

# EXECUTIVE SUMMARY

## 0.1 INTRODUCTION

### 0.1.1 Introduction to Study

Polybutadiene is a term used to denote homopolymer of butadiene C<sub>4</sub>H<sub>6</sub>. Polybutadiene rubber (PBR) is used in various applications - tyre and non-tyre sectors. Polybutadiene latex is used in latex form in the production of ABS resins. Since polybutadiene latex is always produced for captive consumption by ABS resin units, the study therefore focuses only on PBR.

### 0.1.2 Rubbers

Rubbers can be classified into two broad groups - natural and synthetic. In the total global rubber consumption, natural rubber (NR) consumption is approximately 36%. Among the various synthetic rubbers (SR), PBR is the second most important synthetic rubber, next only to styrene butadiene rubber (SBR).

### 0.1.3 Rubber Applications

Traditionally, the tyre application has been the major end-use for rubber : both natural and synthetic. Tyre applications account for 57% of total synthetic rubber consumption. Technical rubber goods for automotive industry rank second. Rubber toughening or rubber modification of thermoplastic and thermoset materials is the third-largest area of applications.

### 0.1.4 Polybutadiene Rubber

Polybutadiene, for the first time was prepared by Lebdev, a Russian in 1910 by using alkali metals as the initiator in diene polymerizations. His work eventually led to the first industrial production facility. During the 1920's and 30's emulsion polymerization process was developed for styrene -butadiene rubber (SBR). Despite the arduous efforts, emulsion polymerized polybutadiene rubber was not accepted as a large scale

commercial prospect in 1940's. Development of stereo- specific catalyst systems in mid 1950s marked a significant development in PBR manufacturing.

#### **0.1.5 PBR Properties**

Depending upon the disposition of the double bonds present in the polymer chain, PBR can be classified into five configuration cis- 1,4; trans-1,4; vinyl-1,2-isotactic; vinyl-1,2-syndiotactic ; and vinyl-1,2 atactic. Depending on the choice of catalyst system, PBR can be prepared ranging from almost 100% cis to 100 % trans or 100% vinyl. Out of these configurations, medium and high cis varieties are of commercial importance.

#### **0.1.6 PBR Manufacturing**

Polybutadiene rubber is prepared by either emulsion or solution polymerisation. In general these processes are based on organo-lithium compounds or co-ordination catalysts. Polymerization is carried out using pure dry butadiene and a solvent. When the desired conversion is achieved, the catalyst is deactivated and polybutadiene is recovered from the unreacted butadiene and solvent, washed to remove the catalyst residue, and dried.

**0.1.7** Hydroxyterminated polybutadienes are valuable intermediates (apart from their potential in block copolymer systems) as they can be used with a wide range of curing, cross-linking and chain extending agents. They are also used as binders for rocket propellants and in mastics and adhesives applications. HTPB is being manufactured by IPCL and Vikram Sarabhai Space Centre has been using it since mid eighties.

#### **0.1.8 PBR Processing**

PBR undergoes mastication, mixing, moulding and curing. It is normally cured with sulphur or peroxide systems after blending with some other elastomers. PBR is normally blended with other elastomers to enhance processability.

#### **0.1.9 PBR Applications**

PBR finds its major outlet in the tyre sector. It is also used in acrylonitrile-butadiene-styrene resins (ABS Resins) and in high-impact polystyrene (HIPS). Various other applications are belts, hoses and footwear. In tyre application, apart from enhanced tread groove cracking

resistance, PBR imparts improved tread-wear resistance and low temperature flexibility. This results in low heat built-up and this property increases tyre life by keeping it cooler. Due to properties like low gel content, low temperature flexibility, narrow molecular weight distribution, better resilience, low water absorption & greater stability, PBR is favoured for the above mentioned non-tyre uses.

#### **0.1.10 Polybutadiene in ABS Resins**

Polybutadiene latex is used in the production of ABS resins, where polybutadiene is grafted with styrene and acrylonitrile and is dispersed in a rigid styrene acrylonitrile (SAN) matrix. ABS is manufactured by emulsion polymerization, mass (bulk) polymerization or combined processes. Although historically emulsion process has dominated, recently mass process has achieved commercial importance.

### **0.2 INDIAN INDUSTRY STRUCTURE AND STATUS**

#### **0.2.1 Indian Rubber Goods Industry**

The origin of the Indian rubber goods industry dates back to the year 1921, when the first rubber goods manufacturing unit was established in West Bengal. Today the rubber goods industry in India consists of 27 automotive tyre manufacturing units, around 170 medium scale units, around 5000 units in small scale sector and numerous tiny ones for misc. rubber products. However even today per capita consumption of rubber in India works out to be very low- 0.6 kg in comparison with other countries- 13 kg. in Japan.

#### **0.2.2 PBR industry in India**

In early 1970s, IPCL set up PBR manufacturing facilities with the know-how from Polymer Corporation of Canada. The commercial production in this plant with the installed capacity of 20,000 TPA started in 1978. PBR's consumption has substantially increased from around 100 tons in 1973-74 to over 30,000 tons today.

#### **0.2.3 PBR Manufacturing Technology**

PBR is currently being produced by only one unit in India i.e., IPCL. The IPCL plant has adopted a technology to produce high

cis-PBR, which involves solution polymerization using stereo-specific Ziegler-Natta type catalyst system, based on cobalt. The process uses benzene as a solvent. The project cost at the time of project implementation was approximately Rs. 30 crores.

#### **0.2.4 PBR Production and Consumption**

With the current production levels of 19,000 TPA, IPCL's PBR plant capacity utilization is 95%. At present IPCL produces only two grades of PBR- CISAMER 1220 and CISAMER G.P. The former which accounts for 60-70% of total production, is used by the tyre sector while the later is being consumed for non-tyre applications. The overall consumption of PBR by Indian rubber industry today is over 33000 TPA (1993-94), amounting to a compounded average growth rate of 6.5% per year in last decade.

Automotive tyres sector is the largest consumer of PBR rubber. Today it accounts for about 70% share, followed by tread rubber- 17%, cycle tyre 6%, and HIPS 3%. PBR consumption forecasts for the years 1994-95 and 1999-2000 are estimated to be approximately 33000 TPA and 65000 TPA respectively.

#### **0.2.5 PBR : Additional Production Capacities**

To meet the increased demand of PBR, IPCL has planned to set up another plant at Baroda. For this plant Japan Synthetic Rubber Co. Ltd. (JSR) has been selected as the process licensor. The cost of the 30,000 TPA PBR project is estimated to be Rs. 150 crores. This project also is based on solution polymerization, but will use nickel based catalyst system. The commercial production is expected to begin in 1995-96.

Apart from IPCL's proposed expansion project, Haldia Petrochemicals, Mr. R. P. Goenka and Mr. A. S. Vaidyanathan have proposed to set up PBR manufacturing units. However, it appears that except for IPCL's proposed expansion project, no other additional production capacity is likely to go on stream in near future. The shortfall in the supplies till then will be met by the imports. It is, therefore, desirable to plan more production facilities of PBR beyond 2000 A.D.

The credit for developing the basic indigenous ABS process goes largely to Shriram Institute for Industrial Research (SRIIR) and National Research Development Corporation (NRDC). License for ABS know-how was obtained by Polychem, ABS Plastics and Synthetics and Chemicals in mid seventies. Besides them two more companies viz., Bhansali Engineering Polymers Ltd., and Gujarat Binil Chemicals Ltd., have established facilities for production of ABS.

1. **ABS Plastics Ltd., Barodak**

The technology for the 2000 TPA plant which was set up in 1978, was obtained for NRDC. However the company has claimed to have made a number of modifications in the original process to produce ABS resin commercially. The original 2000 TPA plant was expanded to 5000 TPA in 1988-89 based on technology supplied by Japan Synthetic Rubber Company, Japan. In the second phase expansion to 14,600 TPA also, JSR know-how was used. Both the original SRIIR and subsequent JSR processes are based on emulsion graft polymerization.

2. **Bhansali Engineering Polymers Ltd., Madhya Pradesh**

The 6000 TPA project with an investment of Rs. 75 crores was commissioned in 1990. The present installed capacity is 7500 TPA. Bhansali have obtained technical know-how from Sumitomo Chemical Engineering Ltd. of Japan. The plant and machinery was obtained from both indigenous and foreign sources. The Sumitomo process adopted by Bhansali Engineering Polymers is a 3 step polymerization process in which polybutadiene latex is produced and the styrene and acrylonitrile are grafted on the latex in a separate reactor. SAN is polymerized separately and latex blended with the rubber latex.

3. **Polychem Ltd., Baroda**

Originally Polychem had obtained the basic know-how from SRIIR/NRDC. For its expansion, Polychem obtained foreign collaboration approval for import of technology for mass (bulk) polymerization process from Panama Ltd. The new process has much lower raw materials and utilities consumption and also has greater flexibility for production of new grades. The original installed capacity was 2000 TPA and present installed capacity is 5000 TPA.

#### 4. Gujarat Binil Chemicals Limited, Ankleshwar

Gujarat Binil's plant is a combined plant for production of ABS, SAN, general purpose polystyrene and high impact polystyrene. The basic process is quite similar to continuous bulk polymerisation of Dow Chemicals, but was developed indigenously. Gujarat Binil have claimed process advantages in their continuous bulk plant in terms of very low air and water pollution, greater control over product properties and lower investment costs.

Their combined installed capacity of engineering thermoplastics (ABS, GPPS, HIPS, SAN) is 2200 TPA. The ABS production in 1991-92 was only 200 tons.

### 0.3 INTERNATIONAL SCENARIO

#### 0.3.1 Developments in Last Three Decades

Discovery of Ziegler-Natta catalyst systems is an important landmark in PBR manufacturing. In less than a decade after discovery, more than two dozen commercial PBR plants were set-up world wide. In the year 1990, PBR accounted for 14% of the synthetic rubber production capacity worldwide. Today, volume-wise, PBR has become second most important synthetic rubber. In the year 1993, global consumption of PBR amounted to 1.4 million tons (excluding Eastern Europe and CPEC) and 1998 consumption is estimated at 1.7 million tons.

#### 0.3.2 R&D Efforts

Major areas in which research is being done in last 3 decades are - high conversion of monomer and low gel formation in the polymerization, production of high (98%) cis-polybutadiene and improved mechanical strength of the polymer. Efforts are also under progress to evolve better catalyst systems and use of safer solvents. A recent significant development in this area is neodymium based catalyst system.

#### 0.3.3 Major Producers of PBR

The major producers of PBR today include - American Synthetic, Asahi Chemical, Australian Synthetic, Bayer, Bridgestone, Coperbo, Enichem, Firestone, Goodyear, Huls, Japan Elastomer, Japan Synthetic,

Karbochem, Korea Kumho, Michelin, Negromex, Nippon Zeon, Petkim Turkey, Petrochim, Repson Ouimica, Taiwan Synthetic, Ube and Romania and CIS. The new plants of PBR under construction are of Goodyear Tyre and Rubber Co. in USA, Autoden in France, Enichem in Italy, Hyundai in Korea, Net Petrochem in Iran and Companhia Perman Bucanade Borracha in Brazil.

#### **0.3.4 Various Manufacturing Processes**

During the 1930s and 1940s polybutadiene rubber was introduced using emulsion polymerization system. Although this system is not considered to be satisfactory, even today it is in use in some plants mainly due to historical reasons. The solution polymerization process, developed in the 1950s is most popular today. Two types of solution PBR have emerged as important commercial rubbers - high cis PBR and medium cis PBR. The production of the later is based on alkyl lithium catalysts, while the former involves co-ordination catalyst systems based on titanium, cobalt, nickel etc. Neodymium based catalyst have emerged in the recent years for production of very high cis PBR.

#### **0.3.5 New Developments**

Thermoplastic elastomers (TPEs), are posing threat to traditional synthetic and natural rubbers, primarily because of ease of processing and recyclability. However, as of now TPEs are used predominantly in non-tyre sectors. Hence, PBR is expected to get least affected as compared to other SRs. Development in this field would be quite relevant to SRs as recyclability of TPEs would become an important consideration in the future.

#### **0.3.6 Polybutadiene in ABS Resins : International Scenario**

##### **1. General**

Consumption of ABS and SAN resins together in 1990 was estimated to be around 2.5 million tons. Today the ABS industry is mainly controlled by major manufactures like Dow Chemicals, Monsanto, GE Plastics, Mitsubishi, JSR, BASF etc.

##### **2. Production Capacities**

Present total world capacity is estimated to be 3 million tons of ABS. New capacity under implementation in the world include plants of

GE Plastics, Tech Corporation, Hannam, Chem Korea, Kumho and Thai Petro.

### 3. Production Process

Amongst various process in use today, emulsion polymerization is quite popular as it can produce a wide variety of ABS grades. Recently, continuous mass (bulk) process is gaining wide acceptance. Generally, the mass polymerization process is more economical than emulsion polymerization process. Both, the fixed capital investments and the operational expenses are reportedly lower in mass process.

## 0.4 R&D EFFORTS, TECHNOLOGY ABSORPTION AND GAPS

### 0.4.1 R&D Efforts

Initially the research team of IPCL was involved in improving the quality and quantity of PBR production. Later the team also studied the role of various reaction parameters on the process. Some of the major areas of work included- developing alternative chain transfer agent, co-catalyst and terminator and modifications of solvent system apart from the work done to improve viscosity, microstructure and removal of trace impurities of PBR.

### 0.4.2 Technology absorption : IPCL

1. Technology adoption efforts include establishing the various grades of PBR as per Polysar's specifications and also the efforts by IPCL to develop and promote various applications of PBR in India.
2. The technology assimilation efforts include the work carried out by research team of IPCL which enabled them to understand the role of various process parameters like impurities of raw materials, catalysts, solvents, etc. on the polymerization reaction. Two successful efforts include development of indigenous sources for catalyst system and the work on the use of off-specification butadiene which was less pure as compared to the licensors specifications.
3. The technology upgradation work include development of alternate chain transfer agent and terminator and co-catalyst which were different from the licensor's process, besides the work on



modifications of solvent system. Also raw materials and solvent consumption have reportedly come down over the years and are in fact less than the licensor's norms, besides a reduction in the energy consumption.

#### **0.4.3 Technology gaps**

PBR industry is more than two decades old in India and by now the prevailing technology has been fully absorbed. IPCL is producing products that are more suited to Indian conditions than those originally specified by the collaborator. Based on market demand, PBR grades have been limited to two. However, there is still scope for improvement in the area of quality consistency. PBRs based on other catalyst systems are also available in world market. IPCL's new 30000 TPA PBR plant will be based on nickel catalyst system.

#### **0.4.4 Technology Absorption Efforts and Technology Gaps in ABS Resins**

##### **1. Technology Absorption Efforts**

One commendable aspect of Indian ABS industry is that all the producers except Bhansali have been involved in scale-up activities from grassroot levels. Both ABS Plastics and Polychem developed the bench level processes into full fledged commercial plants. In ABS Plastics, due to expertise available in the company, their plant investment costs per ton of ABS is least as compared to other Indian companies.

Gujarat Binil also implemented their project based on their own know-how and have overcome teething problems in the initial phases of their operations. Both these companies have tapped local resources for fabrication of critical equipments which otherwise, would have been imported. This has resulted in lower foreign exchange outgo.

##### **2. Technology Gaps**

In this industry significant technological gaps exist. Hence, the dependence on imported technology for ABS still continues. The basic NRDC process itself has draw-backs which include low polymer yields of 90% (as compared to more than 96% conversions in emulsion graft ABS process available abroad) and high batch cycle times.

Although a wide variety of processes (modifications of two basic processes) are available world-wide, Indian companies except for Gujarat Binil have gone for emulsion graft polymerization. Though mass

polymerization is claimed to be most efficient and economical process, it involves sophisticated design of the reactor, and other vital plant equipments.

## **0.5 RECOMMENDATIONS**

### **0.5.1 Recommendations : PBR**

- (i) Since no technology source (for catalyst systems other than cobalt) is available domestically, import of technology for the new plants appears inevitable.
- (ii) In view of the necessity of additional plants and the likely spin off benefits like the possibility of export of technology, efforts in technology development (for catalyst systems based on nickel and neodymium) appear worthwhile.
- (iii) IPCL is in a unique position to undertake this activity since it is the only manufacturer with a strong infrastructure in research and development. For development of superior catalyst systems, IPCL may like to collaborate with a laboratory like National Chemical Laboratory, Pune.

### **0.5.2 Recommendations : Polybutadiene in ABS Resins**

- (i) For the overall indigenous development of process know-how, massive R&D inputs involving new alliance between manufacturers, research institutes and engineering consultants is required.
- (ii) Continuous mass (bulk) polymerization process is quite popular abroad. The plant investments and operational costs are among the lowest in the industry. It is recommended that for ABS resins, technology may be imported using continuous mass (bulk) process.