Introduction, potential applications of new oil-resistant elastomer

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Executive summary

Denka Co. Ltd. recently launched Evolmer, a new elastomer with outstanding performance benefits. Evolmer is a copolymer of acrylonitrile and chloroprene, and it demonstrates good oil resistance, excellent low temperature compression set and superior dynamic properties with appreciably low heat built-up and remarkably high flex-fatigue resistance.

The new elastomer can be used for high performance industrial applications, such as seals, diaphragms, hoses, rubber rollers, rubber linings and transmission belts, among other products.

Polychloroprene rubber (CR) is one of the flagship products of Denka Co. Ltd. Denka currently is the largest producer of CR globally.

Polychloroprene rubber is a special elastomer offering good heat, weather and ozone resistance, fair oil resistance and good balance of mechanical properties. Nitrile rubber (NBR), on the other hand, demonstrates outstanding resistance to petroleum products, but exhibits limited thermal resistance, low temperature flexibility and ozone resistance.

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It is intriguing to strategically and conveniently combine the performance benefits of both CR and NBR. Denka recently has commercially launched a new polymer under the Evolmer brand name. It is a copolymer of acrylonitrile and chloroprene, offering synergistic benefits of both CR and NBR.

Evolmer is produced through controlled free-radical emulsion polymerization technology. It is available in two physical forms: as aqueous colloidal dispersion (latex) and "dry rubber" chips.

Initial investigation of the experimental grade of Evolmer revealed its improved oil resistance and low temperature properties over general purpose polychloroprene rubber and better thermal resistance than NBR.[1] However, the earlier type of Evolmer had challenges with scorch safety[1] and stable cure.

This paper introduces an upgraded version of Evolmer with improved performance benefits. Detailed performance evaluations of the new "dry" Evolmer are featured here with an emphasis on its applicability in high performance seals/O-rings in oils and gas service applications.

Experimental

The rubbers evaluated here are: general-purpose Evolmer (Grade EV 2502); a commercial grade of NBR with ~40 percent acrylonitrile; and two commercially available hydrogenated nitrile rubber (HNBR) grades. One has ~36 percent acrylonitrile and 91 percent saturation (Sulfur curable: designated here as HNBR-S). The other has ~36 percent acrylonitrile, but with 96 percent saturation (Peroxide curable: termed here as HNBR-P).

Compounding and testing

The compounding was done using standard formulations for Evolmer EV 2502 and the other elastomers using commercially available conventional ingredients, as shown in **Table 1**. Standard curing systems were used based on the type of elastomers.

The level of carbon black was adjusted among the elastomers to achieve hardness values in the resultant compounds that were reasonably comparable (about 70 shore A).

All test samples were press-cured (compression molded) at 170°C for 20 minutes, except for button specimens for compression set, where the curing condition used was 170°C for 30 minutes. Compounds with Evolmer EV 2502 and HNBR-P were further post-cured at 175°C for 2 hours. Physical tests on the vulcanizates were carried out based on the standard procedures followed by Denka.

Results and discussion

Some of the basic features of Evolmer EV 2502 rubber are shown in **Table 2**. The glass transition temperature of the current grade of Evolmer was found to be -23°C, with specific gravity of 1.19 and Mooney viscosity of ~53 unit at 100°C.

Mooney viscosity and scorch time of Evolmer EV2502 compound in comparison to NBR and HNBR are shown in **Table 3**. The low Mooney viscosity of the Evolmer compound measured at 100°C indicates its better processability. The scorch time of Evolmer was found to be reasonable in current curing conditions reflecting its good scorch safety.

The moving die rheometer (MDR) results at 160°C for 30 minutes are shown in **Fig. 1**. Evolmer EV 2502 indicates a high and stable state of cure.

The vulcanizate properties of Evolmer EV 2502-based compound are shown in **Table 4** along with compounds of NBR and HNBR.

The Evolmer compound demonstrates comparable tensile properties to those of NBR and HNBR. However, the Evolmer compound shows appreciably better compression set resistance measured at sub-ambient temperatures.

While tested at temperatures of -10°C or below, the compression set resistance of Evolmer was found to be significantly superior than that of NBR and HNBR. As seen in **Table 4**, heat resistance of Evolmer, measured at 120°C, is considerably more improved than NBR; this is comparable to marginally better than HNBR-S; but inferior to that of peroxide cured HNBR (HNBR-P).

The flex fatigue resistance of the Evolmer compound, as measured through De Mattia Flexomer, was found to be remarkably superior than that of the rubbers evaluated here, indicating its ability to withstand repeated flexing or bending without cracking. The heat build-up of Evolmer, measured through a Goodrich Flexometer, also is substantially lower (10+°C lower) than that of NBR and HNBR, indicating its potentially superior performance in dynamic applications.

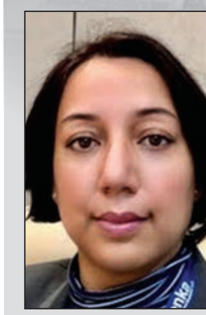
Hot oil resistance of Evolmer compounds at 120°C in terms of changes in specimen volume and elasticity (elongation of break values) are shown in **Table 5**. In general, the peroxide-cured HNBR (HNBR-P) compound shows the best retention of elasticity after being immersed in different standard oils, followed by

Table 1: Basic compounding formulations of Evolmer EV 2502 and other elastomers.

	EV-2502	NBR	HNBR-S	HNBR-P
Ingredients	*Amount (in phr)*			
Rubber	100	100	100	100
Stearic Acid	0.5	0.5	0.5	0.5
Antioxidant (s)	4	4	8	1
Carbon Black	50	62	58	50
Plasticizer/ Softener	10	10	10	10
ZnO	5	5	5	5
MgO (#150)	4			
Accelerator (TMU)	1			
Accelerator (TETD)			2	
Accelerator (TMTM)			1.2	
Sulfur		1.5	0.7	
Accelerator (MBTS)		1.5		
Peroxide (Perbutyl® P)				8

Table 2: Basic features of Evolmer EV 2502.

Molecular weight (by Gel Permeation Chromatography, GPC)	
M_n	14.6 x 10^4
M_w	34.4 x 10^4
PDI	2.4
Glass Transition Temperature (by Differential Scanning Calorimetry, DSC)	-23 °C
Specific Gravity	1.19
Rubber Mooney Viscosity; (ML_{1+4}), 100 °C	53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She has more than 19 years of experience in diverse areas of polymer science and engineering and previously worked at GE Plastics and DuPont.

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Huntsman CEO cautiously optimistic for second quarter

By Simon Robinson
Urethanes Technology International

THE WOODLANDS, Texas—Consumer confidence is the key to recovery in many downstream markets, Huntsman Corp. CEO Peter Huntsman told analysts in a recent conference call. Take, for example, the automotive industry.

Huntsman

"As we speak to our customers, I think there is very little inventory in the supply chain," Huntsman said. "I think you're going to see an impact of the improvement on a month-to-month basis. But, again, when I talk about the visibility that we have—how many units of automobiles will Ford or GM or BMW be running (in the near future)—that hasn't been told to us."

Huntsman contends, however, that consumer sentiment is just one of the many issues that will drive industry recovery.

The impact of the coronavirus pandemic has hit Huntsman's polyurethanes division particularly hard. In April, polyurethane orders fell by around 60 percent across the board. The Americas were down 90 percent and Asia fell by about 20 percent, he said.

Overall, orders for May were down around 50 percent, and June's orders by about 35 percent.

In the composite wood and other construction sectors, demand for Huntsman's products in April were down 35 percent, and could be down by 20 percent in June. Elastomers were down 60 percent in April and up to 45 percent in June.

Despite the drops in demand, Huntsman said the company has no plans for "idling any of our MDI manufacturing facilities. … We'll be matching the rate of production demand."

To this end, capacity is running at about 70 percent for Asia, 50 percent for the Americas, and 60 percent in Europe.

Looking regionally, Huntsman said that volumes in its Asia business were down 8 percent in the quarter with double digit drops in everything apart from insulation—which was up 11 percent—and footwear and adhesives, cast and elastomers, which were down by single digits.

There were, however, "improving trends starting at the end of February through March. We are cautiously optimistic that the worst is behind us in ACE in China," Huntsman said. "Our expectations for May and June are for sequentially improving conditions."

Comparing his company in January with the Huntsman that entered the financial crash in 2008, Huntsman said the polyurethanes business had entered the coronavirus pandemic with low stock levels of benzene—a key raw material for MDI. This means the company will be able to take advantage of low benzene prices soon after demand for MDI picks up.

The business is in better shape, too. Capacity for MDI is 370,00 metric tons higher than it was in 2008. Downstream markets with more stable and higher margins are a bigger share of sales than in 2009.

Finally, he addressed business in China.

"I think that domestic business is doing quite well." Huntsman said. "Over the last quarter, China has gone from restocking to real growth. We've seen about 4 percent growth in the Chinese business of our urethanes versus a year ago. And so, Asia all in all is up about 1 percent.

"As we look to China, we are quite bullish about what we see. Europe … we are definitely coming from the bottom of this particular cycle, and we see gradual rebuilding. The Americas are at that trough, and I think that, in the coming weeks, you'll start to see that pickup of automotive, aerospace and so forth."

Technical

Elastomer

Continued from page 17

Sour Fluid Immersion Test on Evolmer as per API 6A

Sour gas containing hydrogen sulfide (H2S) can have detrimental effects on elastomers. Upon exposure to sour gas, non-resistant elastomers typically become hard and brittle, losing their elastic properties and their ability to seal, ultimately leading to seal failure.[2]

Evolmer EV 2502 has been evaluated here for hot-mixed sour gas resistance as per well-recognized industry standard protocol: American Petroleum Institute (API) 6A/ISO 10423. The test conditions used are shown in **Table 9**.

Dimensions, hardness and tensile properties of the O-ring specimens made from the Evolmer EV 2502 compound, measured before and after sour gas exposure at 100°C, are monitored and the results are provided in **Table 10**. As observed, EV 2502 passes all requirements in API 6A.

Table 9: Experimental conditions of sour fluid immersion test on Evolmer EV 2502 as per API 6A.

Temperature	100 ºC
Pressure	11.1 (min)-11.9 (max)
Test Medium (Class FF/HH)	
Gas Phase	Mixed Sour Gas: **80% CO_2 10% H_2S 10% CH_4**
Liquid Phase	Kerosene (1200 ml); Deionized Water (100 ml)
Test Specimen	Size 325 O-rings
Replicates	5
Exposure Time	160 hrs, minimum

Table 10: Test results of sour fluid immersion test on Evolmer EV 2502 as per API 6A.

	Volume, cc	Hardness (Shore A)	50% Modulus (MPa)	100% Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
Unexposed	3.154	74	1.88	3.97	11.45	180.2
After Exposure	3.372	72	1.52	4.06	10.41	168.8
Change, %	**7%**	**-3% (-2 pts)**	**-19%**	**2%**	**-9%**	**-7%**
Qualification Limits	+25/-5 %	+5/-20 pts	±50%	±50%	±50%	±50%
	PASS	**PASS**	**PASS**	**PASS**	**PASS**	**PASS**

Rapid gas decompression (RGD) test on Evolmer as per NACE TM0192-2012

Rapid gas decompression (RGD), or explosive decompression (ED), is a failure mechanism of elastomer seals and O-rings caused by a rapid reduction in pressure of a gaseous media. Gas that may permeate into the elastomer seal expands violently when the pressure is released rapidly, causing seal failure.

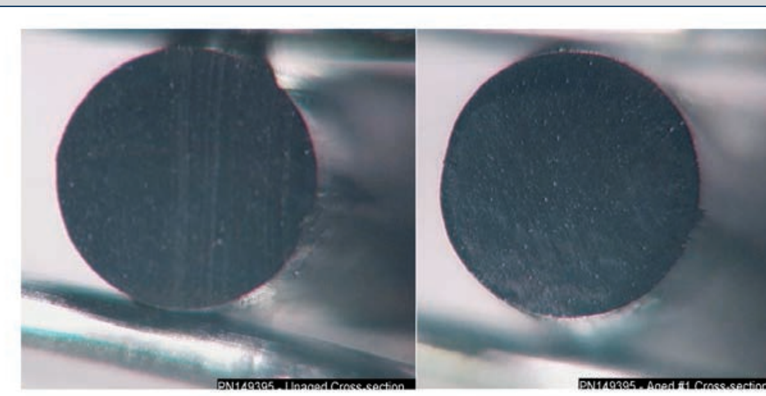
The conditions used as per NACE TM0192-2012 for the RGD test of Evolmer are shown in **Table 11**. After exposure to the test media, the test samples were subjected to a visual inspection for damage. That included both an examination of the whole O-ring under magnification and sectioning of the samples. Any physical damage was noted, and the test samples were given a numbered rating as defined by the system outlined in NACE TM0192-2012.

Table 11: Experimental conditions of rapid gas decompression (RGD) test on Evolmer EV 2502 as per NACE TM0192-2012.

Temperature	25 ºC
Pressure	5.2 MPa
Test Medium	99% Industrial Grade CO_2
Test Specimen	Size 325 O-rings
Replicates	3
Exposure Time	24 hrs., minimum
Pressure Release	≤1 min (~ 20 sec in actual)

With the Evolmer EV 2502-based compound, the surfaces of all three specimens after the test were smooth, free of pitting and blisters, analogous to their pre-testing condition (**Fig. 2**). All three samples were sectioned at randomly selected locations. No section revealed any visible blisters, cracks or other damage. These factors earned all three of the test samples the best possible rating of "1" on the NACE TM0192-2012 scale.

Fig. 2: Test results of rapid gas decompression (RGD) on Evolmer EV 2502 as per NACE TM0192-2012.



(a) Before Test (b) After Test

Conclusion

Evolmer EV 2502 demonstrates improved scorch safety, stable curing, excellent oil resistance, low temperature compression set and superior dynamic properties with appreciably lower heat build-up and remarkably higher flex-fatigue resistance.

In addition, Evolmer EV 2502 qualifies to sour gas resistance as per API 6A and best possible rating "1" in RGD tests as per NACE TM0192-2012, showing its promise in high performance seals and O-rings applications in both static and dynamic conditions.

References

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