Polyphosphazene/Low-Density Polyethylene Blends: Miscibility and Flame-Retardance Studies

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ABSTRACT: The effect of poly(dianilinephosphazene) (PDAP) on the processability, thermal behavior, crystallinity, morphology, mechanical properties, and flammability behavior of low-density polyethylene (LDPE) was studied. Plasticorder traces of PDAP/LDPE blends implied good processability and miscibility. Thermogravimetric analysis showed that PDAP improved the thermal stability of LDPE. X-ray diffraction results indicated that PDAP was a semicrystalline polymer, and the crystallinity of the blends decreased with increasing PDAP content. A new reflection at $2\theta = 23.15°$ was found in wide-angle X-ray diffraction spectra of the blends, indicating that these two components interacted with one another. The scanning electron microscopy microstructures of the blends also supported these findings. Moreover, PDAP substantially enhanced the limited oxygen index and elongation at break of LDPE. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 709–714, 2002

Key words: flame retardance; polyethylene (PE); mechanical properties; polyphosphazene; processability

INTRODUCTION

It is well known that low-density polyethylene (LDPE) has excellent mechanical properties, low-temperature resistance, insulation properties, and chemical corrosion resistance. Therefore, it has been widely used as a commodity thermoplastic polymer. However, being a hydrocarbon polymer, LDPE catches fire easily and burns with dripping. Therefore, it alone cannot meet all the properties required for specific applications. A number of phosphorus-based, halogen-based, and inorganic flame retardants are recommended for LDPE to reduce its flammability.[1–4] Polyphosphazenes constitute a broad class of inorganic polymers with backbones consisting of alternating phosphorus and nitrogen atoms and two substituents at each phosphorus atom. Because of the special skeletal characteristics of the —P=N— system, a tremendous variety of substituents can be attached to the backbone phosphorus atoms,[5] so these inorganic polymers exhibit a very broad spectrum of chemical and physical properties that make them suitable for many applications, especially in flame resistance. It was expected that LDPE modified with poly(dianilinephosphazene) (PDAP) would show a remarkable improvement in flame retardance.

EXPERIMENTAL

Materials

LDPE (0.914 g/cm^3) was supplied by Jin Shan Petrochemical Corp., Ltd. (Shanghai, China).

PDAP was synthesized and further purified in our laboratory as follows. Poly(dichlorophosphazene) was prepared by the ring-opening polymerization of hexachlorocyclotriphosphazene, as suggested by Allcock et al.;[6] BCl$_3$, a Lewis acid, was adopted as a catalyst. Because it was very moisture-sensitive and easily crosslinked, poly(dichlorophosphazene) needed to be treated carefully. Then, PDAP was prepared by a nucleophilic substitution of the chlorine atoms by the appropriate aniline on poly(dichlorophosphazene).

Mixture preparation

The blends were prepared by melt mixing in two shaft internal roller mixers fitted to a Haake Rheometer system (effective chamber volume = 50 cm^3) at a rotation speed of 50 rpm. The temperature of mixing was 150°C, which was higher than the melting temperature of each polymer. The overall mixing schedule was as follows. LDPE was added directly to the mixer and melted. Then, PDAP was added, and mixing continued for 8–15 min until an equilibrium torque was obtained that indicated a homogeneous dispersion of the polymers. After mixing, the samples were hot-pressed to sheets of suitable thickness for 8 min at 160°C under 25 MPa. The sheet size and thickness were dependent on the testing methods used. The

TABLE I
Composition of Samples

Sample	LDPE (%)	PDAP (%)
LDPE	100	0
PDAP10	90	10
PDAP15	85	15
PDAP20	80	20
PDAP	0	100

blend compositions and sample codes are given in Table I.

Characterization

The characterization methods included Fourier transform infrared, solution ^{31}P-NMR, gel permeation chromatography, and elemental analysis. With these techniques, it was established that the polymers were linear with a number-average molecular weight of 32,035, and the weight-average molecular weight/number-average molecular weight ratio of PDAP was 1.646. The ^{31}P-NMR spectra were in agreement with this aniline replacement.

The chemical structure of PDAP is shown in Figure 1.

Thermogravimetric analysis (TGA)

Each sample (6–10 mg) was examined under a nitrogen flow on a PerkinElmer TGA 7/DX with platinum sample holders from room temperature to 800°C at a heating rate of 10°C/min.

Morphology observations

Scanning electron microscopy (SEM; Hitachi S-2150) observations were made for cryofractured specimens of some blends and their surfaces etched by tetrahydrofuran at a magnification of 2000×.

Mechanical properties

The tensile strength and elongation at break were measured on dumbbell specimens at a speed of 50 mm/min at room temperature on an Instron 4465 according to ASTM Standard D 638. The tensile strength and elongation at break were determined from stress–strain curves. The average of four data points was taken, and experimental errors were ±5 and ±3.5%, respectively.

Flammability tests

The oxygen index (ASTM Standard D 2863) was used to characterize the flammability of the samples. The apparatus used was manufactured by Ray-Ran, and

the deviation standard was ±0.4 units. Three or four samples were analyzed for the determination of average values so that reproducible results could be obtained for limited oxygen index (LOI) measurements.

RESULTS AND DISCUSSION

Evaluation of the processability of various blends

Melt-mixing torque–time curves of blends prepared in different compositions are shown in Figure 2. The graphs indicate that torque values gradually decreased with the mixing time. As the PDAP content increased, the torque values of the blends decreased. The intensity for the initial peaks of the various blends also decreased. For example, the torque maximum of the blends decreased from 69 Nm for LDPE to 20 Nm for PDAP20, and the final torque decreased from 20 Nm for LDPE to 11 Nm for PDAP20. This might have resulted from the plasticizing action of PDAP. When the time exceeded 30 s, homogeneous blends could be obtained. However, the final torque values were very low. Both results imply that good miscibility existed between PDAP and LDPE. The miscibility could be further confirmed with SEM experiments, which are in progress.

The miscibility could also be evaluated by the energy requirement for the plasticization of these blends, which was derived from the area under the torque–time curves under the experimental conditions with eq. (1):[7]

$$w = 2\pi R \int_{t_1}^{t_2} \tau_a dt \qquad (1)$$

where R is the rotor speed, t_1 is the initial time, t_2 is the final time, and τ_a is the mixing torque. The plasticization energy for the blends is listed in Table II

The energy requirement for the blends decreased with the addition of PDAP, as listed in Table II. The energy requirement for PDAP20 was half that for LDPE.

TGA

TGA was used to characterize the thermal behaviors of LDPE, PDAP, and their blends.

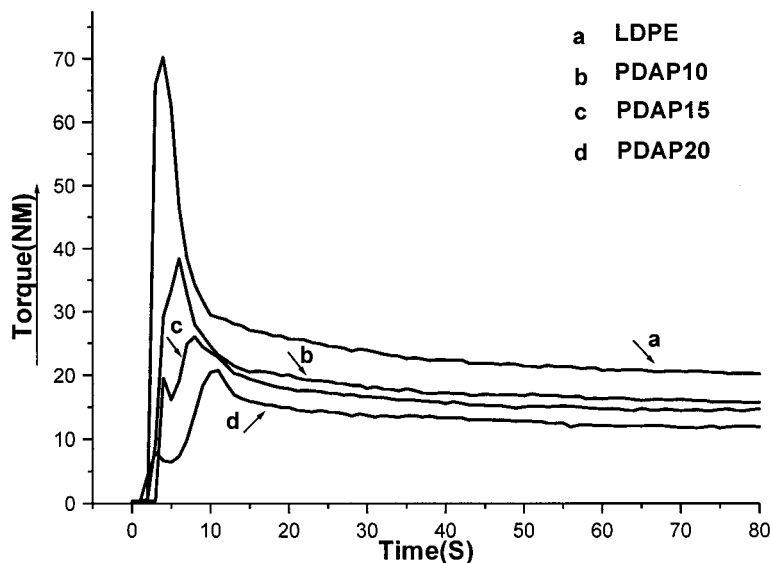**Figure 1** Chemical structure of PDAP.

Figure 2 Haake plasticorder torque profile of PDAP/LDPE at processing.

Figure 3 presents plots of the residual weight fractions of PDAP and LDPE versus temperature at a heating rate of 10°C/min under the protection of nitrogen. PDAP thermally decomposed separately in three different temperature ranges. As for the initial degradation, which occurred around 334°C, this might have been caused by the instability of the oligomer. The subsequent degradation around 443°C should be assigned to the breaking down of the aniline group; the ultimate degradation around 530°C is thought to have resulted from the breaking down of the backbone. The TGA curve obtained for PDAP indicates that PDAP is a thermostable material. As for LDPE, it mainly decomposed in a single process from 400 to 470°C. Moreover, the char yield of PDAP (38%) was much higher than that of LDPE (0%) at 800°C.

Figure 4 shows the TGA curves of the various blends. The temperature for the maximum degradation rate of the various blends increased with increasing PDAP content. The blends retained much more residual char than LDPE at temperatures higher than 500°C. Additionally, the char yield increased steadily with increasing PDAP content. Therefore, it is possible that PDAP can protect an LDPE matrix from further decomposition to some extent. It is also possible that these two components interact with each other at high temperatures.

X-Ray characterization techniques

Figure 5 exhibits the wide-angle X-ray diffraction (WAXD) patterns of LDPE, PDAP, and PDAP/LDPE blends. There are two sharp reflections at $2\theta = 21.6$ and $24.2°$ in the WAXD patterns of LDPE, which are assigned to the 110 and 200 reflections of the orthorhombic subcell.[8,9] As the content of PDAP increased, the intensity of the 110 and 200 reflections decreased; this indicated that the crystallization degree of the blends decreased. It is likely that the crystalline domain of LDPE was disarranged by the addition of PDAP. It is obvious that the positions of the two major diffraction peaks remained unchanged; this implies that the addition of PDAP did not lead to the crystalline structure of LDPE changing.[10] As shown in Figure 5, the WAXD pattern of PDAP has a sharp reflection at $2\theta = 22.25°$. This reflection peak disappeared when PDAP was mixed with LDPE. In the meantime, a new reflection at $2\theta = 23.15°$ was found, which suggests that the crystal structure of the PDAP components in the blends was different from that of pure PDAP. This confirmed that these two components were interacting in the case of blending.

Morphology and miscibility

SEM was employed to investigate the surface morphology of the blends. SEM micrographs of cryofrac-

TABLE II
Energy Requirement of the Blends

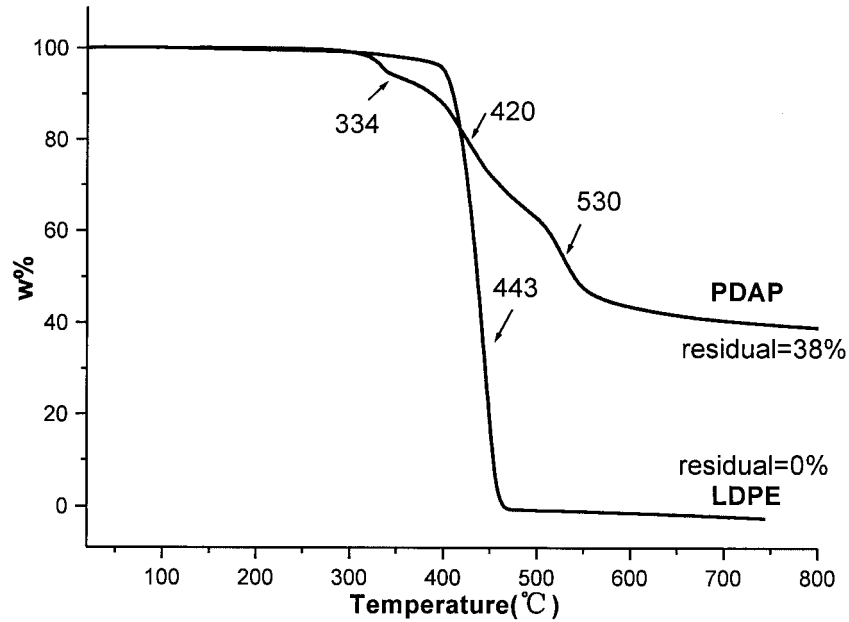| Sample	LDPE	PDAP10	PDAP15	PDAP20
Energy required for plasticization (kJ)	694.3	502.1	480.3	326.5

Figure 3 TGA thermograms of PDAP and LDPE.

tured surfaces and etched specimens free of the PDAP component are given in Figure 6. The surface morphologies of PDAP/LDPE blends with different PDAP contents were similar, so we just took PDAP10 and PDAP20 as examples. It can be seen in Figure 6(a,b) that PDAP10 and PDAP20 had smooth surfaces and few cavities. This indicates that the interfacial adhesion between PDAP and LDPE was relatively good even though the PDAP/LDPE blends remained two-phase; this can be seen in Figure 6(c,d). Etching of the fracture surfaces with tetrahydrofuran for the removal of the PDAP component improved the accuracy of determining the PDAP phase sizes by SEM. It showed a surface for the blends with PDAP embedded in the LDPE matrix and with PDAP domains

dispersed as droplets. The average diameter of the cavities decreased from 2 μm for the PDAP20 sample to 0.5 μm for PDAP10. Morphology investigations undertaken with SEM indicated that PDAP was compatible with LDPE to some extent.

Mechanical properties

The mechanical parameters of various blends are listed in Table III. The elongation at break of the blends linearly increased with increasing PDAP contents. Moreover, the elongation at break of PDAP20 went beyond 1500%, and a few other such cases could be observed in other LDPE blends. The data show that the addition of PDAP to LDPE slightly reduced the
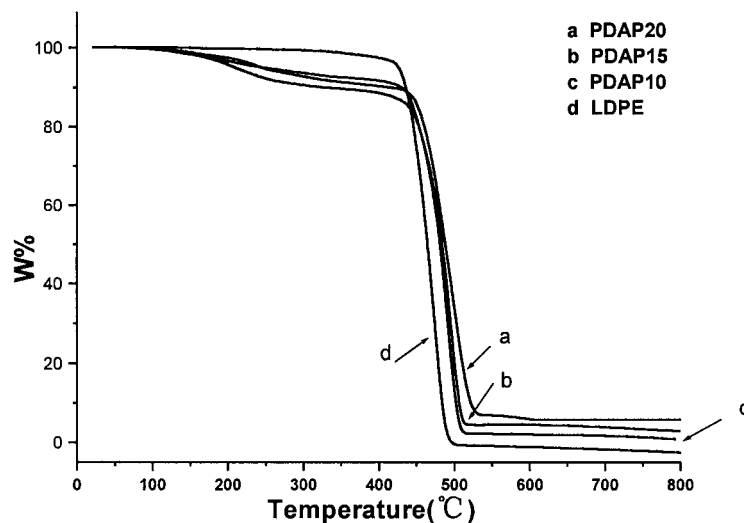

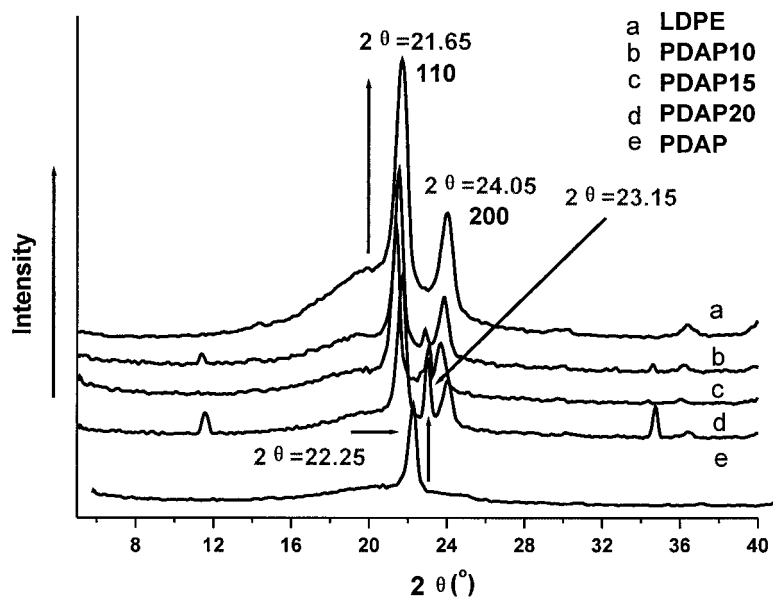**Figure 4** TGA thermograms of PDAP/LDPE blends.
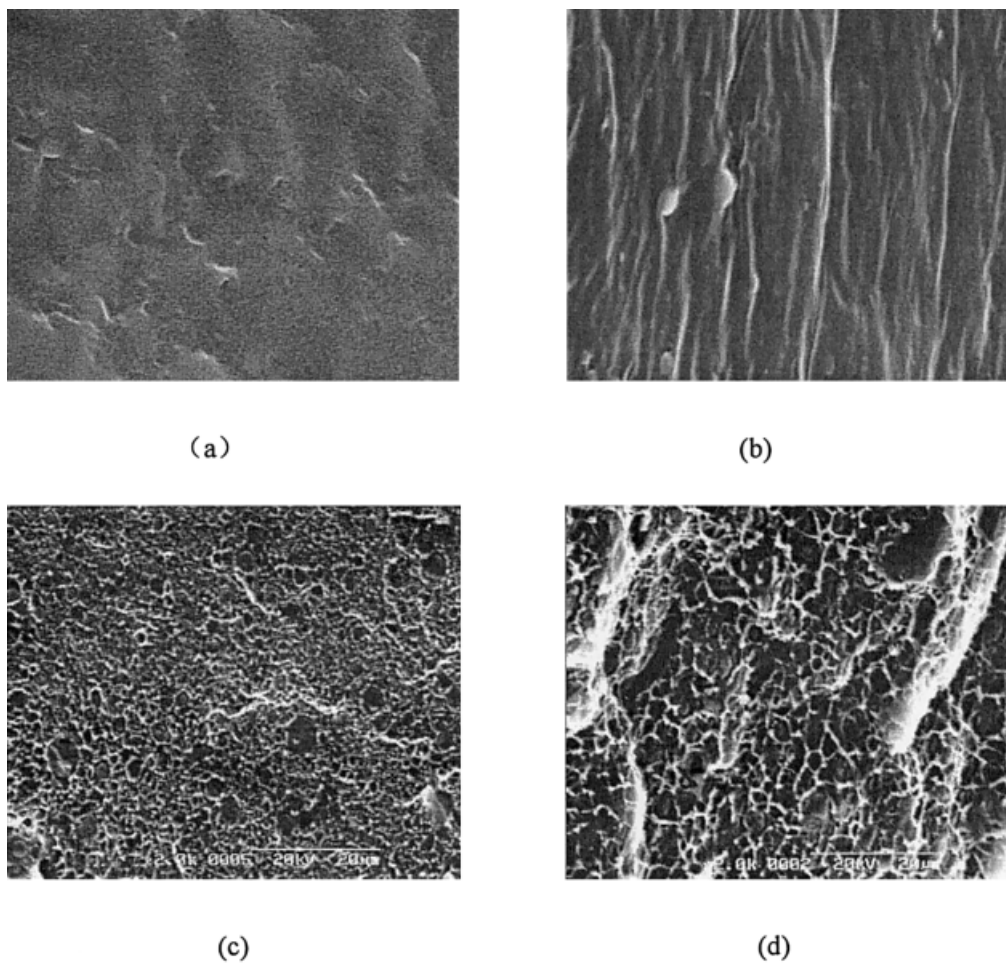
Figure 5 WAXD curves of various blends and LDPE.

Figure 6 SEM micrographs of various blends: (a) PDAP10, (b) PDAP20, (c) PDAP10 (etched), and (d) PDAP20 (etched; magnification, 2000×).

TABLE III
Mechanical Properties and LOI Values
of Various Blends

Sample	Tensile strength (MPa)	Elongation at break (%)	LOI value
PDAP20	16.74	1550	28.4
PDAP15	18.41	1380	26.7
PDAP10	21.33	960	24.6
LDPE	22.84	810	17.4

tensile strength of LDPE. The most important cause was that the crystallinity of the blends decreased in comparison to that of pure LDPE.

Flammability

The LOI values for the various LDPE/PDAP blends are also listed in Table III. It is obvious that the LOI values increased with increasing PDAP content. As is known, both phosphorus and nitrogen elements in PDAP play roles as flame retardants. The mechanism of phosphorus flame retardants appears to function in the condensed phase, in which they can promote char or coat the char surface with various phosphoric acids; in the vapor phase, in which they can function by the free-radical trap theory; or physically by promoting dripping of the burning polymer.[11] However, the mechanism of nitrogen flame retardants appears to function in the vapor phase.[12] It is believed that the coexistence of phosphorus and nitrogen in the same molecule will exert a synergistic effect in PDAP/LDPE blends.

CONCLUSIONS

From the Haake results, we found that the addition of PDAP improved the processability of LDPE and that LDPE was miscible or compatible with PDAP. TGA revealed that the PDAP/LDPE blends were thermally stable. WAXD results showed that PDAP was a semi-crystalline polymer and that the crystallinity of the blends decreased with increasing PDAP content. A new reflection at $2\theta = 23.15°$ indicated that these two components interacted with each other. Morphology investigations indicated that PDAP was compatible with LDPE to some extent. Mechanical testing showed that the addition of PDAP could greatly improve the elongation at break of the blends. Additionally, PDAP could remarkably improve the LOI values of the PDAP/LDPE blends.

References

1. Hsieh, Y.-L.; Yeh, K. Polym Sci Technol 1984, 26, 203.
2. Wang, Z.; Qu, B.; Fan, W.; Huang, P. J Appl Polym Sci 2001, 81, 206.
3. Hornsby, P. R.; Winter, P.; Cusack, P. A. Polym Degrad Stab 1994, 44, 177.
4. Peters, E. N. J Appl Polym Sci 1979, 24, 1457.
5. Potin, P. H.; Jaeger, D. E. Eur Polym J 1991, 27, 341.
6. Allcock, H. R.; Riding, G. H.; Manners, I.; et al. Polym Prepr 1990, 31, 48.
7. Maity, A. K.; Xavier, S. F. Eur Polym J 1999, 35, 173.
8. Wang, Z. G.; Hsiao, B. S.; Sirota, E. B.; Srinivas, S. A. Polym 2000, 41, 8825.
9. Brooks, N. W. J.; Duckett, R. A.; Ward, I. M. Polym 1999, 40, 7367.
10. Zhao, H.; Lei, Z.; Wang, Z.; Huang, B. Eur Polym J 1999, 35, 355.
11. Green, J. J Fire Sci 1996, 14, 426.
12. Horacek, H.; Grabner, R. Polym Degrad Stab 1996, 54, 205.