

WU XINGAN, WU ZUNGHUA, CHEN SHUFA, LIU HANMAO, LI LINGLAN, SHUAI ZHENGQUAN

Chemistry and Chemical Engineering College
Hunan University
410082, Changsha, P. R. China

The selection of the oil-extending process and properties of Nd-catalyzed oil-extended 1,4-*cis*-polybutadiene

Summary — Three methods of oil-extending of the rubber — continuous, one-step and two-step ones have been discussed. Two-step method, leading to the product showing constant, required oil content, appeared to be the best one. This way modified rubber (Nd-catalyzed 1,4-*cis*-polybutadiene) shows better mechanical properties than Nd-catalyzed 1,4-*cis*-polybutadiene, the best butadiene rubber up to now.

Key words: oil-extending of a rubber, 1,4-*cis*-polybutadiene, Nd-catalyst, Ni-catalyst, mechanical properties.

For rare earth catalyst system, such as neodymium catalyst system, the center of catalytic activity is heavy metal whose atomic nucleus has stronger gravitational field than Ni, V, Cr and Ti. Ziegler—Natta catalytic system with Nd or other rare earth metals as catalyst let obtain the 1,4-polybutadiene showing extremely high 1,4-*cis*-unit content, usually more than 97%, high molecular weight, very good mechanical and tensile properties making possible wide and successful application.

In the course of studying polymerization of butadiene with Nd as catalyst, it was hoped to manufacture excellent oil-extended 1,4-*cis*-polybutadiene except of this polybutadiene with high molecular weight.

In general, oil-extension has the following purposes [1]:

- to improve the processing function of non-vulcanized rubber,
- to increase the speed of vulcanization (compared with adding the same amount of oil into the formula),
- to reduce the heat generation in vulcanized rubber,
- to reduce the costs of material shaping,
- to improve wet skid resistance,
- to make low hardness rubber.

So oil-extended rubber such as oil-extended butadiene-styrene and oil-extended 1,4-*cis*-polybutadiene are widely produced and used [2].

At present, the technology of the oil-extending process can be roughly classified in three ways according to location of oil-extension [3—12]:

- oil-extending in front of extrusion press,
- oil-extending in rubber solution,
- oil-extending in the first polymerizing reactor.

Because in the first method an extending oil is not well-distributed in oil-extended rubber, the strength of

vulcanized rubber is low. The third method requires extending oil of good quality or it will influence the polymerization. The best of them second method, *i.e.* the technology of oil-extension in rubber solution, can be classified into three different processes, *i.e.* no step (continuous technology), one step (one-step technology) or two steps (two-step technology).

The polymerization of butadiene catalyzed by rare earth metals or Ni is described elsewhere [14—17]. In this work, the pilot manufacturing methods (mainly second method) for oil-extending process of 1,4-*cis*-polybutadiene, catalyzed by neodymium, is discussed.

VARIANTS OF OIL-EXTENSION PROCESS

Continuous technology of oil-extension

When using hydrogenated petroleum as a solvent and butadiene/solvent ratio is equal 12 g/100 mL, polymerization of butadiene by Nd-catalyst leads to obtain 1,4-*cis*-polybutadiene solution. In order to produce oil-extended rubber, add extending oil to the polymer solution; the polymer solution is coacervated in the hot water, then becomes granular oil-extended rubber. After removing the solvent and water and drying, the rubber becomes the end-product. Figure 1 illustrates the scheme of continuous technology of oil-extension plant.

The technology used is similar to the proposed in the literature [1].

Polymer coming from the polymerizer (1) was diluted by diluting oil (2), then went into the stopper (3). Agitated with stopper, quantitative antiaging agent and extending oil for 2—6 hours in stopper oil-extension reactor (4), the extending oil (6) was well distributed in

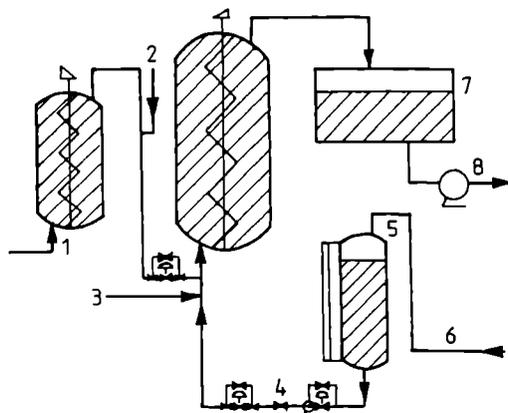


Fig. 1. 200T—500T/a Pilot plant in SINOPEC JINZHOU Petro Chemical Company (Liaoning) P. R. China; 1 — polymerizer, 2 — diluting oil, 3 — stopper, 4 — terminating oil-extension reactor, 5 — measuring tank for extending oil, 6 — extending oil, 7 — oil-extended rubber solution tank, 8 — exit

rubber solution and the solution became orange (or white) and transparent. According to the different Mooney point of oil-extended rubber, it was sent into another rubber solution tank (7), mixed by the spiral pump and then taken out. In order to remove the solvent the solution was coacervated in the coacervate reactor to obtain hydrous granular oil-extended rubber. After being pressed and dried, the rubber became the end-product.

This method had advantages of being a simple process, using economical equipment and energy resources, and a high level of automation. It appeared to be an ideal oil-extension process.

To keep Mooney point and oil content constant within narrow accurate limits, for example $ML(1+4) 100^{\circ}C = 47 \pm 2$, oil/rubber = $(37.5 \pm 1.5)\%$, it was required that in the rubber solution which had been polymerized, the content of dry rubber and the Mooney viscosity $ML(1+4) 100^{\circ}C$ of basic rubber must be kept constant. Moreover, it was also required that extending oil content had to be kept either constant or changing synchronously with the content of dry rubber. The content and flow of impurity in the monomer and catalyst had to be kept constant.

Figure 2 shows the relationship of selected visible variables with rubber Mooney viscosity and oil content of the end product.

From Figure 2 it can be seen that though the most modern electronic measuring instruments were used, the measuring error of the flow rate of catalyst, butadiene and solvent could be controlled within $\pm 0.5\%$. Because there were reactions among catalysts at the time, the invisible changes of trace water, O_2 and many kinds of trace impurities in butadiene and solvent could not be calculated, so the conversion of butadiene during polymerization could not be kept constant, the Mooney viscosity of polymer could not be completely constant and

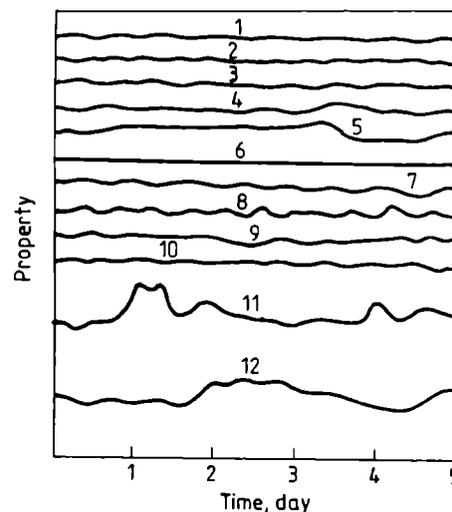


Fig. 2. Influence of visible variable on the properties of end-product rubber in technology of continuous oil-extending process: 1 — monomer flow rate (kg/h), 2 — solvent first flow rate (L/h), 3 — catalyst I flow rate (L/h), 4 — catalyst II flow rate (L/h), 5 — catalyst III flow rate (L/h), 6 — catalyst II/III (mol/mol), 7 — temperature of the first polymerization reactor ($^{\circ}C$), 8 — pressure in the first polymerization reactor (MPa), 9 — extending oil flow rate (kg/h), 10 — rubber Mooney viscosity in stopper $ML(1+4) 100^{\circ}C$, 11 — oil content in the end product (g/100 g), 12 — Mooney viscosity of end-product rubber $ML(1+4) 100^{\circ}C$

the flow rate of extending oil could not be synchronously changed completely with the content of dry rubber in the last polymerization reactor (required error $\leq \pm 0.5\%$).

After one-year experiments, the Mooney viscosity and oil content of end-product rubber in the technology of continuous oil-extension [$ML = 47 \pm 2$, oil/rubber = $(37.5 \pm 1.5)/100$] qualification percent was only ten percent and it was difficult to adapt the method to a new catalyst system, especially during the test period.

One-step technology of oil-extension

Figure 3 shows the scheme of one-step technology of oil-extension plant. When the polymerization was terminated and the rubber solution was well diluted, it went into I oil-extending reactor. When it reached 3/4 of the height of the reactor, the flow should be cut off and the valves changed, so that the rubber solution could flow into II oil-extending reactor.

After the rubber solution had been agitated in the I oil-extending reactor for half an hour, a sample was taken to analyze the content of dry rubber in the solution ($W_{dry}/W_{sol.}$) using the density and volume of the rubber solution in the reactor.

According to the formula $G_1 = (37.5/100) \cdot (W_{dry}/W_{sol.}) \cdot V \cdot d$, the weight of extending oil G_1 could be calculated.

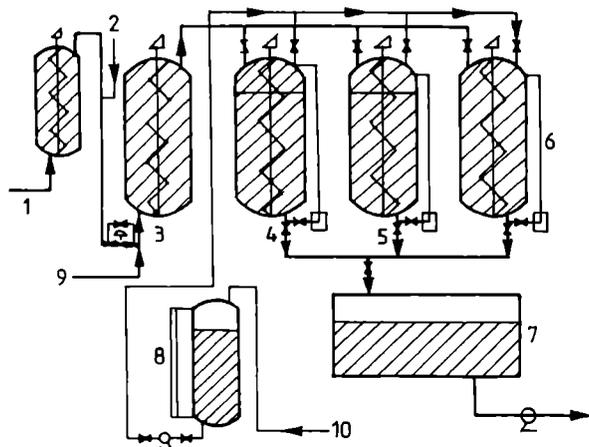


Fig. 3. Scheme of one-step technology of oil-extension. Pilot plant in SINOPEC JINZHOU Petro Chemical Company (Liaoning) P. R. CHINA: 1 — polymerization reactor, 2 — diluting oil, 3 — termination reactor, 4 — I oil-extending reactor, 5 — II oil-extending reactor, 6 — III oil-extending reactor, 7 — rubber solution tank, 8 — measuring tank for extending oil, 9 — terminating agent, 10 — extending-oil

After adding extending oil G_1 from the measuring tank, the solution was agitated until it was well distributed. Then it was poured into another tank of rubber solution, according to different high-low Mooney viscosity, mixed, transported by a spiral pump, and coacervated.

The same work in II and III oil-extending reactors as in I oil-extending reactor was done by changing I, II and III oil-extending reactors in run and then finishing the oil extension process.

By adopting one-step technology of oil-extension according to the index of extending oil $(37.5 \pm 2.5)/100$, its qualification percent could reach 71.5%. To go a step further to narrow the error range of oil content to $(37.5 \pm 1.5)/100$ and to improve its qualification rate, some difficulties were encountered:

- it was difficult to avoid error made by analysis of the dry rubber content $W_{dry}/W_{sol.}$,
- there was great difficulty in surveying each volume of rubber solution accurately,
- because of the influence of temperature and rubber content, the density of rubber solution was not easy to survey accurately.

These factors would directly influence the oil content G_1 , so this method needed further improving.

Two-step technology of oil-extension

The scheme of this method is similar to Figure 3.

The first oil-extending method is the same as in one-step technology, except the changing of the oil-content from 37.5% to $(37.5 - n)/100$, if $n = 7.5\%$. The purpose was to make adding the second oil more convenient. When the first oil-extension was completed, a sample

was taken to analyze the oil content (m_1). Knowing the first oil content G_1 , the oil amount G_2 would be added:

$$G_2 = (37.5 G_1 / m_1) - G_1$$

Any other factors ($W_{dry}/W_{sol.}$, V and d) do not exist in this formula, so the qualification percent of oil content could be improved.

Rubber solution, which had been oil-extended, was well distributed and transparent. Fluctuation scope of oil content of the two methods (one-step and two-step) are compared in Table 1.

Table 1. Comparison of the fluctuation range of oil content in the two methods

Number of experiment cycle	Technology of oil-extension (step)	Oil content ^{a)} %	The highest oil content %	The lowest oil content %	Percent of oil content <35%	Percent of oil content >40%	Qualification rate %
12	1	37.5 ± 2.5	58.82	22.59	27.5	28.2	71.5
13	2	37.5 ± 1.5	53.00	34.80	8.7	13.0	100.0
14	2	37.5 ± 1.5	43.36	34.0	10.0	13.3	100.0

^{a)} Oil content per 100 g rubber.

From the Table 1 it can be seen that the fluctuation range at two-step technology of oil-extension was smaller than at one-step technology and the qualification percent of oil content of end-product rubber (37.5 ± 1.5) reached 100.0%.

The two-step technology of oil extension shows a large permissible elasticity to the change of operation factors such as the flow of polymerizing materials, the content of impurities, the content of dry rubber and the fluctuation of Mooney viscosity. It was applied to the industrial production, but the investments in equipment, energy consumption and operation procedures were high, so the method needed further improving. However for the industrial production the qualification of product quality was the most important.

Properties of oil-extended Nd-system catalyzed 1,4-cis-polybutadiene

Oil-Nd-BR marks are shown in Table 2.

Table 2. Types of Nd-catalyzed 1,4-cis-polybutadiene

Mark classification	40	50
ML (1+4) 100°C	40 ± 2	50 ± 2
Oil basic rubber, phr	37.5 ± 1.5	47.5 ± 2.5

Comparison between oil-Nd-BR and oil-Ni-BR (oil extended Ni-catalyzed 1,4-cis-polybutadiene) which are vulcanized using the same Japanese recipe (BR-31) are

Table 3. Comparison of oil-Nd-BR and oil-Ni-BR

	CHINA Oil-Nd-BR					JSR BR-31 (Oil-Ni-BR)				
	20'	30'	45'	60'	100'	20'	30'	45'	60'	100'
Curing characteristics (at 143°C)										
Hardness, Shore A	57	57	55	53	53	55	55	54	54	52
Tensile strength, MPa	19.3	18.7	18.4	18.5	18.6	15.5	15.3	15.6	15.1	15.7
Elongation at break, %	622	586	588	611	666	547	511	511	543	571
300% Modulus, MPa	7.1	7.5	7.1	6.6	6.0	6.5	6.1	6.8	6.8	6.1
500% Modulus, MPa	15.0	15.5	15.3	14.6	13.4	13.7	14.7	14.6	15.0	13.1
Tension set, %	11	11	9	9	8	11	9	8	8	7
Ageing coefficient, 100°C · 48 h			0.53					0.63		
Tear resistance, MPa			4.7					4.2		
Rebound, %			45					44		
Akron abrasion, cm ³ /1.61 km			0.059					0.153		
Crack generation			1—500000 times					1—240000 times		
Flex growth			6 0 6 ^{*)}					6 6 6 ^{*)}		

^{*)} 0 — no crack.

6 — The cracks are from light to nearly broken.

shown in Table 3. Their properties were measured at the Central Research Institute of Rubber Industry Beijing, China.

As cured compound, oil-Nd-BR shows several advantages in comparison with JSR BR-31 in tensile strength, Akron abrasion, crack generation and flex growth.

CONCLUSIONS

Continuous technology of oil-extension has advantages of being a simple and economical (what concerns energy) process. Non-identical quality and flow of materials could lead to the fluctuation of dry rubber content. At present it is difficult to change the oil content synchronously with the content of dry rubber, so the qualification rate of oil content in the end product rubber is low.

One-step technology of oil-extension needs more equipment investment and energy consumption than continuous technology. It shows a large permissible elasticity to the fluctuation of polymerization conversion rate. Because it is not easy to survey the volume and density of the rubber solution and the content of dry rubber accurately at all times, the fluctuation of oil content is wide.

Two-step technology of oil-extension is an improved method of one-step technology. It appears to be a feasible method for industry. It omits three factors, *i.e.* content of dry rubber, volume and density of rubber solution that are difficult to survey accurately. The qualification percent of end-product rubber oil content (37.5±1.5)/100 and ML (40±2) reached 100%, so it was applied to industrial production. Efforts should be made to reduce energy consumption and operation procedures in the future.

Compared with the best Ni-BR-31 vulcanizate currently used, the oil-Nd-BR vulcanizate had better comprehensive properties including tensile strength, Akron abrasion, crack generation and flex growth.

REFERENCES

1. Whitehouse W. G., Bavnhart R. R.: *Rubber World* 1963, 39, No 2, 150.
2. *Polymer Digest* (Japan) 1978, 30, No 3—4, 97.
3. Ledwith A., Sherrington D. C.: "Reactivity, Mechanism and Structure in Polymer Chemistry" (Eds. Jenkins A. D., Ledwith A.), Wiley & Sons, London 1974, 411—430.
4. Ottino J. M., Ranz W. E., Macosko C. W.: *Chem. Eng. Sic.* 1979, 34, 877.
5. Ravindran Ch., Ottino M.: *Ind. Eng. Chem. Fundam.* 1985, 24, 170.
6. Wu Xingan, et al.: *China Synth. Rubber Ind.* 1980, 3, No 1, 7.
7. Wu Xingan, et al.: *China Synth. Rubber Ind.* 1981, 4, No 2, 82.
8. Wu Xingan: *China Synth. Rubber Ind.* 1984, 7, No 4, 260 (CA 1984, 101, 1727732).
9. Qiao Sanyang: *China Synth. Rubber Ind.* 1993, 16, No 1, 11.
10. Jinag Zhilan, Gong Zhi: *China Synth. Rubber Ind.* 1994, 17, No 1, 23.
11. Zhang Xinhui, Li Bailin, et al.: *China Synth. Rubber Ind.* 1994, 17, No 2, 98.
12. Jiang Liansheng: *China Synth. Rubber Ind.* 1997, 20, No 4, 253.
13. Fan Jikuan: *Modern Chem. Ind. (China)* 2000, 20, No 8, 15.
14. Fu Yanjie, Zhao Zhenhua, Cao Zhengang: *China Synth. Rubber Ind.* 1999, 22, No 3, 140.
15. Wei Rubing, Li Ying, Wang Junzhou: *China Synth. Rubber Ind.* 2001, 24, No 4, 197.
16. Wang Junzhou: *China Synth. Rubber Ind.* 2001, 24, No 6, 321.
17. Huang Jian: *China Synth. Rubber Ind.* 1999, 22, No 1, 1.

Received 5 XII 2001.

Revised version 14 III 2002.