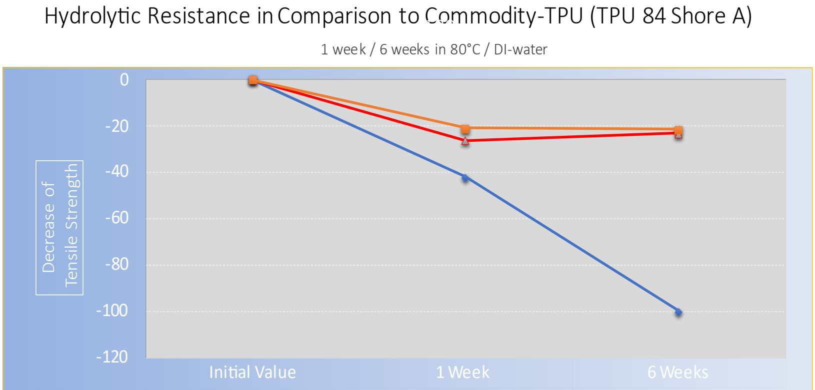
The artificial weathering cycle specified by the customer is defined as follows:

1. 400 hours at 85°C at 93% relative humidity

2. Subsequently, 100 hours in 85°C hot air

It was found that the prescribed weathering cycle does not lead to degradation of the materials VP 020 and VP 026. No significant changes are evident in any of the relevant parameters.

The following table shows the long-term hydrolysis behavior at 85°C in hot water:



	Initial Value	1 Week	6 Weeks
C-TPU 85 A	0	-42	-100
VP 020	0	-26,2	-23,2
VP 026	0	-20,9	-21,4

The course of the tensile strength can be linked to the degradation of the average molecular weight (2).

Ultimately, the ester-based commodity TPU is no longer usable after two weeks. In contrast, the two newly developed TPU materials show slight degradation with a loss of tensile strength of around 22% and continue to perform their function without impairment after 1000 hours.

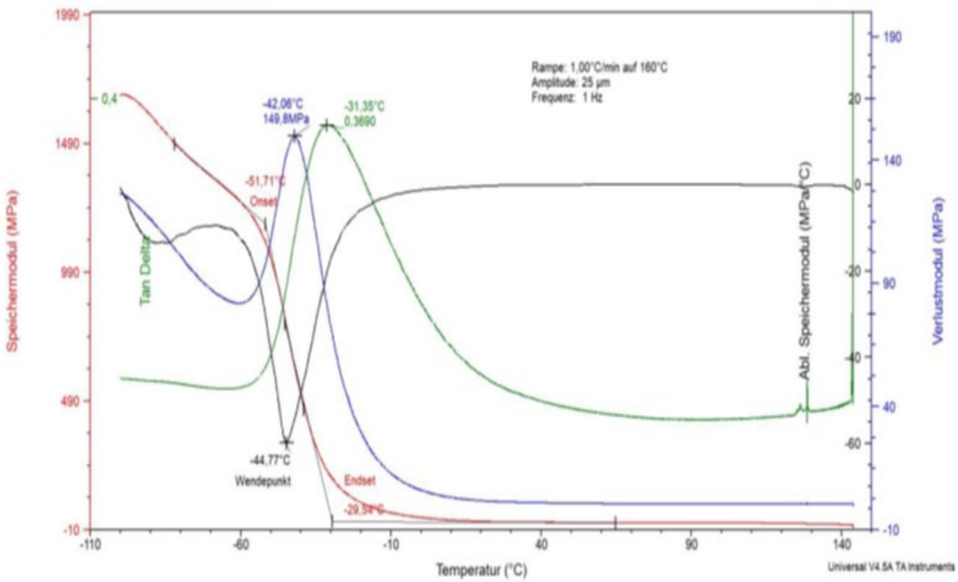
In practice, there are many influences that require stability against hydrolyzing media. Many lubricants, additives or thickeners can generate degradation, especially in conjunction with tropical humidity. Acidic or alkaline cleaning fluids can also break down polyurethanes after a short time. For this reason Hydrolysis-resistant materials can be seen as a high priority in food applications in conjunction with CIP media.

To determine their general suitability for pneumatics, some commercially available types of grease were tested for resistance. Ultimately, the newly developed materials show a very broad range of resistance in commercially available pneumatic greases:

Immersion Testing of VP 020 and VP 026
Testing Conditions: 85°C 168h

		Change in Tensile Strength (MPa)	Volumen Change (%)	Change in Hardness (Shore A)
VP 020	Autol Top 2000 SL	+ 22,3	+5,4	-2,6
VP 026	Autol Top 2000 SL	+6,6	+3,2	-2,3
VP 020	Elkalub GLS 993 H1	+5,9	-0,3	-1,7
VP 026	Elkalub GLS 993 H1	+5,3	-0,7	-1,2
VP 020	Mobilux EP 2 NLG2	+2,0	+2,8	-2,5
VP 026	Mobilux EP 2 NLG2	-1,9	+1,4	-1,9

DMA-Low Temperature Analysis of VP 020



	Onset of the E'-Curve	Turning Point of the E'-Curve
VP 020	-51,7	-44,8
VP 026	-44,7	- 34,9

The low temperature properties of the new TPUs are of crucial importance for the function of the pulse generator piston. The cold behavior of the weathered samples was determined on the basis of a DMA measurement. The heating rate selected was 1K/min at 1 Hz in tension mode. The E' values (red curve) resulting from the DMA measurement describe the elastic behavior of the material.

A turning point of -44.8°C for VP 020 ultimately provides evidence of sufficiently good cold flexibility for the intended application on the pulse generator piston. The soft segment, which is chemically firmly integrated into the PUR matrix, does not allow any negative changes here. Likewise, no post-crosslinking has taken place, triggered by the artificial weathering.

It was therefore obvious that VP 020 would be the preferred choice for the pulse generator piston in the intended series application.

Other target applications for VP 020/VP 026 can be found in pneumatics piston and valve seals as well as flange seals and O-rings (2).

In particular, when standard TPU grades lead to rapid degradation due to chemical influences, these newly developed TPU materials can lead to reliable problem solutions.

The structure of these materials contains relevant proportions of renewable raw materials, which means that with 26% for VP 020 and 45% for VP 026, it has been possible to establish a sustainable sealing product portfolio.

Sources:

[1] “Oleochemical products as building blocks for polymers” Andreas Heidbreder, Rainer Höfer, Roland Grützmacher, Alfred Westfechtel, C. William Blewett Veröffentlichung: Wiley- VCH Verlag GmbH, Weinheim, 1999

[2] „Thermoplastische Polyurethan-Werkstoffe für anspruchsvolle O-Ring Anwendungen in der Fluid-Industrie“ Joachim Möschel Vortrag ISGATEC-Forum 17./18. 11. 2020

https://doi.org/10.61319/CR9CO7U2