Ultra High Molecular Weight NORDEL™ EPDM for TPV and Low Hardness Molded Goods Enabled by Advanced Molecular Catalyst

S. Wu¹, T. Han², V. Thakur³, R. Weeks¹, C. Li Pi Shan¹, and J. Tuberquia¹

¹ The Dow Chemical Company, Lake Jackson, Texas, USA
² Dow Chemical (China) Investment Co. Ltd., Shanghai, China
³ Dow Europe GmbH, Horgen, Switzerland

E-mail: ¹xswu@dow.com, ²than2@dow.com

Abstract. Ethylene propylene diene synthetic rubber (EPDM) is the material of choice to manufacture various automotive parts due to its natural stability and resistance to heat, UV, and ozone. In addition, its polyolefinic nature results in consistent processing and good filler and oil acceptance for use in compounds ranging from automotive weather sealing, under-the-hood belts and coolant hoses, roofing membranes, gaskets and other general rubber articles. Building on a fifty-year history of performance, Dow’s Advanced Molecular Catalyst (AMC) and process technology advancements enable highly tailored design of EPDM molecular architecture including, composition, molecular weight and long chain branching (LCB). This is not only resulting in capacity efficiency and sustainable production but also increasing design options of the molecular features to tailor the performance for high in-use efficiency. This paper summarizes a new ultra high molecular weight (UHMW) NORDEL™ EPDM product and its potential applications. Case studies will be presented to showcase its use in thermoplastic vulcanizate (TPV), black color low hardness compounds, and lighter color (gray) washing machine gasket application. The EPDM polymer structure, compound formulation, mixing performance, compound rheology, vulcanization characteristics, and mechanical property improvements are discussed.

1. Introduction

1.1 EPDM Catalyst Technology

There are six key variables that define the properties of EPDM rubbers: (a) polymer molecular weight, (b) molecular weight distribution, (c) comonomer (propylene) content, (d) comonomer distribution, (e) termonomer type, content and distribution and (f) long chain branching level. The most important factor in controlling these variables is catalyst technology. Commercial olefin polymerization catalysts not only have to produce EPDM products with the desired architectures and properties outlined above, but they also must exhibit high catalytic activity under the desired polymerization conditions. Additionally, precatalysts (neutral, unactivated complexes) need to be thermally stable at and above ambient temperature, as they are often stored for weeks before they are used.
Fig. 1 shows the differences between the different catalyst technologies that exist today to produce EPDM rubbers. The heritage Ziegler-Natta/Vanadium (ZN) catalysts developed in 1960s are still in use. However, this process technology is now antiquated due to its low production efficiency and high energy and water usage. In terms of catalyst and process, the Z-N catalyst suffers from low catalyst efficiency that operates at ambient and sub-ambient reaction temperatures and requires the removal of catalyst residues by steam stripping followed by drying of the polymer crumb [1]. A recent life cycle analysis reports that a Ziegler-Natta EPDM production process can use up to 50% more energy and has 30% more impact on the environment than Dow’s state-of-the-art solution process [2].

Dow first revolutionized the production of EPDM in 1997 with the introduction of its INSITE™ technology and use of metallocene catalysts in a high temperature solution process [3]. The direct advantages included catalyst efficiency, ten times higher than that of a Z-N catalyst and operated at significantly higher reaction temperatures and does not require the removal of catalyst residues. Due to the plants high temperature operation and special plant design, resulted in EPDM grades with almost no gels and improved product consistency that elevated the quality of EPDM and enabled Dow’s industrial partners to extrude products with Class A surface finish and reduced scrap.

Since the introduction of metallocene catalysts, Dow has continued with its generational development of polyolefin catalysts. Using high-throughput (HTR) catalyst screening technology, new catalysts were screened against targeted product-process improvements [4]. In the high-throughput screening and molecular modelling process, thousands of catalyst combinations are screened and optimized. As an output of the high-throughput screening process, Dow has introduced its new Advanced Molecular Catalyst technology (AMC) that leads the EPDM industry by enabling even higher process sustainability and catalyst efficiency. For the end-user of EPDM rubber, Dow’s AMC technology unlocks new molecular capabilities for the development of new products. For instance, the new AMC technology can efficiently produce EPDM with ultra-high molecular weight, higher diene content, and increased levels of long chain branching. In addition to process upgrades, oil-extension capability further extends the possibility to design & produce EPDMs with even higher molecular weights than conventionally used.
1.2 Thermodynamic Vulcanize

Thermoplastic vulcanizate (TPV) is a plastic elastomer alloy which consists of a high volume content fine particle size cross-linked rubber particles dispersed in a low volume content thermoplastic matrix. TPV is produced via dynamic vulcanization of immiscible blends of a rubber and a thermoplastic, i.e., the selective crosslinking of the rubber while melt mixing with the thermoplastic [5-8]. Today, the major commercial available TPVs are based on blends of ethylene propylene diene rubber (EPDM) with polypropylene (PP), and crosslinked with phenolic resin or peroxide curing agents [9].

TPV are considered as a high performance thermoplastic elastomers since they have the excellent elasticity and mechanical properties of thermoset rubbers and robust processability and recyclability of thermoplastics. This unique feature enable TPV to penetrate into many applications previously dominated by thermoset rubber.

TPV has been enjoying fast growth for it offers a number of advantages over thermoset rubbers. First of all, it addresses the light weight trend. TPV weighs 30% less than thermoset EPDM. Another advantage is that any scrap/flash generated, or even the end product itself, can be recycled back into the production. Therefore there’s is less waste. TPVs also require little or no compounding by the converter nor curing. For example, injection molding cycle times can be reduced to seconds rather than the minutes generally needed for molding and cure of thermoset rubbers.

Molecular weight and composition have been identified as the top design parameters for TPV grade EPDM. MW determines viscosity, which in turn has significant impact on phase inversion and morphology development. EPDM Crystallinity of EPDM strongly affects compression set at room temperature and at low temperature, low temperature oil retaining and tensile properties. For TPV applications, an ultra-high MW and tailored composition is desired.

1.3 Molded Rubber Goods

Molded goods are a diverse array of products using a mold to produce the required geometry such as seals, diaphragms, bushings, and mountings [10]. Compression molding, transfer molding, and injection molding are the major molding methods. Natural rubber and variety of synthetic rubbers are being used to produce molded rubber parts for various applications. EPDM has been the material choice to make grommets, boots, bellows, muffler hanger, engine mounts, and washing machine gasket where the weathering and heat resistance are important. In this case study, a low hardness soft compound designed for grommets with excellent elasticity and compression set resistant will be shared. Design a low hardness formulation with excellent mechanical properties is always a challenge. The ultra high molecular weight is required to have large number of chain entanglement therefore to provide the vulcanizate excellent mechanical properties after plasticized with large amount of mineral oil. Without pre-extended with oil, this ultra high molecular weight EPDM will have an extremely high Mooney viscosity and rubber elasticity making the processing a very challenging task therefore 75 phr hydrogenated paraffinic oil has been added to this EPDM rubber to lower the Mooney viscosity to 55 MU (ML1+4@125C) providing it excellent processablity.
2 Experiment

2.1 Materials and Formulations

The product specification of the newly developed ultra high molecular weight NORDEL™ EPDM is listed in the Table 1.

| Polymer          | Mooney Viscosity* | Ethylene content (wt%) | Diene content (wt%) | Oil (phr) |
|------------------|-------------------|------------------------|--------------------|-----------|
| UHMW EPDM        | 55                | 65                     | 4.5                | 75        |

*Note: Rubber Mooney viscosity is measured at 125 °C following ASTM D1646-15.

The phenolic resin cured TPV formulation is listed in Table 2.

| Ingredient                        | PHR   |
|-----------------------------------|-------|
| UHMW EPDM                         | 175   |
| Polypropylene (2 MFR)              | 58    |
| Clay                              | 42    |
| Paraffinic oil                    | 55    |
| Phenolic resin curatives           | 6.26  |
| Zinc oxide                        | 2     |
| Total                             | 338.26|

The low hardness molded compound formulations are listed in Table 3.

| Ingredient                        | Black | Gray  |
|-----------------------------------|-------|-------|
| UHMW EPDM                         | 175   | 175   |
| Zinc oxide                        | 5     | 5     |
| Stearic acid                      | 1     | 1     |
| Carbon black N550                 | 70    | 0.35  |
| TiO2                              | 0     | 10    |
| Mineral fillers                   | 0     | 170   |
| Coupling agent                    | 0     | 2.25  |
| Paraffinic Oil                    | 25    | 50    |
| Processing Aid                    | 3     | 5     |
| Stabilizer                        | 1     | 1     |
| Curatives                         | 6.75  | 6.75  |
| Total (PHR)                       | 286.75| 428.35|
2.2 Sample Preparation

2.2.1 TPV Sample Preparation

A single step compounding process was used for making UHMW EPDM based TPVs. The following components were blended (dry mixed): EPDM, polypropylene, clay filler, stannous chloride, and zinc oxide, to form a pre-blend. The pre-blend was added to a 26-mm twin-screw extruder with a total length-to-diameter ratio (L/D) of 60. Oil (50 PHR) and phenolic resin (5 PHR) were added through an injection port at barrel 3 or barrel 5. Additional oil (40 PHR) was injected at a barrel 5 or barrel 10. Before injection, phenolic resin was dissolved in heated process oil, at 120°C, and the solution was then added to the extruder using a Leistritz Gear Pump cart, with heat traced liquid feed systems. The crosslinked (compounded) composition (TPV) exiting the extruder was then pelletized using an underwater pelletization unit.

The TPV molded sample were injection molded using a Krauss Maffei KM 110-390/390 CL Injection Molder. Each test plaques were 4 inch x 6 inch x 0.125 inches in dimension. About twelve test plaques were prepared for each TPV composition.

The TPV tape sample was extruded using a Haake Rheocord System 9000 torque rheometer with a Rheomix 254 extruder. The Rheomix 254 is a 25 L/D single screw extruder equipped with ¾ inch screw and four zones. The extrusion process parameters were optimized for each material based on its rheological properties. A 0.25 mm thick tape sample with smooth surface was produced with each TPV material.

2.2.2 Low Hardness Molded Rubber Goods Mixing, Molding, and Curing

For the molded parts formulations, all compounds were mixed using an “up-side-down” mixing procedure. All filler, polymer, 2/3 of oil and all chemicals excluding sulfur were mixed for 90 seconds, after which the left over 1/3 oil were added. Mixing was continued for another 120 seconds, after which sulfur was added. The compounds were mixed for another 70 seconds then dropped. The mixer rotor speed was 35 RPM and the fill factor was 0.86. Mixing was completed on a 6” 2 roll mill at ambient conditions, a blanket was sheeted out to use for rheology and mechanical testing.

Compounds were cured on a hot press for t90 + 5 minutes at 180 °C for tensile and tear testing following ASTM D3182-15. Testing specimens were cut from the cured sheets. Compression set specimen were cured for t90+12 minutes at180 °C. Cured specimens were conditioned for at least 18 hours before testing.

2.3 Characterization

2.3.1 TPV Sample Characterization

Atomic Force Microscopy (AFM)

Samples were polished under cryogenic conditions using a Leica UCT/FCS microtome operated at 120°C. Thin sections (about 160 nm) were cut from sample and placed on a mica surface for AFM analysis. Topography and phase images were captured at ambient temperature by using a Digital Instruments (now Veeco) Multi-Mode AFM equipped with a NanoScope IV controller.

Shore A Hardness

Hardness was measured with a Shore A type durometer (ASTM D2240). The durometer was placed onto a plaque of ~0.125 inch thickness, prepared by injection molding procedure described earlier.
Compression set
Compression set was measured according to ASTM D 395 at 70 °C and 120 °C. Pucks with 29.0 mm (±0.5mm) diameter were extracted from the injection molded plaques of ~3 mm thickness. For each sample, four pucks were inspected for notches, uneven thickness and inhomogeneity, and were stacked such that the total height was 12.5 mm (± 0.5 mm), equating to compressive strain of 25% when a 9.5 mm spacer was used.

Stress-strain Properties
Tensile properties were measured at room temperature following the method of ASTM D-412, on micro-tensile specimens that were die cut from the injection molded plaques.

Oil resistance
Sample specimens were die cut from injection molded plaques, which were made as described in the Injection Molding section below, into tensile bars. Oil resistance was measured in accordance with ASTM D471-98 in which the sample was immersed in oil, specifically IRM-903, at 125 °C.

Extrusion Surface Quality
The surface quality of the extruded tape made from the TPV compound was evaluated using a visual rating of the tape appearance and smoothness, including the edge uniformity and surface smoothness. Additionally, the surface roughness can be measured by confocal laser scanning microscopy (CSLM). A coarse surface texture is indicative of poor dispersion of the rubber phase, and may also represent an incomplete phase inversion (when thermoplastic polymer (e.g., PP) becomes the continuous phase).

2.3.2 Low Hardness Molded Rubber Goods Sample Characterization
Mooney Viscosity
Mooney viscosity of gum and compounds were measured using an Alpha Technologies Mooney Viscometer following ASTM D1646-15.

Moving Die Rheometer (MDR)
Cure kinetic profiles at 180 °C were measured using an Alpha Moving Die Rheometer (MDR-2000) following ASTM D5289-15.

Tensile strength
The tensile properties of the solid vulcanizate were acquired following ASTM D1708.

Die-C Tear strength
Die-C tear strengths of the solid vulcanizate were obtained using ASTM D624.

Compression set
The compression set has been measured at three conditions (72 hours @ 100 °C, 150 °C) according to ASTM D 395 Method B.
3 Results and Discussion

3.1 Ultra High Molecular Weight NORDEL™ EPDM based TPV

A new ultra-high MW NORDEL™ EPDM was developed based on the understanding how molecular architecture affects TPV properties. The features of the new polymer include ultra-high molecular weight for better morphology development and mechanical properties, tailored composition for better balance of properties and 75 phr (43 wt%) oil extended for balanced throughput and formulation flexibility. The product specification was listed in Table 1.

Table 4 summarized physical properties of a TPV product based on the UHMW EPDM, compounded on a commercial-scale twin screw extruder with a single step process. TPV sample showed excellent properties such as compression set, tensile strength, tear strength and oil swell. The extruded TPV also demonstrated excellent extrudates surface quality. Surface roughness as characterized by Sq of 25 micron was measured with confocal laser scanner as shown in Fig. 2.

Table 4: Typical physical properties of TPV based on UHMW NORDEL™ EPDM

| TPV Mechanical Properties       | Value   |
|---------------------------------|---------|
| Hardness (Shore A)              | 62      |
| Compression Set % (22 hours @ 70°C) | 27      |
| Compression Set % (70 hours @ 120°C) | 48      |
| Die-C Tear Strength kN/m (MD/CD*) | 25.7/28.5 |
| Elongation % (MD/CD*)           | 222/436 |
| Tensile Strength psi (MD/CD*)   | 5/6.2   |
| Oil Swell % (168 hr @ 120°C)    | 103     |

*Note: MD is machine direction; CD is cross direction.

Fig. 2. Surface Roughness (Sq) measured on Extruded TPV tape by Confocal Laser Scanning (a) left image: surface roughness (b) right image: surface morphology
Fig. 3. Morphology of Dow UHMW EPDM based TPV. Left image: AFM image with scale bar of 20 micrometer (b) right image: AFM image with scale bar of 2 micrometer

Fig. 4. Morphology of Dow UHMW EPDM based TPV sample diluted with PP at 50:50 volume ratio. Left image: AFM image with scale bar of 20 micrometer (b) right image: AFM image with scale bar of 2 micrometer

All TPV morphologies were characterized by agglomerated rubber particles dispersed in the polypropylene matrix. The agglomeration was due to the high volume ratio of the oil-swelled rubber phase. The diluted phase morphologies clearly showed ultra fine EPDM particles at 1-3 micron size depicted by Fig. 4.

Thermoplastic Vulcanizate (TPV) is a unique member of thermoplastic elastomer family as it could be melt processed as thermoplastic and has thermoset rubber like elastic properties. The EPDM/PP type TPV is the most common one, it contains micron-sized fully crosslinked EPDM rubber particles dispersed homogenously in a continuous PP matrix. By tuning the molecular architecture of EPDM produced by Dow’s Advanced Molecular Catalysis and process technology
advancements, a new Ultra-high MW NORDEL™ EPDM was developed to enable TPV with excellent physical properties and superior surface smoothness.

### 3.2 Low Hardness Molded Rubber Goods (Black and Gray Color)

The compound Mooney is simply an indicator of the rubber compound processability; the different processing techniques require different compound Mooney viscosity to provide proper performance. Usually, the suitable compound Mooney range for injection molding is around 25 to 65 MU (tested at 100 °C) and up to 100 MU for compression molding. The compounds Mooney of the two low hardness formulations were listed in Table 5; both compounds showed proper Mooney viscosities suitable for molding process. The curing density, scorch time, and curing time were tested using moving die rheometer (MDR) at 180 °C and the data were summarized in Table 6.

| Compound Mooney Viscosity | Black | Gray |
|---------------------------|-------|------|
| ML (1+4) @ 100°C (MU)     | 51    | 42   |

| Curing Characteristics | Black | Gray |
|------------------------|-------|------|
| ML(dNm)                | 1.35  | 1.34 |
| MH(dNm)                | 8.63  | 7.9  |
| MH-ML(dNm)             | 7.28  | 6.56 |
| ts1 (min)              | 0.11  | 1.12 |
| ts2 (min)              | 0.76  | 1.47 |
| tc10(min)              | 0.95  | 0.97 |
| tc50(min)              | 0.69  | 2.04 |

As shown by both formulations, they were soft with hardness around 40 Shore A, had more than 10 MPa tensile strength with over 600% ultimate elongation which are highly required for many automotive and appliance applications such as grommet, bellows, boots, and washing machine gaskets.
Table 7. Mechanical Properties of Black and Gray Color Low Hardness Molded Goods

| Mechanical Properties | Black  | Gray   |
|-----------------------|--------|--------|
| Density (g/cc)        | 1.02   | 1.23   |
| Hardness (Sh.A)       | 44     | 38.6   |
| Young's Modulus (MPa) | 3.14   | 2.34   |
| 10% modulus(MPa)      | 1.75   | 1.39   |
| 50% modulus(MPa)      | 1.03   | 0.72   |
| 100% modulus(MPa)     | 0.87   | 0.53   |
| Tensile strength (MPa)| 11.77  | 11.2   |
| Elongation at break (%)| 698.71 | 818.1  |
| Die-C tear (kN/m)     | 28.83  | 20.31  |
| Compression set       |        |        |
| 72 hours @ 100 °C (%) | 48     | NA     |
| 72 hours @ 150 °C (%) | 57     | NA     |

From these two 40 Shore A formulation study, we could conclude that the newly developed oil extended ultra high molecular weight NORDEL™ product is an ideal EPDM for the manufacturing of low hardness molded rubber parts which require high mechanical strength and ultimate elongation at break.

4 Conclusion
The rubber industry uses EPDM materials from three different generations of catalyst and process technologies; traditional ZN, metallocene, and now Dow’s new Advanced Molecular Catalyst technology. The new AMC technology developed by Dow Chemical leads the EPDM industry in process sustainability and production efficiency; saving up to 50% less energy and having 30% less impact on the environment in comparison to the traditional ZN process.

By tuning the molecular architecture of EPDM produced with Dow’s Advanced Molecular Catalysis and process technology advancements, a new Ultra-high MW NORDEL™ EPDM was successfully developed and proven to be an ideal EPDM to produce premium TPV with excellent physical properties, excellent surface smoothness and also suitable to manufacture low hardness molded rubber parts where high mechanical strength and ultimate elongation at break are required. Please add some general conclusion on molded parts.

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