

## **Analysis of Organic Solvent-Insoluble Portions Included in Ethylene-Propylene-Diene Terpolymer**

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### **Synopsis**

Organic solvent-insoluble portions included in the varying type of ethylene-propylene-diene terpolymers (EPDM) were analyzed by the solubility test, differential scanning calorimetry, x-ray diffraction, infrared spectrometry and the electron microscope. It was found that insoluble portions are resolved into microcrystalline gel owing to association of the long ethylene linkage and the crosslinking gel based on the presence of the third component by the variety of EPDM. The differences in the analytical results of the microcrystalline gel was ascribed to the differences in the monomer sequence distribution along the polymer chain.

### **INTRODUCTION**

It is well known that EPDM includes insoluble portions in organic solvents. However, the structure of the insoluble portions was not determined and the effect of the insoluble portions on flow properties was never understood from a point of view of processability in the extrusion processes. It was pointed out that insoluble portions directly influence on the processing properties in extrusion processes.

It is very helpful to elucidate the molecular structure of the insoluble portions for understanding the extrusion processing properties with structure terms. Cyclohexane-insoluble portions are said to be the crystalline gel, the crosslinking gel, or the entanglement gel of the ultrahigh molecules. Thus, analysis of insoluble portions in the varying commercial EPDM was carried out by the solubility test, by differential scanning calorimetry (SDC), by x-ray diffraction, by the infrared spectrometer, and by electron microscopy.

### **EXPERIMENTAL**

The commercial samples shown in Table I were supplied for varying analyses.

#### **Separation of Insoluble Portions in Organic Solvents and Solubility**

EPDM, 0.5 g, and antioxidant Sumilizer BHT, 2.5 mg, were added to the varying organic solvents (tetrachloromethane, cyclohexane, xylene, and tetralin), 100 ml, and the mixture was kept without stirring at the varying temperatures for 7 hr. A solution was filtered through 300-mesh

TABLE I  
Characteristics of the Supplied EPDM<sup>a</sup>

	ML <sub>1+4</sub> <sup>100</sup>	C <sub>3</sub> , wt-%	I <sub>2</sub> V	[η], dl/g	Gel, wt-%
EPDM-DCPD					
A	40	50	8.8	1.50	8.7
B	40	51	12	1.37	0.0
C	62	31	10	—	22
D	67	37	13	1.75	16
EPDM-ENB					
E	42	48	9.5	1.62	0.4
F	42	51	9.7	1.72	0.2
G	44	49	18.5	—	20
H	41	49	16.1	1.52	0.3

<sup>a</sup> ENB: Ethylidenenorbornene; DCPD: dicyclopentadiene; ML<sub>1+4</sub><sup>100</sup>: Mooney viscosity; C<sub>3</sub>: propylene content; I<sub>2</sub>V: iodine value. Intrinsic viscosity [η] was measured in xylene at 70°C.

wire netting and the insoluble portions (swollen gel) were dried under reduced pressure at 50°C to constant weight.

A large amount of insoluble portions in cyclohexane was recovered with stirring at room temperature for the varying analyses, except solubility test.

#### Analyses of Cyclohexane-Insoluble Portions and Soluble Portions

Infrared absorption was measured by a Hitachi Grating Infrared Spectrometer EPI-G3 in the usual manner. Samples were prepared by drying swollen polymer film on the NaCl plate. Propylene composition was calculated from the ratios of peaks at 1460 and 1380 cm<sup>-1</sup>.

Samples used for DSC, x-ray, and electron microscopy measurements were prepared by pressing pads of the polymer between stainless steel plates in a press at ca. 160°C under a pressure of 100 kg/cm<sup>2</sup> for 5 min after preheating for 2 min and by pressing at 20°C for 5 min.

The glass transition temperature  $T_g$  was measured by a Perkin Elmer Model DSC 1B. The diffraction pattern was obtained by a Rigaku-Denki Geiger Flex 2035. The fraction of the polymer in the crystalline state was determined by an adaptation of the procedures reported by Matthews et al.<sup>1</sup> The diffraction pattern was resolved into an area  $A_a$  attributable to the amorphous phase and areas  $A_c^{(110)}$  and  $A_c^{(200)}$  attributable to the crystalline phase at (110) and (200) planes, respectively. The weight fraction  $F_c$  of the polymer in the crystalline phase is obtained from the following equation:

$$F_c = \frac{1.0A_c^{(110)} + 1.43A_c^{(200)}}{0.69A_a + 1.0A_c^{(110)} + 1.43A_c^{(200)}}$$

A Hitachi HV11-E electron microscope was used for determination of the microstructure.

### Synthesis of Ethylene-Propylene Block Copolymer

TiCl<sub>4</sub>, 4 mmoles, was dispersed in ca. 800 ml hexane and activated with 8 mmoles AlClEt<sub>2</sub> and 6 mmoles AlEt<sub>3</sub>. At about room temperature, propylene was introduced with stirring up to a pressure of 1.0 kg/cm<sup>2</sup>. This pressure was maintained for a certain time. The residual propylene was then expelled with a vigorous stream of nitrogen and the nitrogen in turn removed by the application of a water pump vacuum. Ethylene was then fed up to a pressure of 0.5 kg/cm<sup>2</sup> and polymerization was carried out for the same time as propylene polymerization. The residual ethylene was then expelled with nitrogen. After the two olefins had been changed 5 and 10 times, the suspension was treated with methanol and hydrochloric acid. The summarized time of polymerization was adjusted to be 60 min for the former, (—EP—)<sub>5</sub>, and 30 min for the latter, (—EP—)<sub>10</sub>. The solid products were filtered off and washed with methanol. The obtained block copolymers are shown in Table II.

TABLE II  
Characteristics of Block Copolymers

Sample	<i>n</i>	Yield, g	[ $\eta$ ], <sup>a</sup> dl/g	Propylene, <sup>b</sup> mole-%	Crystallinity, %	Insoluble portions in toluene, wt-%
I	5	21.1	1.74	51.8	39.4(26.9) <sup>b</sup>	53.9
J	10	16.9	—	—	42.2(25.9) <sup>b</sup>	63.0

<sup>a</sup> Intrinsic viscosity, *o*-dichlorobenzene, 110°C.

<sup>b</sup> Sample: soluble portion in chloroform.

### RESULTS

The results of the solubility test of samples G and H in tetrachloromethane, cyclohexane, xylene, and tetralin are given in Figure 1. The content of insoluble portion of every sample decreases with increasing temperature, except for sample G; sample G showed a solubility behavior independent of temperature. The content of insoluble portion was sensitive to the thermal history of the sample, i.e., (1) pressing at 160°C for 5 min and pressing at 20°C, or (2) pressing at 160°C for 5 min and no pressing at 20°C. The content of the insoluble portions in samples B, F, and H was variable in the range of 10–20 wt-%, under the above described pre-treatment while that of the insoluble portion in other samples was approximately constant within the experimental error. All the results of the solubility tests are summarized in Table V.

The propylene composition of cyclohexane-soluble and insoluble portions is shown in Table III. Sample B was not variable in propylene composition, while the propylene composition of the soluble portion in samples A, G, and H was 10% higher than that of the insoluble portion.

Infrared spectra of cyclohexane-soluble portions and insoluble portions in all of samples were analyzed carefully between 700 and 750 cm<sup>-1</sup> in order

TABLE III  
Propylene Composition of Cyclohexane-Soluble Portions and Insoluble Portions

Propylene, mole-%	Sample A		B		G		H	
	Sol.	Insol.	Sol.	Insol.	Sol.	Insol.	Sol.	Insol.
	43.1	33.9	39.9	39.4	46.5	37.6	40.7	31.8

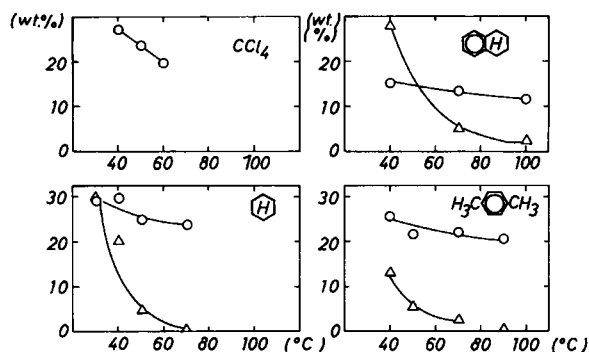


Fig. 1. Temperature effect on solubility: (O) G; ( $\Delta$ ) H.

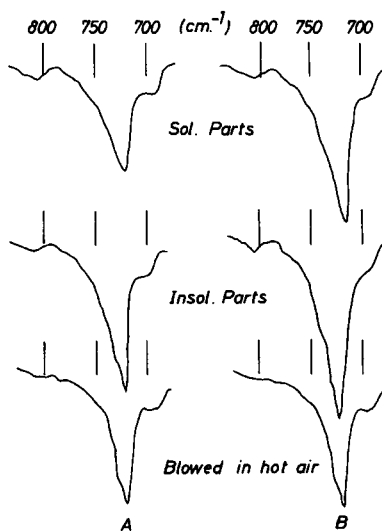


Fig. 2. Infrared spectra.

to obtain information on crystallinity based on methylene linkage. Representative spectra are shown in Figure 2. Infrared spectra of insoluble portions indicated absorption at  $730\text{ cm}^{-1}$ , except for sample G (Table IV). Furthermore, absorption at  $730\text{ cm}^{-1}$  disappeared when the sample was blown with hot air (at ca.  $90^\circ\text{C}$ ) (Fig. 2).

Cyclohexane-insoluble portions and soluble portions prepared by pressing were annealed at  $50^\circ$ ,  $70^\circ$ ,  $90^\circ$ , and  $120^\circ\text{C}$  for 48 hr. The glass transition

TABLE IV  
Appearance of Absorption at  $730\text{ cm}^{-1}$ <sup>a</sup>

Sample	A	B	G	H
Insol. portion	○	○	×	○
Sol. portion	×	×	×	×

<sup>a</sup> ○: Absorption; ×: no absorption.

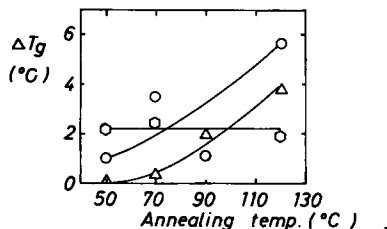


Fig. 3. Plot of  $T_g$  vs. annealing temperature: (○) A; (Δ) B; (○) G.

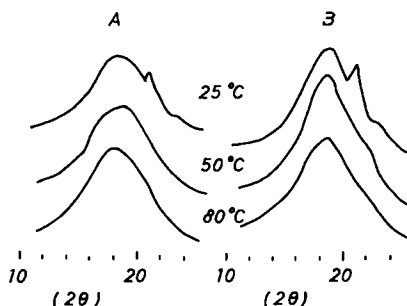


Fig. 4. X-Ray diffraction patterns of insoluble portions.

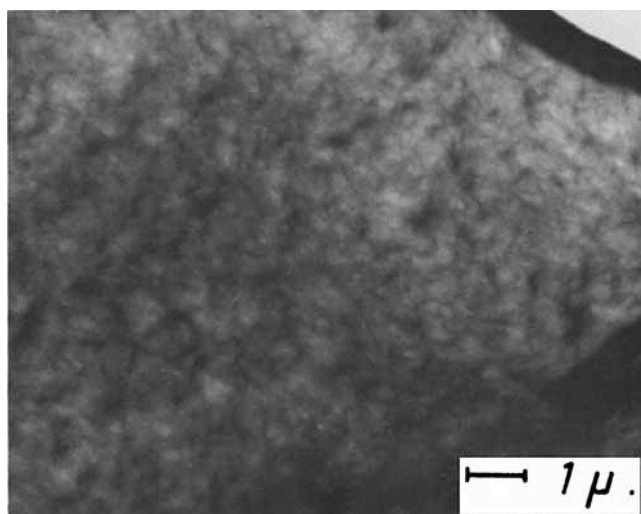
temperature of all the samples was extremely dependent on the thermal and aging history. The differences in  $T_g$  values of insoluble portions and soluble portions,

$$\Delta T_g = T_g^{\text{insol.p}} - T_g^{\text{sol.p}}$$

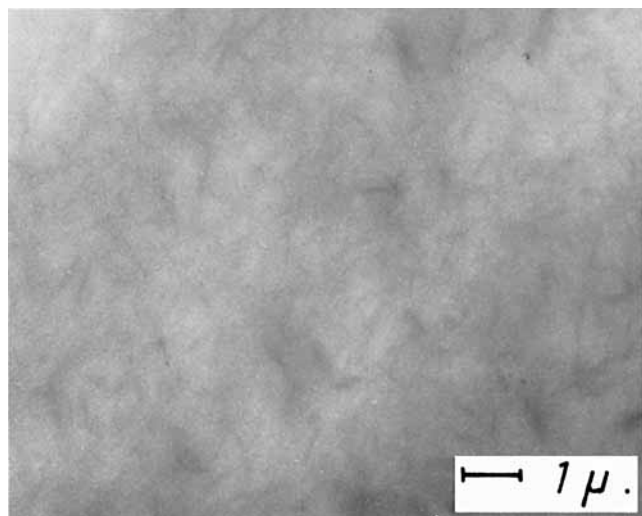
were plotted against the annealing temperatures (Fig. 3). The  $\Delta T_g$  values of samples A and B increase positively with increase in annealing temperature under the employed conditions (Fig. 3).

The strong x-ray diffraction peak appeared at (110), (200) planes for the insoluble portion of sample B and at the (110) plane for the insoluble portion of sample A. A negligibly weak diffraction peak was observed at the (110) plane for the insoluble portion of sample G. All the soluble portions indicated a broad peak based on an amorphous polymer. Crystallinity of insoluble portions in samples A and B, calculated from the x-ray diffraction peak, was as follows: 23.3% for sample A and 32.0% for sample B. It should be noted that the diffraction peak from the (110) and (200) planes disappears with increase in temperature (Fig. 4).

The microstructure of samples B, D, F, and H observed by the electron microscope gave the heterogeneous phase distribution in the polymer



(a)

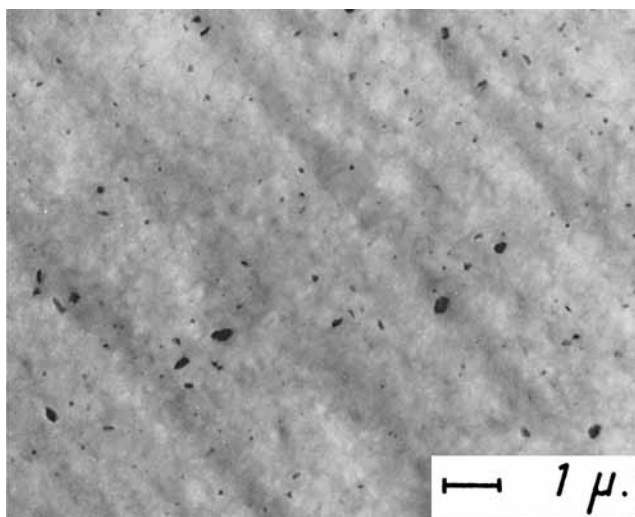


(b)

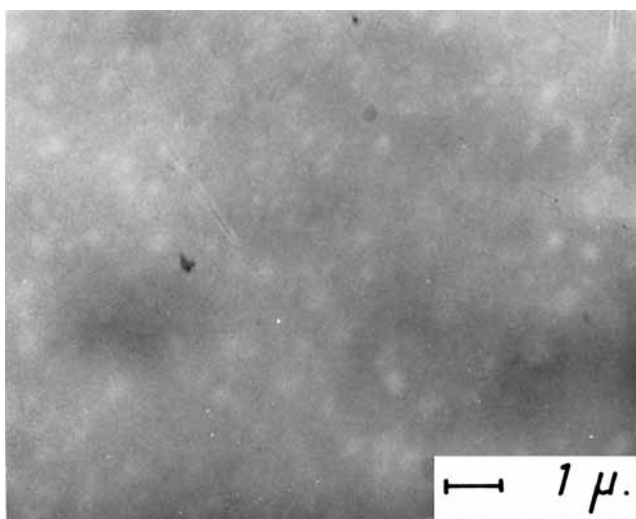
Fig. 5. Representative microstructure of sample B: (a) insoluble portion; (b) soluble portion.

domain. Especially the insoluble portions of samples B and H indicated a discontinuous, microphase separation. However, such a heterogeneous phase distribution was not observed in the polymer domain of samples A and G. Representative microstructures are shown in Figures 5 and 6.

The microstructure of the ethylene-propylene block copolymers (EPB) showed an extremely clear, microseparated phase distribution in the polymer domain, based on differences in density. Representative microstructures are given in Figure 7.



(a)

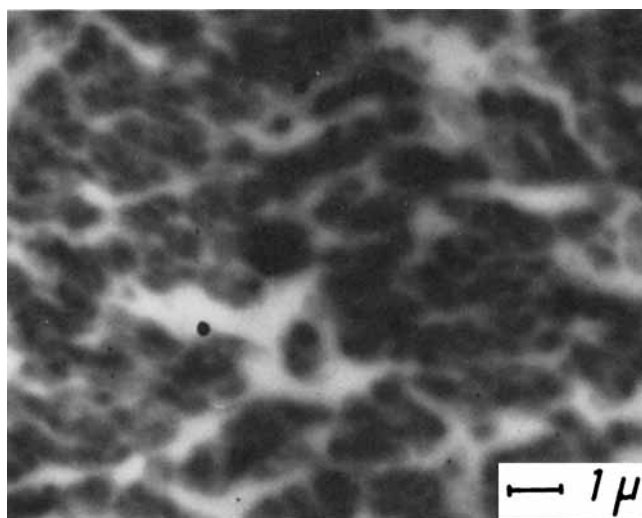


(b)

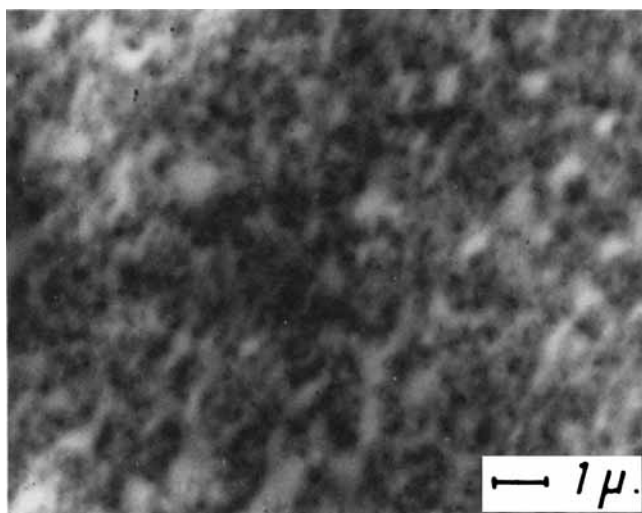
Fig. 6. Representative microstructure of sample A: (a) insoluble portion; (b) soluble portion.

### DISCUSSION

The results of analyses of all samples are summarized in Table V. Infrared absorption at  $730\text{ cm}^{-1}$  was found due to the crystalline region in polyethylene.<sup>2</sup> The insoluble portions indicated absorption at  $730\text{ cm}^{-1}$ , with the exception of sample G. The differences in  $T_g$  values between insoluble portion and soluble portion,  $\Delta T_g$ , could supply the information of the association degree between polymer chains, that is, the concentration of the microcrystalline structures. Fox and Loshaek<sup>3</sup> pointed out



(a)



(b)

Fig. 7. Microstructure of samples I (a) and J (b) EPB.

that  $\Delta T_g$  is related to the molecular weight between the physically interacted points, i.e., the microcrystalline region. The  $T_g$  values of samples A, B, and H greatly depended on the annealing temperature, except sample G. This was confirmed by the x-ray diffraction peak at (110) and (200) planes based on the presence of the crystalline region. Thus, it is concluded that organic solvent-insoluble portions are resolved into the crystalline gel attributable to the intra- or intermolecular association of the long ethylene linkage and the intra- or intermolecular crosslinking gel attributable to the active double bond included in the diene monomer. Since



TABLE V  
Summary of Results of Physical Tests\*

	Sample A		B		C		D		E		F		G		H	
	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S
Physical tests																
Solubility																
temperature																
thermal history																
Propylene composition, mole-%	33.9	43.1	39.4	39.9	-	-	-	-	-	-	-	-	37.6	46.5	31.8	40.7
Infrared absorption at 730 $\text{cm}^{-1}$																
$T_g$ annealing temperature																
X-ray diffraction																
	23.3%		32.0%													
Electron microscope heterogeneous domain																
	X	X	O	X	-	-	-	-	-	-	-	-	-	-	-	-

\* O: Dependent or observed; X: independent or unobserved; I: insoluble portion; S: soluble portion.

sample G includes a high content of ENB along the polymer chain, it could be assumed that the crosslinking gel is produced during the polymerization processes. It is interesting that sample H, having the high iodine value, includes a crystalline gel without a crosslinking gel. This could be ascribed to the differences in the polymerization system.

We should pay attention to the essential difference in the various analytical results of the crystalline gel in the various samples. For example, solubility of samples A, C, D, E, and G is independent on the thermal history of the samples, whereas that of samples B, F, and H depends on the thermal history. It is interesting to compare sample A and sample B in the above sense. The propylene composition of sample B is approximately equal in both portions. For sample A, the propylene composition of the insoluble portion is less than 10% relative to that of the soluble portion. Furthermore, the insoluble portion of sample B shows a higher value than 6% in propylene composition in comparison with that of sample A. It is surprising that the crystallinity of sample B is higher than that of sample A. A remarkable difference was observed in the microstructure of sample A and sample B. The microstructure of sample B approximates that of EPB, I, and J. Hence, it might be ascribed to the formation of the microcrystalline region based on the inter- or intramolecular association of the long ethylene linkage. This also reflects that the methylene sequence distribution along the polymer chain is efficiently ordered for sample B, relative to sample A. This agrees with the results obtained from the solution properties.<sup>4</sup>

## CONCLUSIONS

It was found that the insoluble portions in the organic solvent which are included in commercial EPDM are composed of a crystalline gel, with the exception of the crosslinking gel in sample G. There are distinctive differences in the physical properties of crystalline gel between samples A, C, and E and samples B, D, F, and H.

Especially the latter crystalline gel is due to the strong association of long ethylene linkages regularly distributed along the polymer chain.

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