EPDM Technical Report

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1. Introduction

This report, reviews the technology for producing ethylene propylene-diene (EPDM). This report also reviews some cases of random ethylene-propylene copolymer (EPM) production. A technology review for ethylene-propylene copolymers—the highly crystalline, stereoregular, and block copolymers, in particular—is, however, not included.

EPDM elastomers are produced by three different processes: the solution process, the suspension process (also known as the slurry process), and the gas-phase process. Conventional Ziegler-Natta catalyst systems based on transition metals, such as V and Ti, are commercially used for most of these processes. Currently, metallocene catalyst systems based on Zr, Ti, or Hf also attract the industry's attention for EPDM production. Du Pont/Dow Elastomer, a joint venture between Du Pont and Dow Chemical, has started to produce EPDM by a solution process using Dow's Insite™ metallocene catalyst. The gas-phase process developed by Union Carbide is also recently commercialized. In this report, we evaluate and compare these processes, which use either ethylidene norbornene (ENB) or 1,4-hexadiene (HD) as the nonconjugated diene in the terpolymer, and either Ziegler-Natta or metallocene catalyst systems for polymerization. The processes can be briefly described thus:

- Solution process for EPDM containing HD by Ziegler-Natta catalyst—the EPDM(HD) elastomer is made in a process presumably used commercially by Du Pont; the polymer is recovered without steam-stripping.
- Solution process for EPDM containing ENB by Insite™ metallocene catalyst—the EPDM(ENB) elastomer is produced in a manner similar to the solution process for EPDM(HD), but this process uses a high polymerization temperature, which allows a high resin concentration in the reactor effluent.
- Solution process for EPDM containing ENB by Ziegler-Natta catalyst—the EPDM(ENB) elastomer is produced in a conventional process with steam-stripping to recover the polymer.
- Gas-phase process for EPDM containing ENB by pre–polymerized Ziegler-Natta catalyst—the EPDM(ENB) elastomer is made in a process presumably similar to the commercial process used by Union Carbide.
- Suspension process for EPDM containing ENB by Ziegler-Natta catalyst—the EPDM(ENB) elastomer is produced in excess propylene.

In the EP elastomer industry, it is difficult to differentiate the market share of EPDM elastomers from EPM elastomers. We estimated that EPDM elastomers account for about 80–85% of total worldwide EP elastomer production. The supply and demand given in this report, however, include both types of elastomers. The worldwide production capacity for EP elastomers as of July 1998 was estimated at about 2.5 billion lb/y (1.14 million t/yr), of which 50% is accounted for by producers in the United States, 26% in Western Europe, and 19% in Japan. World consumption of EP elastomers for 1997 is estimated at about 1.59 billion lb/yr (720,000 t/yr).

GENERAL ASPECTS

In 1998, worldwide production capacity for ethylene-propylene (EP) elastomers is estimated at 2.5 billion lb/yr (1.14 million t/yr). The United States, Western Europe, and Japan are major producing regions, accounting for more than 90% of the total. World consumption of EP elastomers in 1997 was estimated at 1.59 billion lb/yr (720,000 t/yr), of which 86% is consumed in the three major regions. Automotive applications account for the majority of EP elastomer market share: in the United States, 45%; in Western Europe, 55%; and in Japan, 60%. Therefore, the performance of the automotive industry in these regions significantly affects the demand for EP elastomers.

For the next five years, the average growth of worldwide demand for ethylene-propylenediene (EPDM) is estimated at 2–3%/yr. Apparently, the EP elastomer industry will experience overcapacity for the rest of this century. Because the trading of EP elastomers is more global than ever, the effects of oversupply will prevail worldwide, particularly with the recovery of the Asian economies still in doubt.

TECHNICAL ASPECTS

Commercially, three processes are used for producing EPDM: the solution process, the suspension (or slurry) process, and the gas-phase process. The majority of EP elastomer producers use the solution process, with only two producers using suspension and one producer using gas phase. All commercial EPDM plants in the world—except one of Du Pont/Dow Elastomer’s plants at Plaquemine, Louisiana—use Ziegler-Natta catalyst systems for their polymerization. The Plaquemine plant, which began operations early in 1998, uses Dow’s Insite™ metallocene catalyst technology for producing EPDM in the solution process. Also started in 1998 is Union Carbide’s plant at Seadrift, Texas, which uses the company’s Unipol® gas-phase process involving a Ziegler-Natta catalyst.

This report presents a technology review and an economic evaluation of commercially used EPDM processes. Tables 2.1 through 2.3 summarize the design bases and assumptions for three EPDM processes. Table 2.4 presents a summary of capital investment and production costs for these processes, each with a design production capacity of 200 million lb/yr (90,700 t/yr).

Solution Process: EPDM by the Insite™ Metallocene Catalyst

In June 1997, Du Pont/Dow Elastomer, a 50/50 joint venture between Du Pont and Dow Chemical formed in April 1996, started producing a new line of EPDM elastomers designated Nordel IP, which are made by a solution process using Dow's Insite™ metallocene catalyst. We evaluated the process using information derived from the Du Pont patents for the solution process and from the Dow patents for the titanocene catalyst system and reaction conditions. We also made an economic comparison between the present process and two conventional solution processes—one that Du Pont presumably uses to produce its EPDM(HD), and one that produces EPDM(ENB) with steam-stripping to recover monomers and solvent (see Table 2.5). One characteristic of the present process is high thermal efficiency, which results in a lower capital investment for the process than the capital investment required for the two other processes, as shown in Table 2.5.

In the Du Pont/Dow Elastomer process, the monomers are pretreated before polymerization, which is carried out continuously in a horizontal reactor equipped with a set of outer ribbon blades pitched in a direction opposite to a set of inner ribbon blades. The heat of polymerization is dissipated partly by precooled feed streams and partly by evaporative removal of some of the volatile reaction mixture. Using the titanocene catalyst allows the polymerization to be performed at a high temperature, such that a higher EPDM concentration (16.4 wt%) in the reactor effluent than that from a conventional solution process (10–13 wt% at 30–50°C [86–122°F]) can be achieved without operation difficulties. The double ribbon agitators used in the horizontal reactor certainly make the operation easier. The high operating pressure used in the process helps to recover unreacted monomers and solvent and makes the process more energy efficient.

EPDM product is recovered from the polymer solution through a phase separation conducted at less than 238°C (460°F) and 3.4 MPa (500 psia), conditions similar to those claimed in the Du Pont patents for separating EPDM(HD) from its solution. Since the type of diene is the only major difference between these two cases, it is our assumption that the EPDM product in the present process could be separated with such a technique. Nevertheless, one would need to confirm such an assumption in a laboratory.

Gas-Phase Process: EPDM by the Prepolymerized Ziegler-Natta Catalyst

In 1997, Union Carbide announced plans to build a 198 million lb/yr (90,000 t/yr) EPDM plant at Seadrift, Texas, using its Unipol® gas-phase technology. In the gas-phase process, polymerization is carried out in the presence of a Ziegler-Natta catalyst, which can either be charged as a prepolymerized catalyst system or can be nonprepolymerized. In the latter case, using a fluidization aid, such as carbon black or silica, is necessary to maintain stable fluidization and to avoid agglomeration of polymer particles and sheeting on the reactor walls. Using carbon black limits the production to black EPDM product.

Carbon black in the product might also make removal of residual ethylidene norbornene (ENB) from the product more difficult. Using silica in the polymerization delivers an EPDM product with silica impurity, which may not be desirable in certain applications. For these reasons, we chose the prepolymerized Ziegler-Natta catalyst system for our design of the gas-phase process.

The prepolymerized catalyst system is made in a batch operation that begins with preparing a catalyst precursor from vanadium dichloride (VCl_3) and diethylaluminum chloride (DEAC) in the presence of tetrahydrofuran (THF) and isopentane. The precursor is then used to prepare prepolymerized catalyst in the second-step prepolymerization with ethylene and propylene. The prepolymerized particles have nonsticky polymeric surfaces, or shells, with active catalyst sites in the interior of the particles. It is important to make prepolymerized particles with shells of high elasticity and a high degree of prepolymerization. The final resin product generated from the catalyst must retain a sufficiently thick wall without ultimate breaks. Such breaks can result in diffusion of sticky polymer, causing agglomeration.

As indicated in Table 2.4, the gas-phase process has advantages in both capital investment and production costs compared to the solution and suspension processes. However, the long retention time required for polymerization in this process makes producing multiple grades less desirable than in the other processes.

Suspension Process: EPDM by the Ziegler-Natta Catalyst

The suspension process can handle polymer concentrations in the reactor effluent up to 30 wt%—a much higher concentration than that in the solution processes presented in this report. These higher concentrations are attributable to the characteristics of the suspension process.

The polymerization in this process is carried out in a jacketed stirred-tank reactor in the presence of a Ziegler-Natta catalyst. Most of the unreacted monomers that leave the reactor are compressed, cooled, and recycled to the reactor along with the makeup monomers. The polymer slurry from the reactor is mixed with a small amount of polypropylene glycol to deactivate the catalyst before the slurry is washed with aqueous caustic soda and steam-stripped to remove the residual monomers.

The monomers recovered from the steam-stripping are decanted, distilled, and dried before they are recycled for polymerization. The stripped polymer slurry in aqueous solution is drained of excess water, compressed to remove residual water, and dried through an expander-dryer. The dried EPDM is packed in bales rather than pelletized as in the other processes.

Table 2.1

SOLUTION PROCESS FOR EPDM(ENB) BY INSITE™ METALLOCENE CATALYST

DESIGN BASES

References	306587, 306615, 306616, 372992, 435484, 463623, 463630, 463632
Polymerization conditions	
Temperature, °C (°F)	120 (248)
Pressure, MPa (psia)	3.4 (500)
Residence time, minutes	15
Reactor type	Horizontal, with double ribbon blades
Solvent	n-Hexane
Conversion per pass, %	
Ethylene	25.0
Propylene	3.8
ENB	12.9
Overall yield, %	
Ethylene	99.95
Propylene	99.91
ENB	95.57
Catalyst type	Titanocene
Catalyst efficiency, g of resin/g of Ti	258,500
Polymer composition, wt%	
Ethylene	62.3
Propylene	32.7
ENB	5.0
Recovery of polymer	Phase separation at 6.9 MPa (1,000 psia) and 238°C (460°F)

Table 2.2

GAS-PHASE PROCESS FOR EPDM(ENB) BY PREPOLYMERIZED ZIEGLER-NATTA CATALYST

DESIGN BASES

References	438472, 438473, 463383, 463385, 463393, 463456, 463463, 463469, 463472, 463473, 463485, 463488, 463508
Polymerization conditions	
Temperature, °C (°F)	75 (167)
Pressure, MPa (psia)	2.0 (294)
Gas superficial velocity, ft/s	2.75
Residence time, hours	4
Reactor type	Fluidized-bed
Catalyst type	Prepolymerized Ziegler-Natta
Ethylene:propylene in feed, by mole	2.38:1
Conversion per pass, %	
Ethylene	3.8
Propylene	0.8
ENB	90.0
Overall yield, %	
Ethylene	98.9
Propylene	94.2
ENB	99.7
Catalyst precursor composition, wt%	
DEAC	13.8
THF	6.6
VCl_3	3.6
Silica	76.0
Prepolymerization conditions	
Temperature, °C (°F)	30–50 (86–122)
Pressure, MPa (psia)	0.3–0.44 (44.1–64.7)
Cycle time, hours	6
Reactor type	Stirred-tank, with cone-shaped bottom
Catalyst type	Catalyst precursor, plus promoters
Ethylene:propylene, by mole	80:1
Conversion of monomers, %	100

Table 2.3

SUSPENSION PROCESS FOR EPDM(ENB) BY ZIEGLER-NATTA CATALYST

DESIGN BASES

References	306642, 306643, 306644
Polymerization conditions	
Temperature, °C (°F)	20 (68)
Pressure, MPa (psia)	1.1 (180)
Residence time, minutes	25
Ethylene:propylene in feed, by mole	1:3.75
Conversion per pass, %	
Ethylene	27.85
Propylene	2.75
ENB	64.0
Overall yield, %	
Ethylene	99.7
Propylene	97.0
ENB	88.3
Reactor type	Stirred-tank
Catalyst type	Vanadium-based Ziegler-Natta
Catalyst composition, wt%	
$V(AcAc)_3$	2.6
DEAC	61.5
Ethyl dichloromalonate	6.0
Ethyl chloromalonate	29.9
Polymer composition, wt%	
Ethylene	60.1
Propylene	33.3
ENB	6.6

Table 2.4

ECONOMIC COMPARISON OF THREE EPDM(ENB) PROCESSES

	SOLUTION PROCESS FOR EPDM(ENB) BY INSITE™ CATALYST	GAS-PHASE PROCESS FOR EPDM(ENB) BY PREPOLYMERIZED Z-N CATALYST	SUSPENSION PROCESS FOR EPDM(ENB) BY Z-N CATALYST
CAPACITY (MILLION LB/YR)	**200**	**200**	**200**
INVESTMENT ($ MILLIONS)			
BATTERY LIMITS	79.5	84.4	80.8
OFFSITE	43.4	33.0	46.8
TOTAL FIXED CAPITAL (TFC)	122.9	117.4	127.6
PRODUCTION COSTS (¢/LB)			
RAW MATERIALS	53.57	38.89	44.86
UTILITIES	2.30	1.08	3.38
VARIABLE COSTS	55.87	39.97	48.24
OPERATORS/SHIFT	5	5	6
LABOR COSTS	1.99	2.07	2.18
OTHER DIRECT COSTS	1.26	1.34	1.29
INDIRECT COSTS	2.82	2.83	3.02
PLANT CASH COSTS	61.94	46.21	54.73
DEPRECIATION, 10%/YR OF TFC	6.15	5.87	6.38
G&A, SALES, RESEARCH	15.00	15.00	15.00
TOTAL PRODUCTION COST	83.09	67.08	76.11
25% ROI	15.37	14.67	15.95
PRODUCT VALUE	98.46	81.75	92.06

Table 2.5

ECONOMIC COMPARISON OF THREE EPDM SOLUTION PROCESSES

	SOLUTION PROCESS FOR EPDM(ENB) BY INSITE™ CATALYST	**SOLUTION PROCESS FOR EPDM(HD) BY Z-N CATALYST**	**SOLUTION PROCESS FOR EPDM(ENB) BY Z-N CATALYST**
CAPACITY (MILLION LB/YR)	**200**	**200**	**200**
INVESTMENT ($ MILLION)			
BATTERY LIMITS	79.5	80.3	95.5
OFFSITE	43.4	49.2	94.6
TOTAL FIXED CAPITAL	122.9	129.5	190.1
PRODUCTION COSTS (¢/LB)			
RAW MATERIALS	53.57	35.04	47.75
UTILITIES	2.30	2.96	10.88
VARIABLE COSTS	55.87	38.00	58.63
OPERATORS, MEN/SHIFT	5	5	6
LABOR COSTS	1.99	2.00	2.40
OTHER DIRECT COSTS	1.26	1.27	1.51
INDIRECT COSTS	2.82	2.89	3.82
PLANT CASH COSTS	61.94	44.16	66.36
DEPRECIATION, 10%/YR OF TFC	6.15	6.47	9.5
G&A, SALES, RESEARCH	15.00	15.00	15.00
TOTAL PRODUCTION COST	83.09	65.63	90.86
25% ROI	15.37	16.18	23.76
PRODUCT VALUE	98.46	81.81	114.62