

# Morphology and Properties of HDPE/Zinc-Neutralized Sulfonated EPDM Blends

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## SYNOPSIS

The compatibility of zinc-neutralized sulfonated EPDM (Zn-SEPDM) and its effect on crystallizing behavior of high-density polyethylene (HDPE) as well as the morphology of the blend were studied through wide-angle X-ray diffractometer (WAXD), differential scanning calorimetry (DSC), transition electron micrography (TEM), scanning electron micrography (SEM), a capillary rheometer, and mechanical property test. The results show that addition of Zn-SEPDM decreases both the melting point and the crystallizing temperature of HDPE. The apparent viscosity of the blend decreases with increasing of shear rate and stress. As Zn-SEPDM content exceeds 20%, Zn-SEPDM in the blend becomes continuous and an abrupt change in impact strength occurs. Owing to the incorporation of ionic groups into EPDM, the strong interactions between the chains make the impact strength of HDPE incredibly increased without sacrificing much of its tensile strength.

## INTRODUCTION

The toughness of high-density polyethylene (HDPE) could be improved by mechanically blending it with ethylene-propylene-diene monomer terpolymer (EPDM); the tensile strength of it, however, is much decreased. The zinc sulfonate groups serving as physical crosslinks incorporated in EPDM can associate within the nonpolar rubber matrix; thus, a higher tensile strength may be obtained, as compared with that of HDPE/EPDM blends. In this article, the crystallizing behavior of HDPE/Zn-SEPDM as well as the morphology correlated with their property were studied by wide-angle X-ray diffractometer (WAXD), differential scanning calorimetry (DSC), scanning electron micrography (SEM), transition electron micrography (TEM), a capillary rheometer, and mechanical property test.

## EXPERIMENTAL

### Materials

Materials used were EPDM EP<sub>35</sub> (Japan), double bond content 1.29 mol/kg, and HDPE 5000S (China), MI 0.66 g/10 min.

### Preparation of Zinc-Neutralized Sulfonated EPDM

To a 5% EPDM solution of cyclohexane, acetyl sulfonate was added at room temperature. The reaction was terminated after 30 min by ethyl alcohol. The aging-resistant agent was added in, then neutralized with zinc acetate, flashed for evaporation of the solvent, and vacuum dried. Sulfonation level: 1.1075 mol/kg.

### Preparation of HDPE Blends

Zn-SEPDM (90%) was blended with zinc stearate (10%) in a twin roller at 170°C for a period of 5 min

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**Table I Impact Strength (J/M) of the Blend**

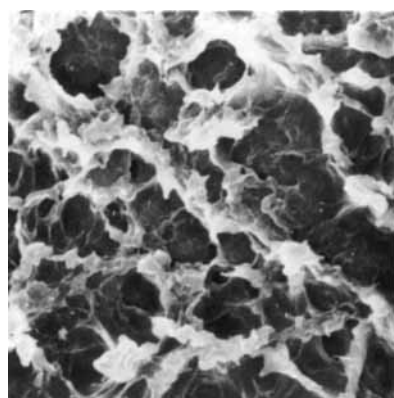
	100/0	95/5	90/10	85/15	80/20	70/30	60/40
HDPE/EPDM	178	388	420	439	685	≥ 685	≥ 685
HDPE/Zn SEPDM	178	393	541	571	920	≥ 920	≥ 920

**Table II Tensile Strength (MPa) of the Blend**

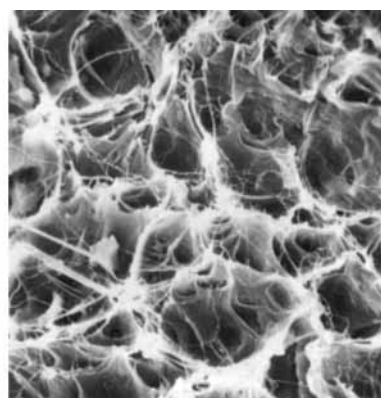
	100/0	95/5	90/10	85/15	80/20	70/30	60/40
HDPE/EPDM	32.79	24.41	21.91	19.50	17.36	13.41	10.29
HDPE/Zn-SEPDM	32.79	28.99	26.53	22.45	19.00	27.73	21.44

**Table III Elongation (%) of the Blend**

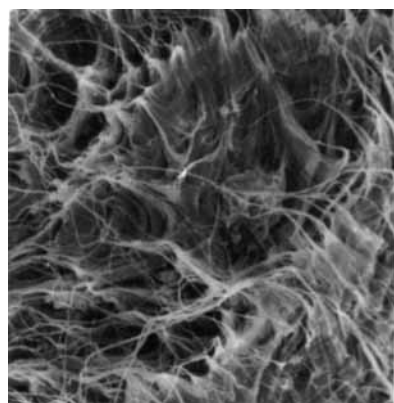
	100/0	95/5	90/10	85/15	80/20	70/30	60/40
HDPE/EPDM	40	182	82	39	31	32	42
HDPE/Zn-SEPDM	40	340	474	306	370	520	793



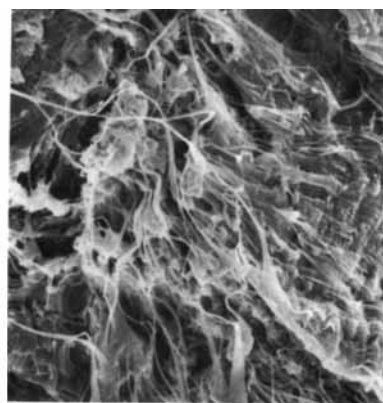
(a) 100/0



(b) 95/5

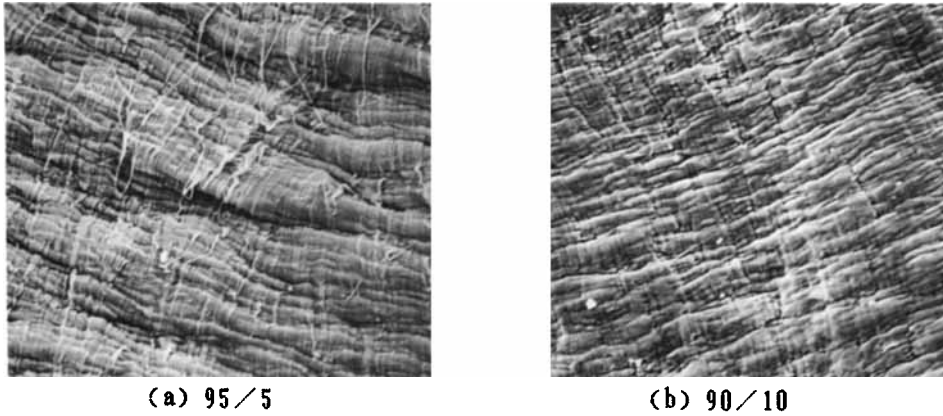


(c) 90/10

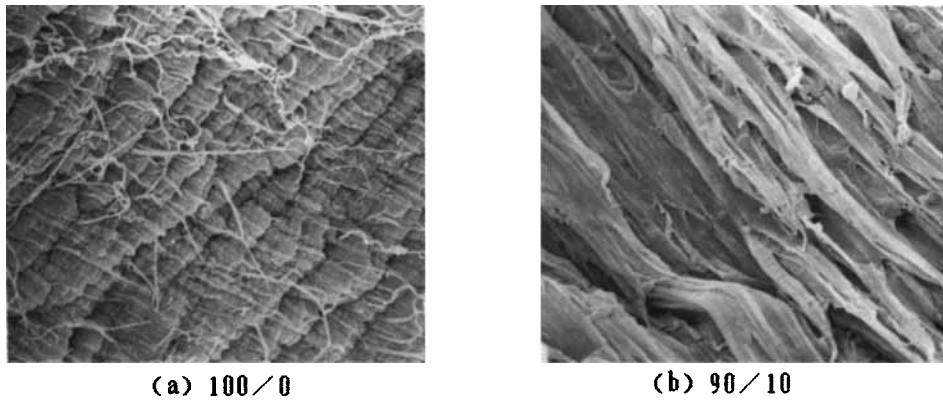


(d) 85/15

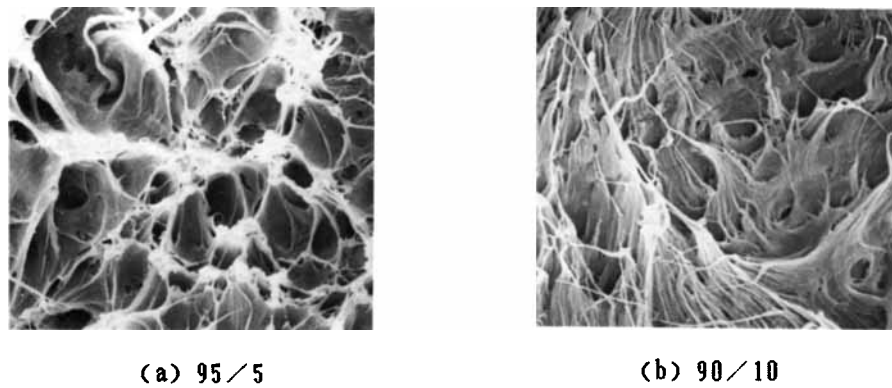
**Figure 1 (a)** SEMs of impact-fractured surfaces of HDPE/Zn-SEPDM blends ( $\times 1,000$ ).



**Figure 1 (b)** SEMs of impact-fractured surfaces of HDPE/EPDM blends ( $\times 2,000$ ).



**Figure 2** SEMs of tensile-fractured surfaces of HDPE/Zn-SEPDM blends ( $\times 2,000$ ).



**Figure 3** SEMs of impact-fractured surfaces of HDPE/Zn-SEPDM blends etched with cyclohexane/tetrahydrofuran ( $\times 1,000$ ).

and then with HDPE at 140°C for a period of 15 min. The specimens for WAXD, DSC, SEM, TEM, and rheological and mechanical property tests were cut from the molded sheets of 1 and 4 mm thick.

#### Measurement and Characterization

An impact test was conducted according to regulation mentioned in GB1843-80. Stress and strain behavior was measured with an autograph electron tensile testing machine (AG-10TA, Japan). Specimen: 25 × 15 × 1 mm, Speed: 100 mm/min.

DSC analysis was performed with a Perkin-Elmer DSC-7 instrument. The test specimen (5–10 mg) was heated to 200°C at a rate of 20°C/min, kept at 200°C for 5 min, then cooled to 30°C at the same rate. The melting point, crystallizing temperature,

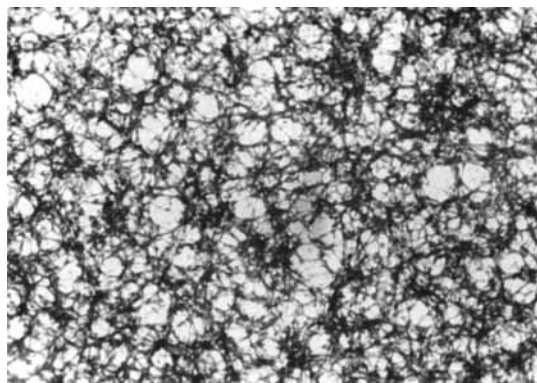
and melting enthalpy of HDPE in the blend were recorded. The crystallinity of HDPE in the blend was calculated according to:

$$X_c = (\Delta H / \Delta H^\circ) \times 100\%$$

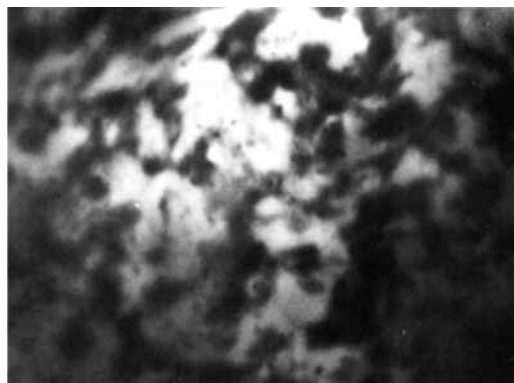
where  $\Delta H^\circ = 68.4 \text{ cal/g}^1$  is the enthalpy of HDPE of 100% crystallinity and  $\Delta H$  is the enthalpy of HDPE in the blend.

A wide angle X-ray diffractometer of D/Max-II A type with  $\text{CuK}_\alpha$  radiation was used. Accelerating voltage and electric current used were 40 KV and 30 mA, respectively.

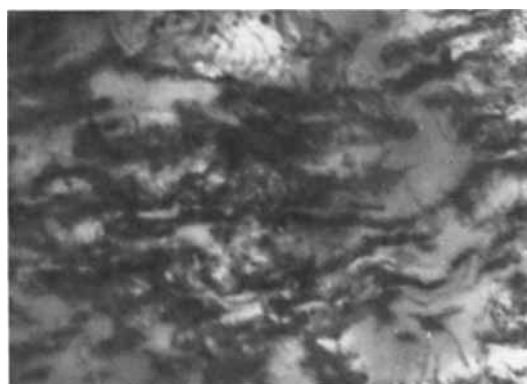
The specimen was microtomed with a LKB-2088 ultramicrotometer at low temperature, dyed with 1%  $\text{OsO}_4$ , and then observed with an electron microscope (JEM-100 CX, Japan).



(a) 80/20

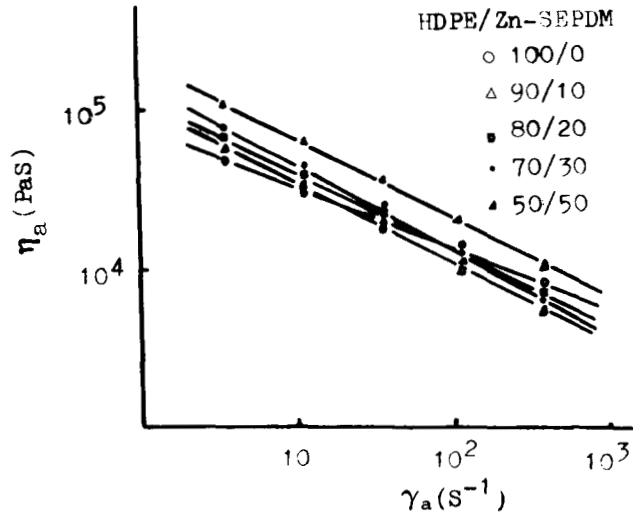


(b) 60/40



(c) 50/50

**Figure 4** TEMs of HDPE/Zn-SEPDM blends ( $\times 6,000$ ).



**Figure 5** Dependence of apparent melt viscosity of HDPE/Zn-SEPDM blends on shear rate (190°C).

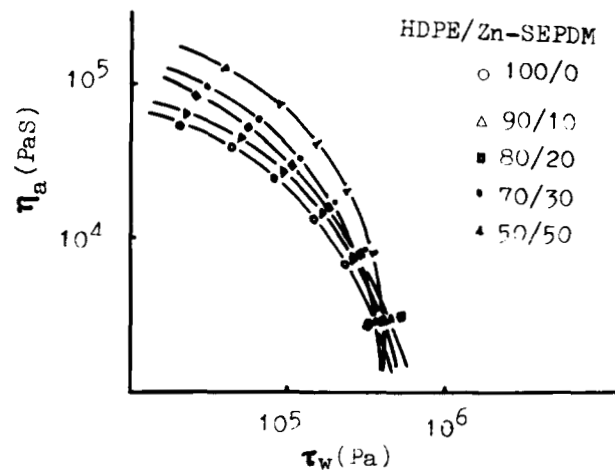
Rheological behavior was measured with Instron 3211 capillary rheometer. The diameter of capillary: 1.273 mm,  $L/D = 40$ , the shear rate corrected by Rabinowitsch equation.

The ruptured surfaces of tensile and impact specimens were observed through SEM (HITACHI-S520, Japan).

## RESULTS AND DISCUSSION

### Morphology and Properties of HDPE/Zn-SEPDM

The data listed in Tables I and II show that when Zn-SEPDM content exceeds 20% an abrupt change



**Figure 6** Dependence of apparent melt viscosity of HDPE/Zn-SEPDM blends on shear stress (190°C).

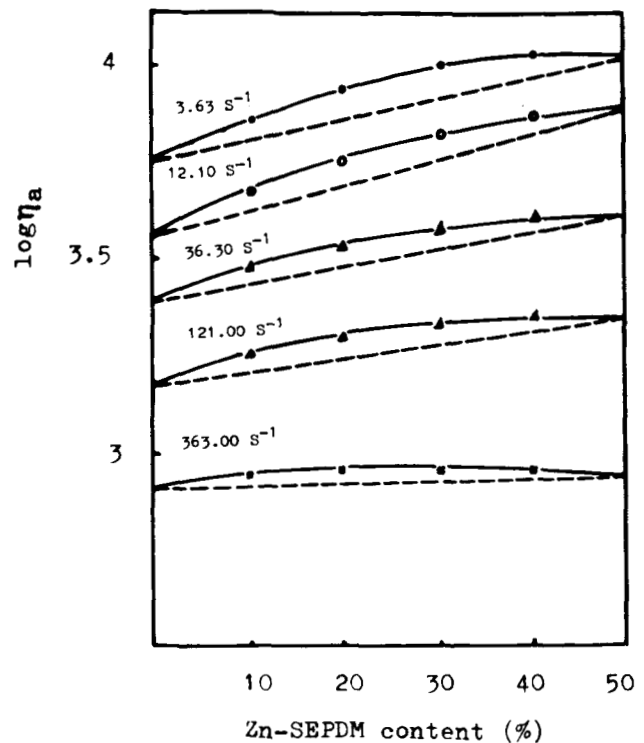
**Table IV** Measured and Calculated  $\eta_a$  of HDPE/Zn-SEPDM Blends at Shear Stress  $10^5$  Pa and 230°C

HDPE/Zn-SEPDM	Calculated <sup>a</sup> $\eta_a$ (PaS)	Measured $\eta_a$ (PaS)	$\Delta\eta_a$ (PaS)
100/0		2300	
0/100		11000	
90/10	2689	3000	311
80/20	3146	3800	654
70/30	3681	4600	919
50/50	5039	8000	2961

<sup>a</sup> By log-additivity rule,  $\ln(\eta_a)_{\text{blend}} = \sum W_i \ln(\eta_a)_i$ .

in impact strength occurs and the tensile strength is much higher than that of HDPE/EPDM. The elongation of HDPE/Zn-SEPDM is also higher than that of HDPE/EPDM (Table III). Obviously, these results are attributed to the physical association of Zn-SEPDM within the nonpolar rubber matrix.

As shown both in Figures 1(a) and 2, much interpenetrated fibriform Zn-SEPDM are formed on the fractured surfaces of the specimen. With the in-



**Figure 7** Dependence of apparent melt viscosity on the Zn-SEPDM content at different shear rate (230°C).

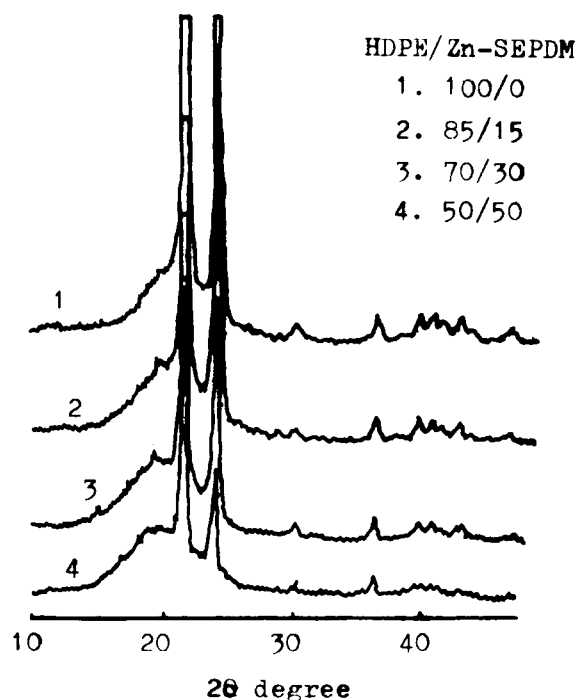
**Table V** WAXD Analysis of HDPE/Zn-SEPDM

HDPE/Zn-SEPDM	<i>d</i> -Spacings of Crystal Planes (Å)					
	110	200	210	020	011	111
100/0	4.124	3.712	2.968	2.475	2.271	2.162
85/15	4.123	3.709	2.966	2.473	2.269	2.163
70/30	4.131	3.713	2.975	2.478	2.269	
50/50	4.100	3.690		2.455	2.254	

**Table VI** DSC Analysis of HDPE/Zn-SEPDM

HDPE/Zn-SEPDM	100/0	90/10	70/30	60/40	50/50
Crystallinity (%)	60/33	60.00	59.00	57.70	56.44
Melting range (K)	372.58	371.99	372.56	372.74	373.24
	413.52	412.34	410.26	410.72	407.60
Melting point (K)	399.13	398.93	397.30	397.01	395.39

crease of the content of Zn-SEPDM, the fibring effect is more obvious and the flexibility of the blend increases. The cool flow occurs in the blend containing 10% Zn-SEPDM and the flexible fibers orient (Fig. 2), indicating the presence of interactions between Zn-SEPDM and the amorphous region of

**Figure 8** WAXD patterns of HDPE/Zn-SEPDM.

HDPE. In the case of HDPE/EPDM, the fibril network does not exist on the fractured surfaces of the blends [Fig. 1(b)].

Figure 3 shows the micrographs of the etched specimens, demonstrating that the fibril networks exist in the whole lot of the specimen.<sup>2</sup> As Zn-SEPDM content amounts to 20%, blend becomes interpenetrating polymer network in structure (Fig. 4) as a result of higher compatibility of its component.<sup>3</sup> In case Zn-SEPDM content exceeds 20%, disperse state appears again.<sup>4</sup>

The melt viscosity of the blends is higher than that of HDPE, especially as Zn-SEPDM content exceeds 30% and at lower shear rate (Fig. 5) or stress (Fig. 6). Since the interactions between Zn-SEPDM and the amorphous region of HDPE become weak under stress, the apparent melt viscosity of the blend will be decreased.

The positive deviation of measured viscosities of the blends from those calculated (Table IV) indicates the existence of strong interactions between the components, resulting in a higher resistance to flow.<sup>5</sup> The deviation decreases with the increase of shear rate (Fig. 7) due to the reduction of interactions between the molecules in the blends.

The *d*-spacings of (110), (200), (020), and (011) planes of HDPE in the blends do not vary with Zn-SEPDM content (Table V), indicating that Zn-SEPDM has no effect on crystal planes. As shown in Figure 8, with the increase of Zn-SEPDM content the diffraction peaks of (111) and (210) disappear

on the WAXD patterns of HDPE/Zn-SEPDM (50/50), showing that Zn-SEPDM has some retarding effect on the propagation of (111) and (210).

The data listed in Table VI show that with the amount of Zn-SEPDM added melting point and crystallinity of the blend decrease and the melting range gets more narrow, illustrating that HDPE and Zn-SEPDM are compatible.

## CONCLUSION

HDPE is partially compatible with Zn-SEPDM. Owing to the incorporation of ionic groups into EPDM, the interactions between the chains are much increased. Both a higher impact and tensile strength of HDPE may be obtained after blending

it with a sufficient amount of Zn-SEPDM not less than 20%.

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