

## **Catalysts**

### **Ethylene/Propylene/5-Ethylidene-2-Norbornene Terpolymerization with a Highly Active Supported Ti Catalyst System: MgCl<sub>2</sub>/TiCl<sub>4</sub>/C<sub>6</sub>H<sub>5</sub>COOC<sub>2</sub>H<sub>5</sub> - AliBu<sub>3</sub>/di-iso-Amyl Ether**

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#### SUMMARY

Ethylene/propylene/5-ethylidene-2-norbornene (ENB) terpolymerization was carried out with a highly active Ti catalyst system (MgCl<sub>2</sub>/TiCl<sub>4</sub>/C<sub>6</sub>H<sub>5</sub>COOC<sub>2</sub>H<sub>5</sub> (EB) - AliBu<sub>3</sub>/di-iso-amyl ether (IAE)). The obtained terpolymer could be vulcanized with sulfur, but the increase of torque value through the vulcanization measured by curelasmeter for the terpolymer obtained with this catalyst was considerably lower than that for the terpolymer obtained with the conventional VOCl<sub>3</sub> catalyst system. It was suggested that lower torque value would be attributed to the heterogeneous diene distribution in the obtained terpolymer, particularly lower ENB content in the high molecular weight fraction.

#### INTRODUCTION

Ethylene/propylene/ENB terpolymer (EPDM) has been produced commercially with the conventional vanadium catalyst system. On the other hand, it is well known that a MgCl<sub>2</sub>-supported TiCl<sub>4</sub> catalyst combined with alkyl aluminum shows very high activity in olefin polymerization. In the present study, ethylene/propylene/ENB terpolymerization was carried out with MgCl<sub>2</sub>/TiCl<sub>4</sub>/EB - AliBu<sub>3</sub>/IAE catalyst system. The obtained terpolymer was vulcanized with sulfur and cure data by curelasmeter were compared with those of terpolymer obtained with the conventional vanadium catalyst system and as well as with those of commercial EPDM.

#### EXPERIMENTAL

Materials; Ethylene, propylene and hydrogen: commercial grade gases produced by Mitsui Petrochemical Industries, Ltd.; toluene, *n*-hexane, MgCl<sub>2</sub>, ethyl benzoate (EB), di-iso-amyl ether (IAE), AliBu<sub>3</sub> and AlEt<sub>1.5</sub>Cl<sub>1.5</sub>: commercially available reagents; 5-ethylidene-2-norbornene (ENB): commercial grade monomer produced by Union Carbide Corporation; Commercial grade EPDM: Mitsui EPT #3045, #3070 and #4070 produced by Mitsui Petrochemical Industries Ltd.

Preparation of the catalyst; Supported Ti catalyst (MgCl<sub>2</sub>/TiCl<sub>4</sub>/EB) was prepared by the same method described in a previous paper(1).

Terpolymerization; Terpolymerization was carried out continuously by using a 2 l glass reactor. Pre-determined amount of ENB and IAE (if it was used), Ti or V catalyst and alkyl aluminum were fed into the reactor as toluene or *n*-hexane solution at rates of 800 ml/hr, 600 ml/hr and 600 ml/hr, respectively. The polymer solution was continuously discharged at 2 l/hr. The resident time of the solution in the reactor was kept to be 30 min. A mixture gas of ethylene, propylene and hydrogen (if it was used) was introduced into the polymer solution at 300 ml/hr. The polymer solution discharged from the bottom of the reactor, was introduced into a large amount of

mixture of methanol and acetone (vol. ratio 1:1). The obtained precipitate was separated and dried in vacuo.

Terpolymer characterization; Any peaks assigned to homopolymer of ethylene and propylene were not detected by the DSC analysis. Ethylene content (mol%) was determined by IR method. The iodine value (IV: I<sub>2</sub>g/100g polymer) for the measure of the content of ENB was determined by the iodine monochloride method(2). Mooney viscosity (ML<sub>1+4</sub>(100°C)) was measured by a Shimadzu Mooney Viscometer. Fractional precipitation was carried out by using the mixture solvent of toluene as good solvent and acetone as poor solvent.

Vulcanization; The obtained terpolymer was compounded with the following recipe (by weight): 100 parts of terpolymer, 5 parts of ZnO, 1 part of stearic acid, 1 part of tetramethylthiuram disulfide and 1 part of sulfur. The compound was vulcanized by using JSR-type Curelastometer (produced by Imanaka Kikai Co.Ltd.) at 160°C. The values of T<sub>15</sub>, T<sub>90</sub>, F<sub>max.</sub> and F<sub>min.</sub> were determined from the vulcanization curve. F<sub>max.</sub> and F<sub>min.</sub> denote the maximum and minimum torque values (Kg·cm), respectively, and T<sub>15</sub> and T<sub>90</sub> denote the times (minute) which are required to attain 15% and 90% of F<sub>max.</sub>, respectively.

#### RESULTS AND DISCUSSION

Tables 1 and 2 show the results of ethylene, propylene and ENB terpolymerization by the MgCl<sub>2</sub>/TiCl<sub>4</sub>/EB - AliBu<sub>3</sub>/IAE catalyst system (cat-[Ti]) and by the VOCl<sub>3</sub> - AlEt<sub>1.5</sub>Cl<sub>1.5</sub> catalyst system (cat-[V]), respectively. As seen in Table 1, by the introduction of ENB, the activity in the terpolymerization with cat-[Ti] was reduced to about one-third of that in ethylene/propylene copolymerization. However, the activity of the system was still 10 times higher than the case of the conventional vanadium catalyst system (cat-[V] in Table 2), which is well known as a typical catalyst in the commercial production of EPDM. On the other hand, as seen in Table 2, ENB was incorporated into copolymers with much higher efficiency by cat-[V] as compared with cat-[Ti] (ENB conversion: cat-[Ti]=16~18%, cat-[V]=98~99%).

Table 1. Ethylene - propylene-ENB terpolymerization with MgCl<sub>2</sub>/TiCl<sub>4</sub>/EB - AliBu<sub>3</sub>/IAE catalyst system

Run No.	Conditions <sup>1)</sup>			Terpolymers				
	Ti mmol/l	Ethylene/ Propylene in feed (mol/mol)	ENB in feed (ml/l)	Activity <sup>2)</sup>	Ethylene content in terpolymer (mol%)	ML <sub>100°C</sub> 1+4	IV <sup>3)</sup>	ENB conversion (%)
1	0.01	40/60	0	4.2	63.2	-	-	-
2	0.03	40/60	15	1.5	61.3	27	11.1	17.7
3	0.05	50/50	30	1.1	72.3	43	16.7	16.3

1) Terpolymerization conditions: mole ratio Al/Ti=50, mole ratio Al/IAE=3.0, temp.=60°C, solvent=toluene.

2) Terpolymer yield in Kg per mmol of Ti.

3) IV: Iodine value.

Table 2. Ethylene-propylene-ENB terpolymerization with  $\text{VOCl}_3 - \text{AlEt}_{1.5}\text{Cl}_{1.5}$  catalyst system

Run No.	Conditions <sup>1)</sup>		Terpolymers				
	Ethylene/ propylene in feed (mol/mol)	H <sub>2</sub> in feed (%)	Activity <sup>2)</sup>	Ethylene content in terpolymer (mol%)	ML <sub>1+4</sub> <sup>100°C</sup>	IV <sup>3)</sup>	ENB conversion (%)
1	25/75	10	0.086	63.3	62	8.7	98.3
2	40/60	25	0.133	59.9	32	5.6	98.6

1) Terpolymerization conditions:  $[\text{Al}] = 5 \text{ mmol/l}$ ,  $[\text{V}] = 0.5 \text{ mmol/l}$ ,  $[\text{ENB}] = 2 \text{ ml/l}$ ,  
temp. = 20°C, solvent = n-hexane.

2) Terpolymer yield in Kg per mmol of V

3) IV: Iodine value.

The quality evaluation of the obtained terpolymer was performed on the basis of the cure rate (calculated by an equation;  $(0.9 F_{\text{max}} - 0.15 F_{\text{min}}) / (T_{90} - T_{15})$ ) and  $\Delta F (= F_{\text{max}} - F_{\text{min}})$ . Table 3 shows the cure data for the obtained terpolymers and for commercially available EPDM. In Fig.1, the relation between the cure rate and IV is shown. All of the obtained data could be plotted on a same line, therefore from the stand point of the cure rate there is no significant difference among these terpolymer.

Table 3. Cure data for the obtained terpolymer and commercially available EPDM.

Terpolymer	ML <sub>1+4</sub> <sup>100°C</sup>	IV	T <sub>15</sub> (min.)	T <sub>90</sub> (min.)	F <sub>min.</sub> (Kg·cm)	F <sub>max.</sub> (Kg·cm)	$\Delta F$ (Kg·cm)	cure rate (Kg·cm/min.)
A	27	11.1	7.25	11.5	0.95	13.9	13.0	2.45
B	43	16.7	6.00	8.25	0.81	16.3	15.5	5.43
C	63	8.7	4.25	11.0	1.76	29	27	3.22
D	32	5.6	6.00	15.5	0.88	23	22	1.82
E	40	12.7	7.25	15.0	1.28	22	21	2.13
F	65	14.4	6.75	13.25	2.6	37	34	4.27
G	66	22.5	7.00	12.0	3.0	38	35	5.7

1) A: Run No.2 in Table 1, B: Run No.3 in Table 1, C: Run No.1 in Table 2,  
D: Run No.2 in Table 2, E: Mitsui EPT #3045, F: Mitsui EPT #3070,  
G: Mitsui EPT #4070.

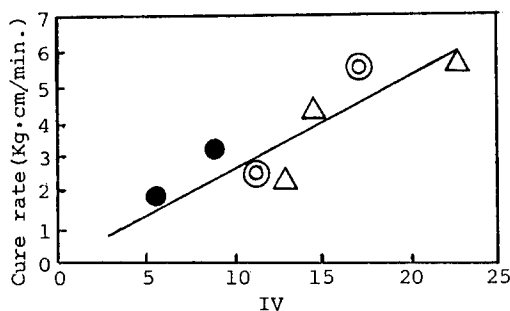


Fig.1 Relation between cure rate and IV

△ : commercially available EPDM  
● : terpolymer obtained with cat-[V]  
⊙ : terpolymer obtained with cat-[Ti]

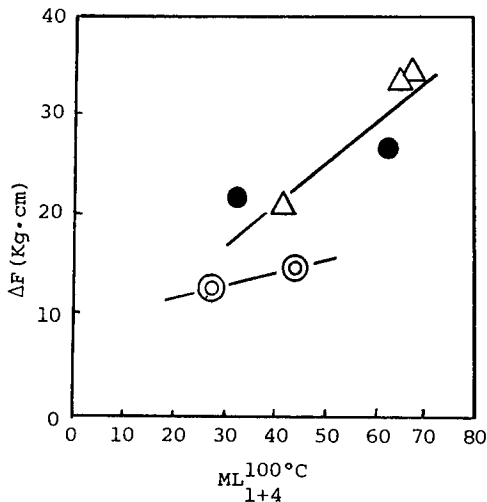


Fig.2 Relation between  $\Delta F$  and  $ML_{1+4}^{100^\circ C}$

$\triangle$  : commercially available EPDM  
 $\bullet$  : terpolymer obtained with cat-[V]  
 $\odot$  : terpolymer obtained with cat-[Ti]

Fig.2 shows the relation between  $\Delta F$  and mooney viscosity. It is known that  $\Delta F$  (the change of torque value through the vulcanization) increases with the increase of crosslink density or mooney viscosity. As seen in Fig. 2,  $\Delta F$  for the terpolymer with cat-[Ti] is lower than that with cat-[V] and commercially available EPDM, which shows that cured terpolymer with cat-[Ti] has poor crosslink density.

To study the cause of low  $\Delta F$ , the fractional precipitation was carried out for the terpolymer with cat-[Ti] (Run No.2 in Table 1). The obtained results are shown in Table 4.

Table 4. Results of the fractionation and cure data for the terpolymer (Run No. 2 in Table 1)

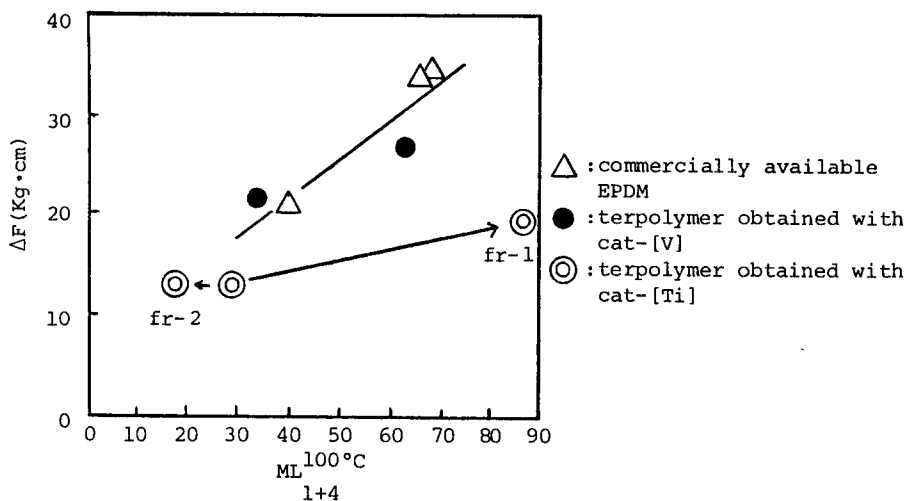
Sample	wt%	$ML_{1+4}^{100^\circ C}$	IV	Cure data					cure rate (Kg·cm/min.)
				$T_{15}$ (min.)	$T_{90}$ (min.)	$F_{min.}$ (Kg·cm)	$F_{max.}$ (Kg·cm)	$\Delta F$ (Kg·cm)	
Whole <sup>1)</sup>	-	27	11	7.25	11.5	0.95	11.5	13	2.45
fr-1	28	87	9	4.00	9.75	4.5	9.75	20	3.1
fr-2	67	18	14	6.75	10.25	0.27	10.25	13	2.9
fr-3	5	<18 (1.2) <sup>2)</sup>	20	-	-	-	-	-	-

1) Ethylene content = 61.3 mol%.

2) Intrinsic viscosity (in decaline at 135°C)

The terpolymer was fractionated to three fractions having different mooney viscosities. Each fraction was found to have the different IV. The fraction having lower mooney viscosity had higher IV, which means that ENB is incorporated preferentially into the polymer having lower molecular weight portion. The relation between  $\Delta F$  and mooney viscosity for the fr-1 and fr-2 was plotted in Fig.3 together with the original terpolymer and the other terpolymers. Fr-2, lower mooney viscosity portion, is comparable to the terpolymer with vanadium catalyst system, while fr-1, higher mooney

Fig.3 Relation between  $\Delta F$  and  $ML_{1+4}^{100^\circ C}$



viscosity portion, shows lower  $\Delta F$ . From these results, the lower  $\Delta F$  could be attributed to the fact that the distribution of diene unit of the terpolymer with cat-[Ti] is not homogeneous and the diene content of higher molecular weight fraction is lower than that of lower molecular weight fraction. Thus, the smaller contribution of higher molecular weight fraction gives rise to low  $\Delta F$  value.

In conclusion, a supported Ti catalyst system shows high activity for the ethylene/propylene/ENB terpolymerization and the obtained terpolymer can be vulcanized with sulfur but the torque value by curelaxometer is lower than that with the conventional vanadium catalyst system.

#### REFERENCES

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- (2) T.S.Lee, I.M.Kttoff and E.Johnson, Anal.Chem. **22**,995(1950)

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