Ultrasonic Improvement of the Compatibility and Rheological Behavior of High-Density Polyethylene/Polystyrene Blends

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ABSTRACT: The effects of ultrasonic oscillations on the rheological behavior, mechanical properties, and morphology of high-density polyethylene (HDPE)/polystyrene (PS) blends were studied. The experimental results show that the die pressure and apparent viscosity of HDPE/PS blends are remarkably reduced in the presence of ultrasonic oscillations and that mechanical properties of the blends are improved. The particle size of the dispersed phase in HDPE/PS blends becomes smaller, its distribution becomes narrower, and the interfacial interaction of the blends becomes stronger if the blends are extruded in the presence of ultrasonic oscillations. Ultraviolet spectra and Soxhlet extraction results show the formation of a polyethylene–PS copolymer during extrusion in the presence of ultrasonic oscillations, which improves the compatibility of HDPE/PS blends. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 23–32, 2002

Key words: high-density polyethylene; polystyrene; ultrasound; compatibility; rheology

INTRODUCTION

The blending of polymers offers attractive opportunities for developing new materials with unique property combinations.[1,2] The majority of polymers are incompatible. It has been increasingly recognized that the interfacial adhesion and morphology control in multiphase polymer blends play an important role in their overall performance.[3,4] Methods to improve interfacial adhesion between two immiscible phases have been the subject of considerable research activity. In general, there exist the following routes for the improvement of compatibility:

1. The addition of a block or graft copolymer compatibilizer with bifunctional properties capable of interacting with both the dispersed phase and matrix.[2,5,6]
2. The introduction of a functional polymer component that forms an interfacially active compatibilizer in situ during processing.[7–10]
3. The in situ formation of an interchain copolymer compatibilizer through reactive blending of the functionalized polymer components and cocrosslinking components.[11–15]
4. An increase in the polarity of the matrix through partial oxidation, γ-ray, electron-beam, microwave, or ultraviolet (UV) irradiation, or polar grafting to improve the wettability of the matrix to the polar dispersed phase.[16–18]
5. The self-compatibilization of polymer blends via mechanochemical reactions and novel melt vibration technology during processing.[19–26]

Although block/graft copolymers have been demonstrated to effectively solve the compatibility problem for polymer blends, a limitation to practical implementation is the lack of adequate chemical routes for economically producing block/graft copolymers that would be appropriate for important systems. An alternative is to form these block or graft copolymers in situ during processing by the reaction of suitably chosen functionalized polymer components. The effective routes for the introduction of functional groups such as carboxyl, hydroxyl, epoxy, and anhydride groups to the molecular chains of nonpolar polymers such as polyethylene (PE), polypropylene, and polystyrene (PS) are reactive processing, γ-ray, electron-beam, microwave, and UV irradiation, and so forth. The key to these results is to avoid crosslinking or degradation during functionalization processing. The functionalized common plastics through the previous routes can greatly improve the interfacial adhesion of
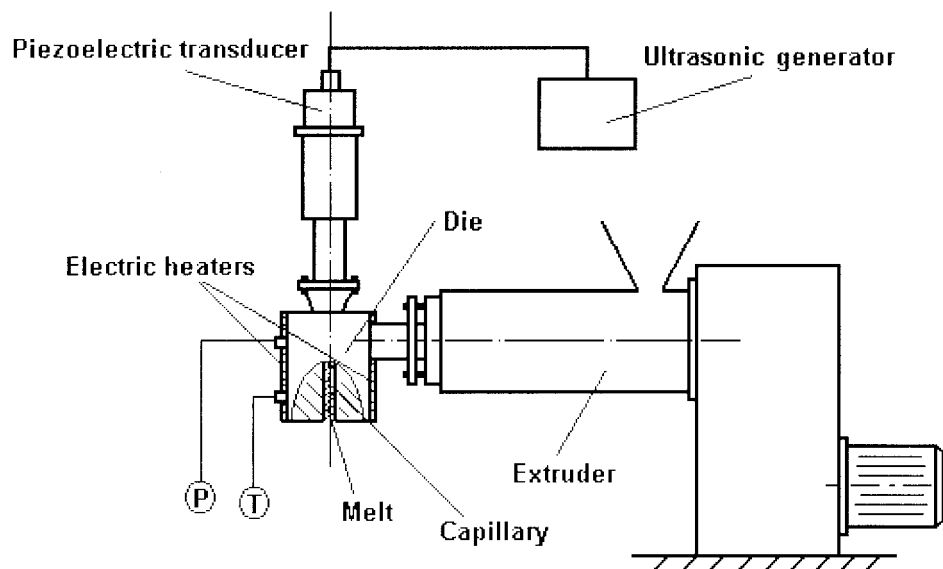
Figure 1 Schematic diagram of the ultrasonic irradiation extrusion system.

their blends with engineering plastics (e.g., polyamide and polyester) and fillers, resulting in great increases in the mechanical properties of the blends and composites.[27]

A recently suggested novel and economical alternative for the compatibilization of incompatible blends is mechanochemical compatibilization under a high shear rate and melt vibration technology during processing. The melt viscosity, dispersed phase size, and size distribution of the polymer blends and composites are reduced, and their mechanical properties are improved because of oscillation compatibilization when oscillations are induced during polymer processing. Ultrasonic oscillations can cause the devulcanization of crosslinked elastomers during extrusion. The devulcanized elastomers can be reprocessed like virgin elastomers.[28,29]

In our previous work,[30–32] ultrasonic oscillations were induced in an extruder. The experimental results show that ultrasonic oscillations can remarkably reduce the die pressure (P), die swell, and apparent viscosity (η_a) of polymer melts. Ultrasonic oscillations can also inhibit the unstable flow of PS and linear low-density polyethylene (LLDPE), and the appearance of PS and LLDPE extrudates during extrusion are improved. The interfacial adhesion of filler-filled high-density polyethylene (HDPE) is enhanced, and the dispersion of filler particles in the matrix is improved in the presence of ultrasonic oscillations.

In this article, the effects of ultrasonic oscillations on the rheological behavior, mechanical properties, and compatibility of HDPE/PS blends are discussed. The morphological development of HDPE/PS blends in the presence of ultrasonic oscillations is characterized through scanning electron microscopy (SEM), UV spectra, differential scanning calorimetry (DSC), and extraction.

EXPERIMENTAL

Figure 1 shows an outline of a specially designed ultrasonic oscillation extrusion system developed in our laboratory. It consists of a single-screw extruder and a cylinder die connected to a generator of ultrasonic oscillations. The die includes a special horn serving as a capillary. The maximum power output and frequency of the generator are 300 W and 20 kHz, respectively. The ultrasonic oscillations are in the direction parallel to the flow of the polymer melt. A pressure transducer and a thermocouple at the die entry were installed for continuous recording of the variation of P and temperature during extrusion.
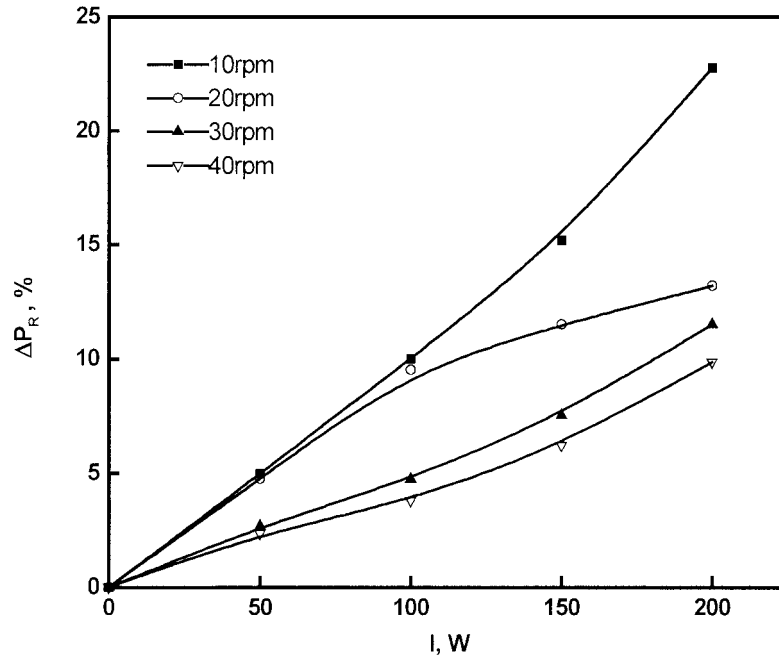
TABLE I
Sample Code and Preparation Conditions

Sample code	Repeated extrusion number	Ultrasound intensity (W)		
		First extrusion	Second extrusion	Third extrusion
0	1	0	—	—
1	1	100	—	—
2	1	200	—	—
00	2	0	0	—
01	2	0	100	—
10	2	100	0	—
11	2	100	100	—
20	2	200	0	—
22	2	200	200	—
000	3	0	0	0
111	3	100	100	100
222	3	200	200	200

Figure 2 ΔP_r versus the ultrasound intensity for HDPE/PS (80/20) blends at different screw rotation speeds.

The shear stress at the capillary wall, τ_w, is given by the equation

$$\tau_w = \frac{PR}{2L}$$

where R and L are the radius and length of the capillary, respectively.

The apparent shear rate, γ_a, is given by the equation

$$\gamma_a = \frac{4Q}{\pi R^3}$$

where Q is the volumetric flow rate. η_a is defined as

$$\eta_a = \frac{\tau_w}{\gamma_a} = \frac{\pi P R^4}{8QL}$$

Two typical examples of HDPE/PS blends (80/20 and 20/80) were studied. Mixtures of HDPE with PS were
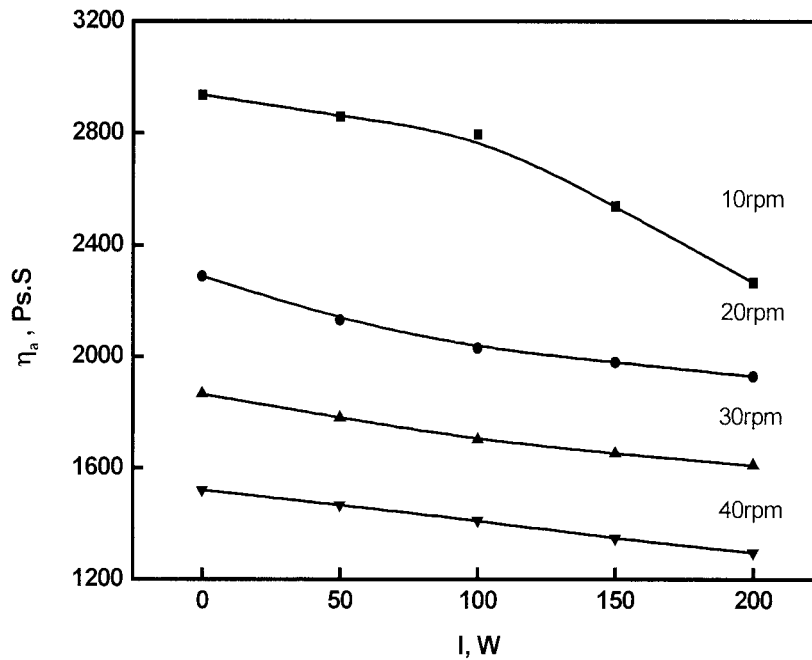

Figure 3 η_a for HDPE/PS (80/20) blends versus the ultrasound intensity at different screw rotation speeds.
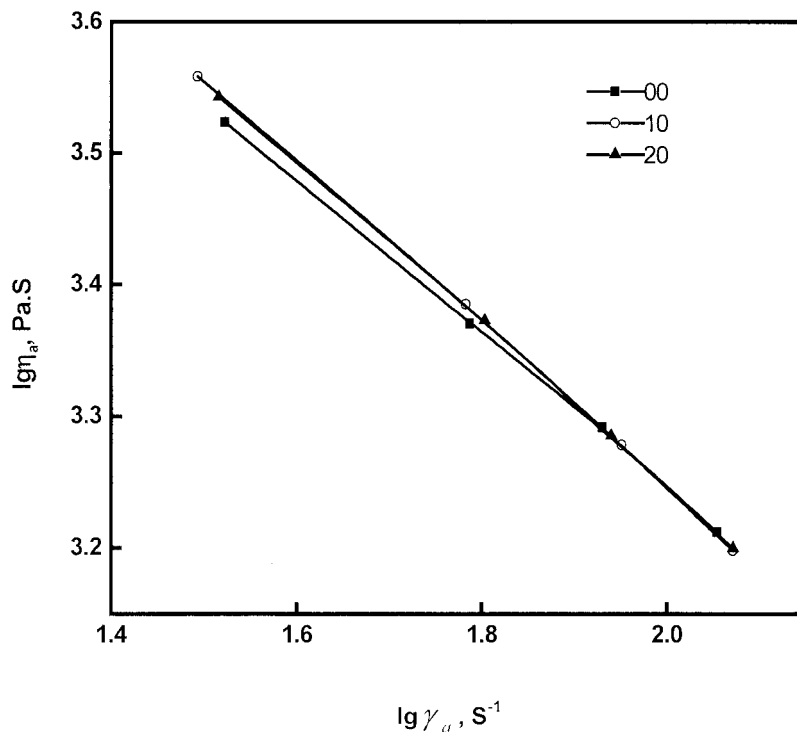
Figure 4 Log η_a versus log γ_a for HDPE/PS (80/20) blends prepared under different conditions.

extruded in an extruder, as shown in Figure 1, and then pelletized. To obtain some specimens for measuring the mechanical properties of the extruded materials, we compression-molded these pellets into 1- and 4-mm sheets. To study the effects of ultrasonic oscillations on the mechanical properties and morphology development of HDPE/PS blends, we took specimens exposed repeatedly to ultrasonic oscillations with different ultrasound intensities. The preparation conditions were as follows: the screw rotation speed was 10 rpm, and the temperatures from hopper to die were

160, 180, 210, and 210°C. The sample codes are listed in Table I.

The stress–strain behavior of HDPE/PS blends was measured on an Instron 4302 tension machine (Canton, MA) with specimen dimensions of 25 mm × 6.5 mm × 1 mm and a crosshead speed of 100 mm/min. Impact strength testing was conducted according to the regulation mentioned in GB1843-80. The morphology of the blends was examined with a Hitachi X-650 scanning electron micrograph (SEM) (Tokyo, Japan). SEM observations were made on the impact fracture
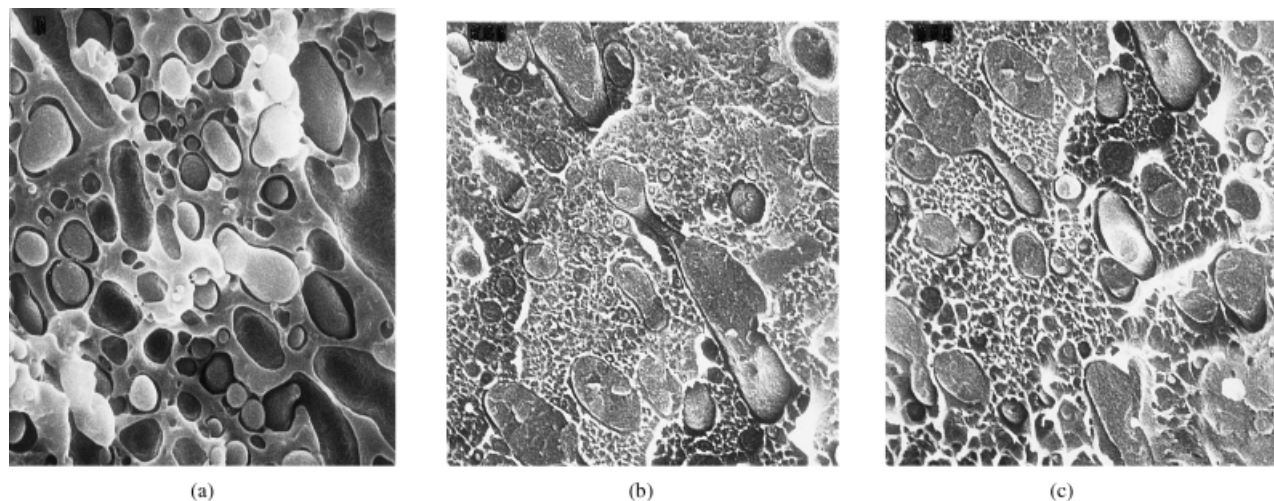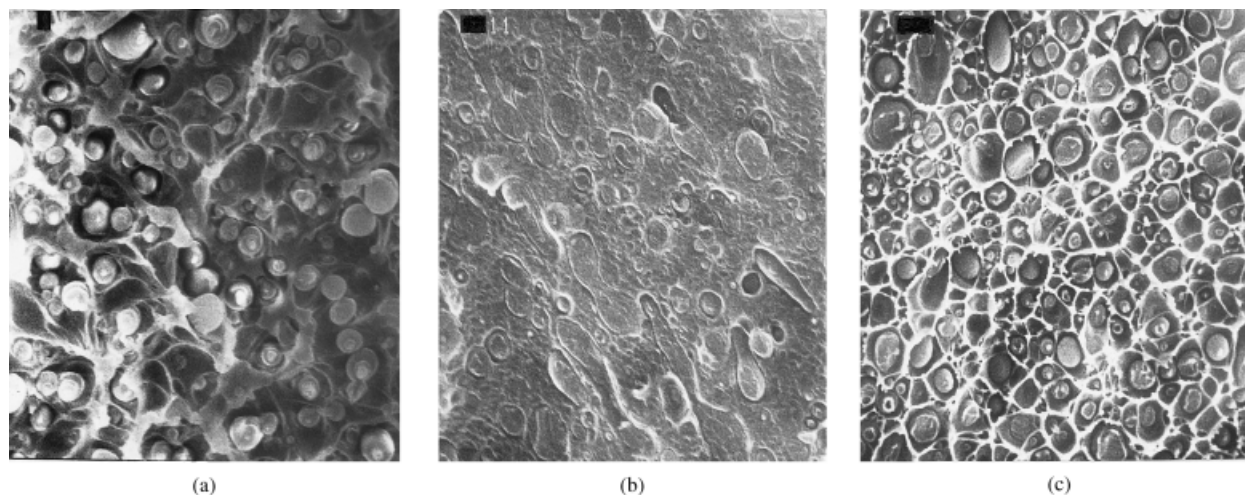

Figure 5 SEM micrographs of the fracture surfaces of HDPE/PS (80/20) blends extruded repeatedly at 10 rpm in the absence of ultrasonic oscillations (×3000). Repeat extrusions: (a) 1, (b) 2, and (c) 3.

Figure 6 SEM micrographs of the fracture surfaces of HDPE/PS (80/20) blends extruded repeatedly at 10 rpm in the presence of ultrasonic oscillations (×3000; ultrasound intensity = 200 W). Repeat extrusions: (a) 1, (b) 2, and (c) 3.

surfaces at the temperature of liquid nitrogen. Gold was sputtered on the surfaces before the SEM observations. SEM micrographs of HDPE/PS (80/20) were analyzed with a Bencher digital image processing system (Leitz, Germany) to obtain the PS particle size and its distribution in the blends.

The blends were pressed into membranes and extracted with 1,2-dichloroethane for 48 h for dissolving out PS, and then the extracted samples were dried in vacuum until their weights were constant. The weight loss of the extracted samples was calculated with the following equation:

$$\text{weight loss} = \frac{W_1 - W_2}{W_1} \times 100\%$$

where W_1 and W_2 are the weights of samples before and after extraction, respectively. Meanwhile, the samples before and after extraction were analyzed with an ultraviolet–visible UV-240 spectrophotometer (Shimadzu Corp., Kyoto, Japan) to investigate the formation of the PE–PS copolymer when the blends were extruded in the presence of ultrasonic oscillations.
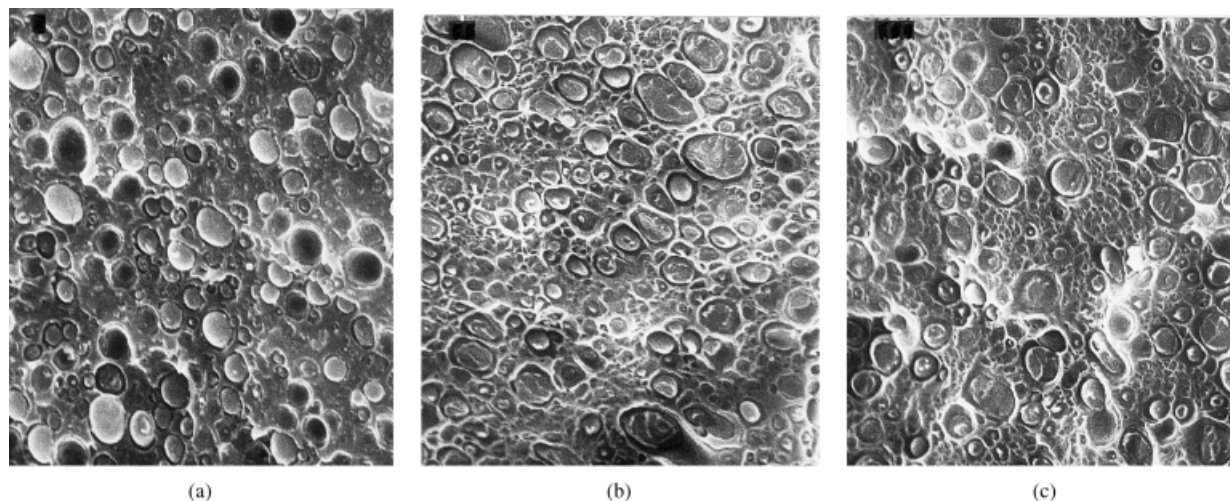
RESULTS AND DISCUSSION

### Effects of ultrasonic oscillations on the rheological behavior of the HDPE/PS (80/20) blends

The relative P drop, ΔP_r, in the presence of ultrasonic oscillations can be written as

$$\Delta P_r = \frac{P_1 - P_2}{P_1} \times 100\%$$

where P_1 and P_2 are the P values in the absence and presence of ultrasonic oscillations, respectively. As

Figure 7 SEM micrographs of the fracture surfaces of HDPE/PS (80/20) blends extruded repeatedly at 10 rpm in the presence of ultrasonic oscillations (×3000; ultrasound intensity = 200 W). Repeat extrusions: (a) 1, (b) 2, and (c) 3.
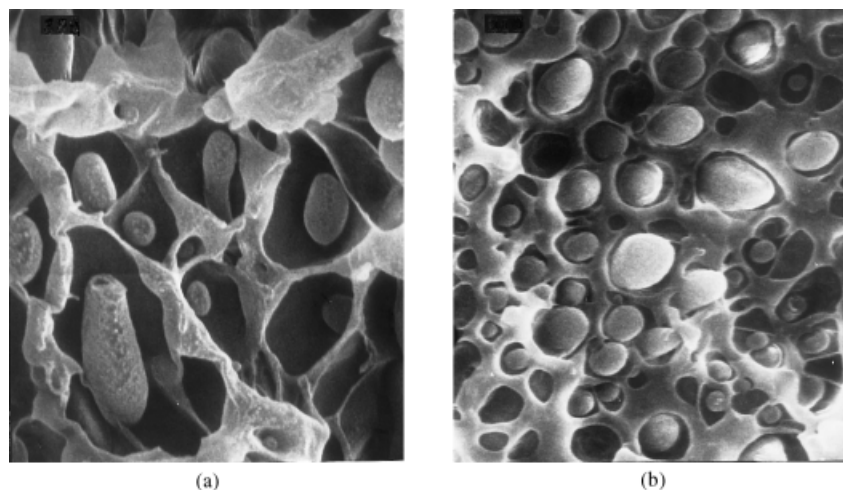
Figure 8 SEM micrographs of the fracture surfaces of HDPE/PS (80/20) blends prepared by two extrusions at 10 rpm (×5000): (a) sample 00 and (b) sample 10.

shown in Figure 2, ΔP_r of the HDPE/PS (80/20) blends increases as the ultrasound intensity rises and decreases with an increase in the screw rotation speed; for a given ultrasound intensity (especially at higher values), the P drop is greater for a lower screw rotation speed and vice versa, indicating that in the presence of ultrasonic oscillations, P for the HDPE/PS (80/20) blends is reduced during extrusion, and the processability of the blends is improved.

Figure 3 shows that η_a of the HDPE/PS (80/20) blends goes down with increasing ultrasound intensity and screw rotation speed. The lower the screw rotation speed is, the more significant the η_a reduction is.

To confirm the permanent change in the viscosity of the HDPE/PS (80/20) blends caused by ultrasonic oscillations, we performed repeated extrusions of the blends. Figure 4 shows the viscosity change of the HDPE/PS (80/20) blends after two extrusions. When ultrasonic oscillations were induced for the first extrusion and ultrasonic oscillations were not induced for the second extrusion, η_a of the prepared blends was higher than that of the blend prepared in the absence of ultrasonic oscillations for two extrusions, indicating that ultrasonic oscillations caused a permanent change in η_a for the HDPE/PS (80/20) blends and that the interfacial interactions of the blends increased.

Ultrasonic compatibilization of the HDPE/PS blends during extrusion

SEM micrographs of the fracture surfaces of the HDPE/PS (80/20) blends are shown in Figures 5–8. Figure 5 shows the morphology of repeatedly ex-
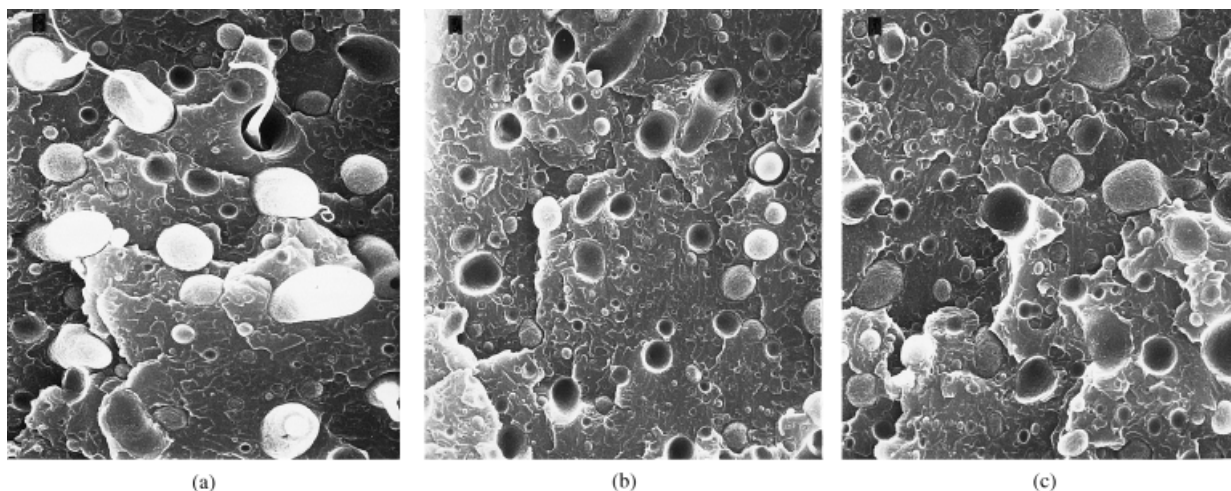
Figure 9 SEM micrographs of the fracture surfaces of HDPE/PS (20/80) blends extruded twice under different conditions (×2000): (a) sample 00, (b) sample 20, and (c) sample 22.
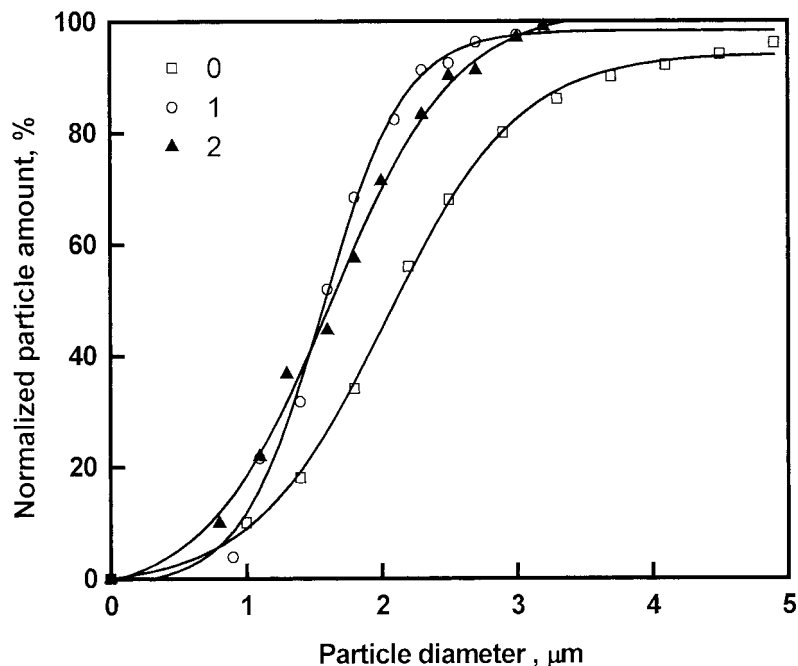
Figure 10 Particle size distribution of the dispersed phase in PS/HDPE (80/20) blends prepared under different conditions

truded HDPE/PS (80/20) blends in the absence of ultrasonic oscillations. Large and irregular PS domains are dispersed in the HDPE matrix. Repeated extrusion hardly influences the large and irregular PS domains. Therefore, HDPE/PS blends are thought to be essentially incompatible in conventional extrusion.

As shown in Figure 6, small PS spheres about 1.5 μm in diameter on average are dispersed in the HDPE matrix when HDPE/PS (80/20) blends are repeatedly extruded in the presence of ultrasonic oscillations with an intensity of 100 W. The particle size and its distribution are evidently decreased in comparison with those shown in Figure 5. The PS particle size is slightly decreased with the increase of repeated extrusions in the presence of ultrasonic oscillations. The same morphology is also observed on the fracture surface of HDPE/PS (80/20) extruded repeatedly in the presence of ultrasonic oscillations with an intensity of 200 W, as shown in Figure 7. As shown in Figure 8, when an HDPE/PS (80/20) blend is first extruded in the presence of ultrasonic oscillations with an intensity of

100 W and then extruded in the absence of ultrasonic oscillations, it also shows small PS spheres about 1.5 μm in diameter on average dispersed in the HDPE matrix, indicating a very stable morphology. Figure 9 also shows that the dispersed HDPE particle size in PS/HDPE (80/20) blends is reduced in the presence of ultrasonic oscillations.

Figure 10 shows the dispersed PS particle size distribution in HDPE/PS (80/20) blends extruded in the presence and absence of ultrasonic oscillations. The particle size and its distribution decrease in the presence of ultrasonic oscillations.

In general, when a compatibilizer is added to a completely incompatible polymer blend, the dispersed phase tends to become spherical, and the spherical particle size and its distribution are decreased. The compatibility of the blends is improved. As described previously, when ultrasonic oscillations are induced during the extrusion of HDPE/PS blends, the irregularly dispersed PS phase disappears, and the PS sphere size and its distribution are greatly reduced, indicating that the ultrasonic oscillations can greatly enhance the compatibility of HDPE/PS blends.

To confirm what causes the ultrasonic compatibilization of HDPE/PS blends, we characterized the morphological structure of HDPE/PS blends through extraction, UV spectrometry, and DSC to study the mechanism for the ultrasonic compatibilization of HDPE/PS blends.
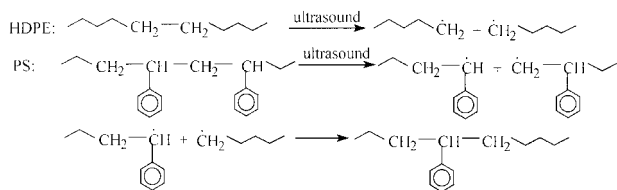
PS could form a block copolymer with HDPE as the following model shows:

TABLE II
1,2-Dichloroethane Extraction Results for the
HDPE/PS (80/20) Blends

Sample Code	Weight Loss (%)
0	20.0
2	8.0
00	20.0
11	18.0
22	15.0
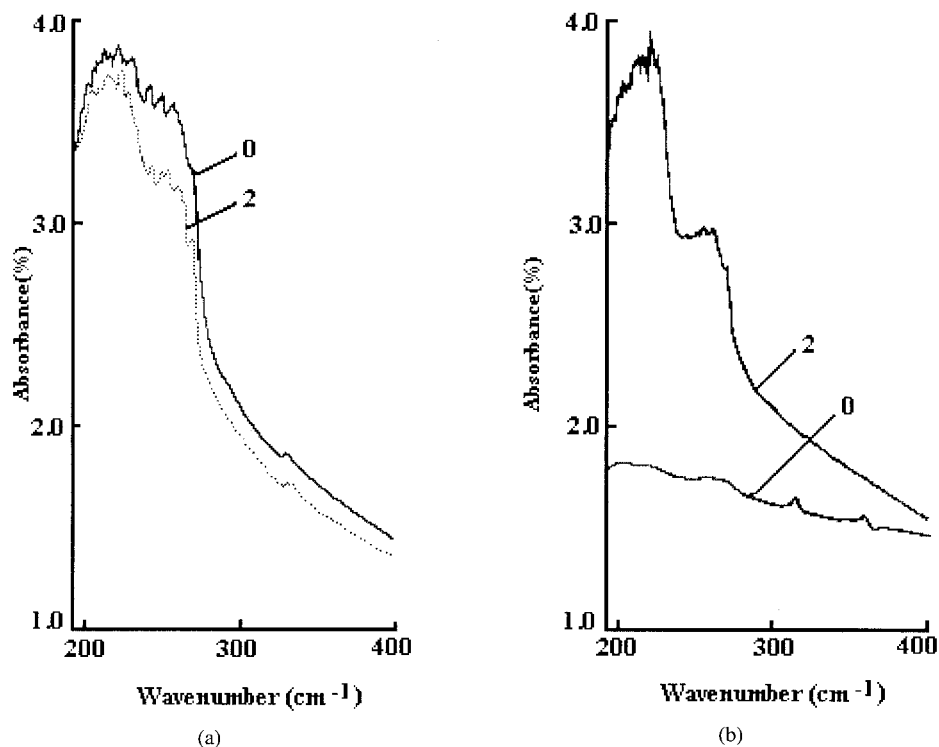
Figure 11 Effect of the ultrasound intensity on UV absorbance spectra of HDPE/PS (80/20) blends: (a) before extraction and (b) after extraction.

Some PS in HDPE/PS blends could not be extracted from the blends by a solvent for PS. The data listed in Table II show that when PS and HDPE/PS (80/20) blends extruded in the presence and absence of ultrasonic oscillations were extracted with 1,2-dichloroethane for 48 h, PS and PS in HDPE/PS (80/20) blends extruded in the absence of ultrasonic oscillations were completely removed, whereas some PS in HDPE/PS (80/20) blends extruded in the presence of ultrasonic oscillations could not be removed. As shown in Figure 11, all of the UV spectra of HDPE/PS (80/20) blends

extruded in the absence of ultrasonic oscillations and in the presence of ultrasonic oscillations with an intensity of 200 W show characteristic absorptions of PS before extraction, whereas the characteristic absorptions of PS in HDPE/PS (80/20) blends extruded in the absence of ultrasonic oscillations disappear in the UV spectrum after extraction. However, the characteristic absorptions of PS in HDPE/PS (80/20) blends extruded in the presence of ultrasonic oscillations with an intensity of 200 W are still seen in the spectrum after extraction, indicating the formation of the HDPE–PS block copolymer during the extrusion of HDPE/PS blends when ultrasonic oscillations are induced.
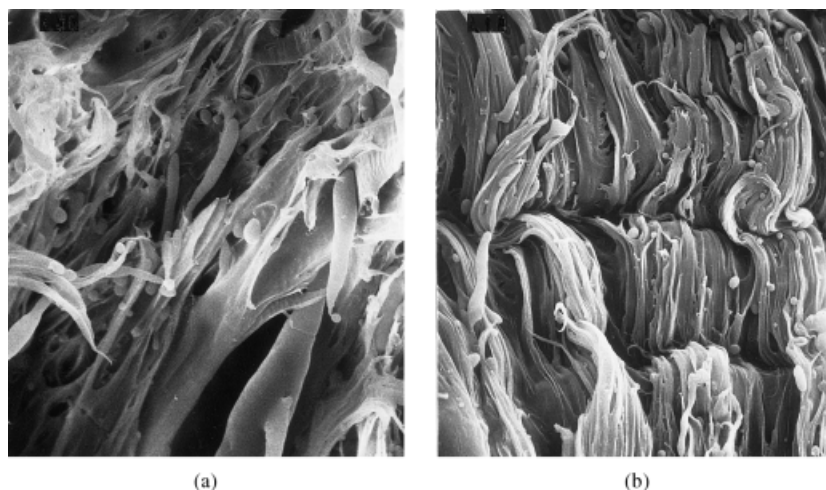
TABLE III
Effect of Ultrasonic Oscillations on the DSC Results of the HDPE/PS (80/20) Blends

Sample Code	ΔH_m (J/g)	ΔH_c (J/g)	T_m (°C)	T_c (°C)
00	151.1	143.1	130.7	115.8
10	139.4	133.4	130.1	117.1
11	137.9	135.2	130.9	116.9
000	141.2	139.2	130.8	116.6
111	136.2	136.8	130.9	116.2
222	139.5	138.3	130.2	117.0

TABLE IV
Effect of Ultrasonic Oscillations on the Mechanical Properties of the HDPE/PS (80/20) Blends

Sample Code	Young's modulus (MPa)	Yield stress (MPa)	Elongation at break (%)	Impact strength (J/m)
0	950.4	21.1	89.1	35.7
2	903.5	19.7	175.7	54.3
00	893.9	18.9	43.36	35.7
01	905.4	19.7	300.2	—
10	962.5	20.1	426.6	52.7
11	932.3	19.5	249.3	52.5
20	909.8	20.0	481.9	39.2
22	913.8	20.1	412.1	37.3

Figure 12 SEM micrographs of the fracture surfaces of HDPE/PS (80/20) blends extruded twice under different conditions (×1000): (a) sample 00 and (b) sample 10.

The data listed in Table III show that the melting enthalpy (ΔH_m) and crystallizing enthalpy (ΔH_c) of HDPE in the HDPE/PD (80/20) blends are reduced in the presence of ultrasonic oscillations, and the melting point (T_m) and crystallization temperature (T_c) are slightly changed, indicating that the crystallization of HDPE in the HDPE/PS (80/20) blends is inhibited by ultrasonic compatibilization during extrusion.

Effects of ultrasonic oscillations on the mechanical properties of the HDPE/PS blends

The data listed in Table IV show that ultrasonic oscillations can greatly increase the elongation at break and impact strength of HDPE/PS (80/20) blends. The yield strength and Young's modulus of the blends increase slightly in the presence of ultrasonic oscillations during extrusion. However, the elongation at break and impact strength of 10 sample increased by 900 and 50%, respectively, with respect to those of the 00 sample. The yield strength and Young's modulus of HDPE/PS (20/80) blends are greatly increased in the presence of ultrasonic oscillations during extrusion (Table V), indicating strong interfacial adhesion in the presence of ultrasonic oscillations during extrusion. As shown in Figure 12, for HDPE/PS (80/20) blends, many debonded PS particles are pulled out on the

tensile fracture surface of the 00 sample, showing poor interfacial adhesion. However, no debonded PS particles are observed on the tensile fracture surface of the 10 sample, indicating that PS particles are well bonded with the HDPE matrix. All of these are ascribed to ultrasonic compatibilization of HDPE/PS blends caused by HDPE–PS block copolymer formed in situ during extrusion.

CONCLUSIONS

1. Ultrasonic oscillations can improve the processing behavior of HDPE/PS blends during extrusion; P and η_a values of the blends remarkably decrease with the increase in ultrasound intensity.
2. In the presence of ultrasonic oscillations, the particle size of the dispersed phase and its distribution in HDPE/PS blends are reduced, and the interfacial adhesion between HDPE and PS is improved. The compatibility of HDPE/PS blends can be improved if the blends are extruded in the presence of ultrasonic oscillations; this is ascribed to the in situ formation of HDPE–PS copolymers under ultrasonic oscillations.
3. Ultrasonic oscillations can greatly increase the elongation at break and impact strength of HDPE/PS blends because of the enhancement of the interfacial adhesion and the compatibility of the blends.

TABLE V
Effect of Ultrasonic Oscillations on the Mechanical Properties of the HDPE/PS (20/80) Blends

Sample Code	Young's modulus (MPa)	Yield stress (MPa)	Elongation at break (%)	Impact strength (kJ/m^2)
00	2451	19.7	0.97	3.2
20	2522	24.0	1.04	3.2
22	2732	21.0	0.90	3.2

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