

Polyethylene–Polyethylene Blends Modified with an Additive of Isotactic Polypropylene

MARIETTA GRIGOROVA and MARIN MIHAILOV*

Institute of Polymers, Bulgarian Academy of Sciences, 1113-Sofia, Bulgaria

SYNOPSIS

The blends of very high molecular weight high-density polyethylene (VHMW–HDPE) or ultrahigh molecular weight high-density polyethylene (UHMW–HDPE) and low-density polyethylene with normal molecular weight (LDPE) in equal or prevailing concentrations of the first component have excellent mechanical properties but very high viscosity in a molten state. The present investigations are a continuation of the fact, established by us for the first time, that the addition of a third polymer, isotactic polypropylene (I-PP), at optimal low concentrations increases the melt flowability of these systems without considerable deterioration of their very good mechanical properties in the solid semicrystalline state. The comparison between the thermomechanical behavior and the sorption in organic media of the systems leads to the supposition that an uninterrupted physical network from the VHMW–HDPE has been formed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

It is well-known that the polyethylene–polyethylene systems (PE–PE) have been studied in theoretical and practical aspects.^{1–5} It has been established that their properties depend, first of all, on the molecular weight characteristics and on the mass ratio of the polyethylene components.^{6–8}

Especially interesting are the binary systems of very high molecular weight/ultrahigh molecular weight high-density polyethylene (VHMW–HDPE/UHMW–HDPE) and normal molecular weight polyethylene with high (HDPE) or low density (LDPE).^{9–13} The information about VHMW–HDPE/LDPE blends^{14,15} is rather limited. In our previous paper,¹⁵ it was reported that these blends possess an excellent complex of mechanical properties by equal or prevailing concentration of the first component; the melt flow is increased in comparison with that of VHMW–HDPE but remains relatively low. In another work,¹⁶ we were the first to report on the observed trends to decrease the melt

viscosity of the systems by the addition of isotactic polypropylene (I-PP).

The present work continues these investigations. It discusses the influence of I-PP additive upon the basic properties of VHMW–HDPE/LDPE blends in a molten and solid semicrystalline state. We had not found data in the literature about investigations of PE/PE/PP systems of this type.

EXPERIMENTAL

The following polyolefins, produced by Neftochim-Burgas (Bulgaria), were used: VHMW–HDPE in powder “nascent” with melt flow index (MFI) = 0.1 g/10 min (210°C, 21.6 kg) and $M_n = 860,000$ (in dekalin); LDPE “Ropoten-FB-02-201” with MFI = 0.18 g/10 min (190°C, 2.16 kg); I-PP “Buplen 6523” with MFI = 7.7 g/10 min (230°C, 2.16 kg). The crystallinity degree of the polyolefins is shown in Table III.

The initial components as well as their blends were rolled for 12 min at 185°C with subsequent compression molding into plaques for 5 min at 185°C under the pressure of 30 MPa (prepressing for 5

* To whom correspondence should be addressed.

min at the same temperature), followed by cooling to 40°C under the same pressure (average cooling rate was 13°C/min).

The tensile properties yield stress (σ_y), tensile strength (σ_b), and elongation at break (ϵ) were determined by monoaxial deformation at a rate of 100 mm/min and room temperature. Thermomechanical investigation was carried out on an apparatus UIP-70-M (Ex-USSR) by heating the pressed samples at a rate 2.5°C/min under 3 kg/cm² pressure (stock diameter 1.78 mm) in air. DSC analysis were performed on a Perkin-Elmer DSC-7 at a heating rate of 5°C/min under argon. The degree of swelling in benzene was determined gravimetrically as $\frac{m - m_0}{m_0} \times 100$, where m_0 is the initial mass and m is the mass of the pressed samples after swelling for a certain time at room temperature. MFI tests of the rolled specimens were performed on a standard capillary viscometer (Ex-USSR). The die swell was calculated as $\frac{d_e}{d_c}$, where d_e is a diameter of the extrudates measured 24 h after the MFI test, and d_c is the initial diameter of the viscometer capillary.

RESULTS AND DISCUSSION

The results from our rheological investigations are difficult to compare since they were carried out under different experimental conditions due to the great differences in the melt viscosity of the investigated systems.

Nevertheless, the data presented in Figures 1–3 show that the MFI of the two polyethylenes and their blends in equiweight ratio is nonlinearly dependent on the concentration of I-PP. The viscosity of LDPE/I-PP blend (Fig. 1) decreases considerably

in the presence of very low I-PP concentration. For VHMW-HDPE/I-PP systems, this effect is rather smaller. A more notable increase of the melt flow is observed at I-PP concentration ≥ 5 wt %. Very interesting are the data, presented in Figure 3, which reveal the I-PP influence upon the rheological properties of the two polyethylenes in equiweight ratio. The nonlinear change of the MFI is characterized by one peculiarity: I-PP at a certain very low concentration decreases the melt flow of the blends, though it improves the flowidity of the initial components at the same concentrations. Moreover, the blends of the two components containing I-PP at this characteristic concentration and at limited intervals around it have a lower melt flow than the blends without I-PP. The additive of I-PP by ≥ 5 wt % noticeably decreases the viscosity of the three-component PE/PE/PP systems, or it is evident that the melt flow of the 1 : 1 VHMW-HDPE/LDPE blend increases visually by the use of an optimum concentration of I-PP. The reliable interpretation of the data needs further investigations. It should be emphasized that the results are double in connection with the differences in the thermodynamic compatibility of the two polyethylenes and I-PP, as well as with the thermodynamic compatibility between the two polymers in the presence of I-PP.

Table I shows the influence of I-PP upon the post-extrusion swelling of the samples after the MFI tests. It is evident that the die swell decreases measurably at the I-PP concentration dependent on the type of polyethylenes. This concentration is the highest for VHMW-HDPE, ≥ 5 wt %, and is considerably lower for LDPE, 0.5 wt %. The swelling coefficient of the extrudates for PE/PE and PE/PE/PP blends is quite close to those of VHMW-HDPE.

The study of the tensile properties reveals that σ_y , σ_b , and ϵ of the both PE and their 1 : 1 VHMW-

Table I Die Swell Versus Composition of Systems Extrudate by 190°C, 5 kg (A), and 210°C, 21.6 kg (B)

Sample No.	Components (wt %)			Die Swell	
	VHMW-HDPE	LDPE	I-PP	A	B
1	100	—	—	—	1.20
2	—	100	—	1.90	—
3	—	—	100	—	1.50
4	50	50	—	—	1.38
5	49.75	49.75	0.5	—	1.35
6	49	49	2	—	1.33
7	47.5	47.5	5	—	1.30
8	45	45	10	—	1.25

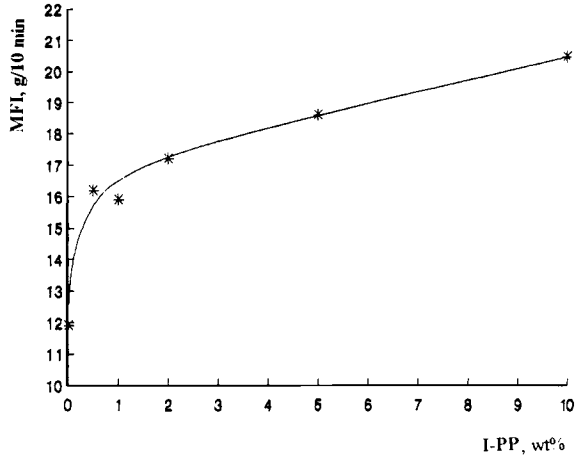


Figure 1 MFI versus composition LDPE/I-PP blends at 190°C, 21.6 kg.

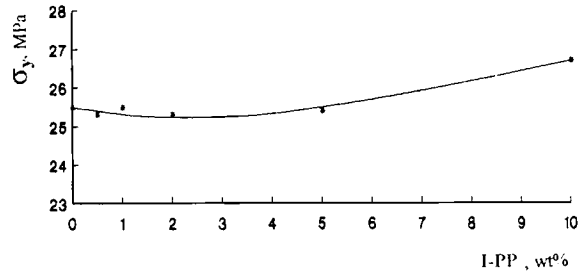


Figure 4 σ_y versus I-PP concentration added to 1 : 1 VHMW-HDPE/LDPE blend.

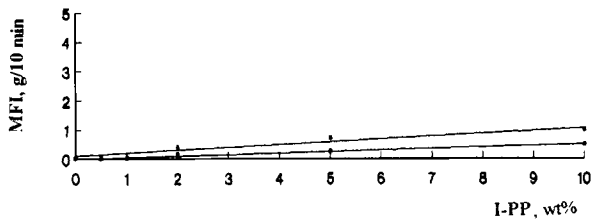


Figure 2 MFI versus composition VHMW-HDPE/I-PP blends at 190°C, 21.6 kg (1), and 230°C, 21.6 kg (2).

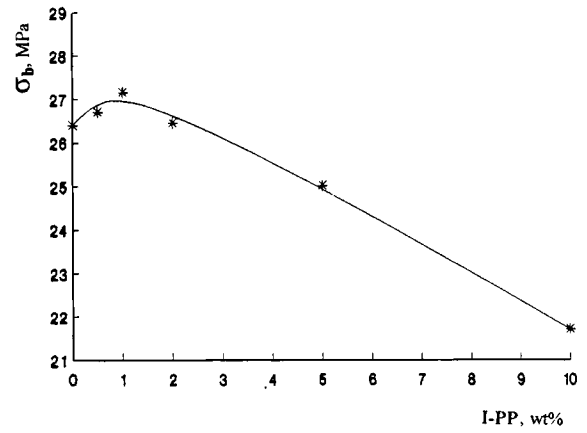


Figure 5 σ_b versus I-PP concentration added to 1 : 1 VHMW-HDPE/LDPE blend.

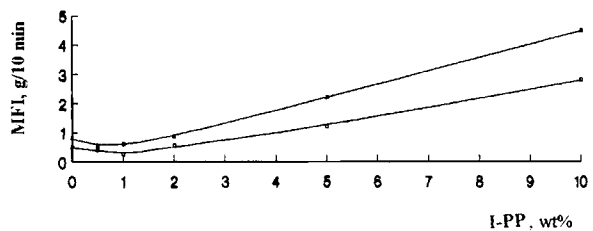


Figure 3 MFI versus I-PP concentration added to 1 : 1 VHMW-HDPE/LDPE blend at 190°C, 21.6 kg (1), and 230°C, 21.6 kg (2).

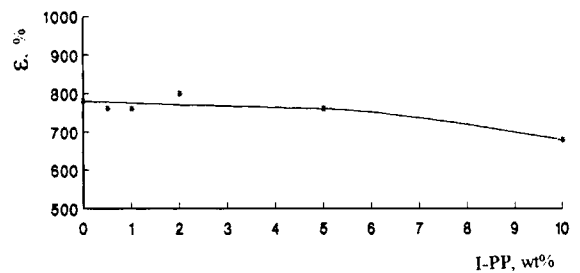


Figure 6 ϵ versus I-PP concentration added to 1 : 1 VHMW-HDPE/LDPE blend.

Table II Impact Strength by Sharpy Versus Polymer Composition of Selected Systems

Sample No.	Components (wt %)			Nondestroyed Samples (%)	
	VHMW-HDPE	LDPE	I-PP	Without Notch	With Notch
1	100	—	—	100	100
2	—	100	—	100	100
3	—	—	100	0	0
4	50	50	—	100	100
5	49.75	49.75	0.5	100	100
6	49	49	2	100	100
7	47.5	47.5	5	100	100
8	45	45	10	100	100

HDPE/LDPE blend depend nonlinearly on I-PP concentration also. Skipping the detailed discussion on the composition-tensile properties dependencies given in Figures 4–6, we should underline some specific features. I-PP concentration changes σ_b most of all. The polyethylene systems preserve their high ductility in the presence of I-PP, which is known to be a brittle fracturing polymer. σ_y , σ_b , and ϵ in the investigated PE/PE and PE/PE/PP blends are close to those of VHMW-HDPE. It is also very important that the PE/PE/PP system preserves its excellent impact strength. The number of undes-

troyed samples determined by the Sharpy method without and with notch remains 100% (Table II). This indicates once more that VHMW-HDPE keeps on being a dominating factor for the very good basic mechanical properties in the PE/PE/PP blends in the presence of optimal I-PP concentration.

The results from our initial DSC investigations on the phase structure of selected systems are shown in Figure 7 and Table III. As expected, the endotherms of I-PP and both polyethylenes are monomodal and VHMW-HDPE has a higher melting point (T_m) than LDPE. The VHMW-HDPE melt-

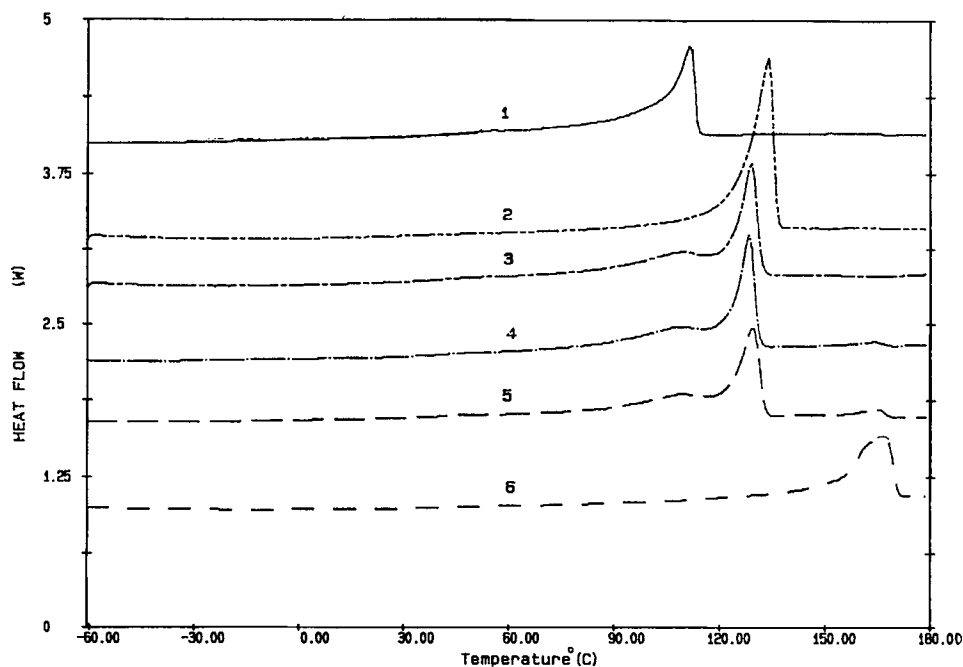


Figure 7 DSC melting thermograms of LDPE (1), VHMW-HDPE (2), 1 : 1 VHMW-HDPE/LDPE blend (3), the same blend containing 5 wt % I-PP (4), the same blend containing 10 wt % I-PP (5), and I-PP (6).

Table III DSC Data of Selected Systems

Sample No.	Components (wt %)			T_m (°C)	Crystallinity (%)	
	VHMW-HDPE	LDPE	I-PP		α exp	α add
1	100	—	—	134	56	—
2	—	100	—	111	32	—
3	—	—	100	116	46	—
4	50	50	—	111, 129	42	44
5	47.5	47.5	5	110, 128, 164	44	44
6	45	45	10	110, 129, 164	46	44

ing temperature decreases in about 5°C in PE-PE systems regardless of the I-PP concentration. It could be assumed that the decrease of VHMW-HDPE T_m is due to the crystallization conditions in the presence of LDPE, as well as to the probable formation of metastable mixed PE/PE crystals. Three crystal phases were observed in the PE/PE/PP blends comprising exclusively or chiefly VHMW-HDPE, LDPE, and I-PP. A crystal phase

of I-PP is detected event at contents of 5 wt %; the component concentration does not influence its melting peak. A very slight tendency to increasing the crystallinity (as compared to the additive one) exists for PE/PE systems by the addition of I-PP.

The thermomechanical investigations on VHMW-HDPE, LDPE, and their blend in equiweight ratio without and with 5 wt % I-PP are shown in Figure 8. The dependencies are noteworthy. Dilatation = f

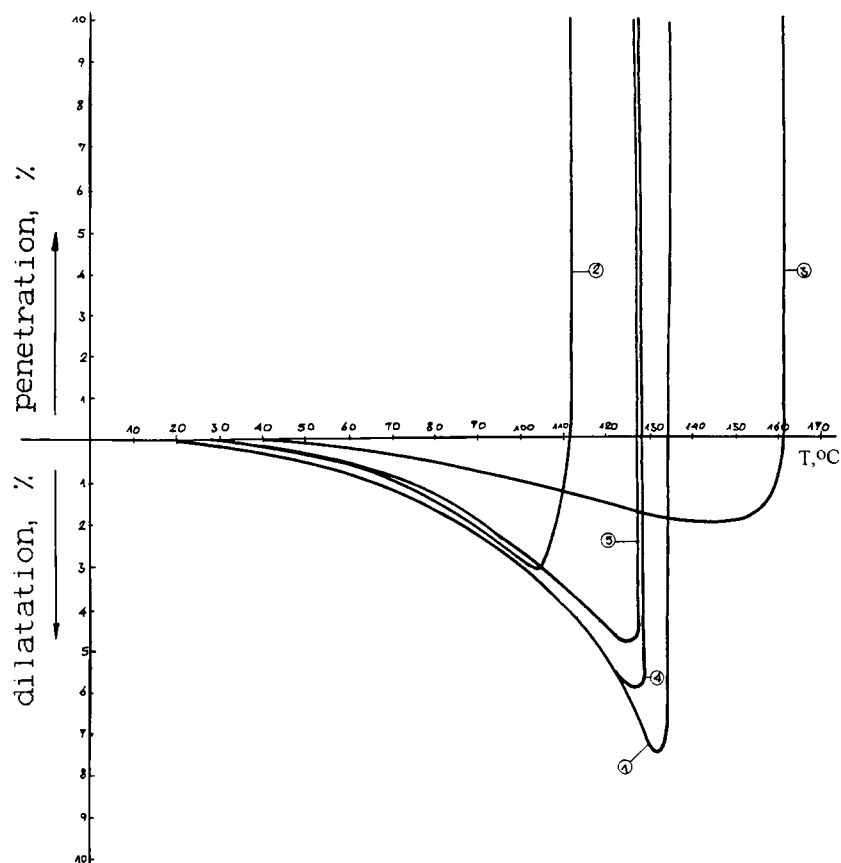


Figure 8 Thermomechanical curves of VHMW-HDPE (1); LDPE (2); I-PP (3); 1 : 1 VHMW-HDPE/LDPE blend (4); and the same blend containing 5 wt % I-PP (5).

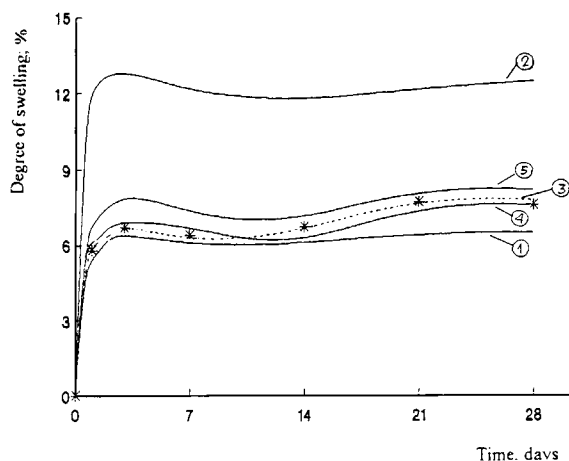


Figure 9 Isothermal time dependence of the swelling degree in benzene of VHMW-HDPE (1), LDPE (2), I-PP (3), 1 : 1 VHMW-HDPE/LDPE blend (4), and the same blend containing 5 wt % I-PP (5).

(temperature) for the PE/PE and PE/PE/PP blends, which are quite close to those of VHMW-HDPE even after LDPE melting. It is evident that the I-PP presence does not change the character of PE/PE blend behavior. This leads to the assumption that VHMW-HDPE forms an uninterrupted physical net in the investigated three-component systems.

The experiments we carried out to confirm this assumption by studying the sorption kinetic of the same systems in organic media are of interest (Fig. 9). We did not find data about the comparative investigation performed in such aspects. The sorption isotherms illustrate that the swelling degree of two- and three-component systems, as their changes within four weeks are characterized by a negative deviation from the linear additivity. They are close to those of VHMW-HDPE and much lower than that of LDPE. Consequently, the stability of the same systems in benzene is comparable to that of VHMW-HDPE and remarkably higher than that of LDPE. Probably, the reason is the high concentration of entangling chains, which is typical for VHMW-HDPE forming the possible uninterrupted physical net.

Further work is needed to confirm this presumption.

CONCLUSION

In conclusion, we must underline that the addition of I-PP in optimal concentration increase the melt flow of the blends of VHMW-HDPE and LDPE without remarkable change in their very good mechanical properties. VHMW-HDPE preserves its dominating influence upon the behavior of the investigated PE/PE/PP systems in the solid semicrystalline state.

The financial support of the National Scientific Research Fund is gratefully acknowledged.

REFERENCES

1. B. H. Clampitt, *J. Polym. Sci., Polym. Chem. Ed.*, **3**, 671 (1965).
2. H. Datta and A. Birley, *Plast. Rubb. Proc. Appl.*, **2**, 237 (1982).
3. M. Grigorova, I. Mladenov, T. Zlatkov, and M. Michailov, *Acta Polym.*, **36**, 230 (1985).
4. J. Barham, M. J. Hill, A. Keller, and C. C. A. Rosney, *J. Mat. Sci. Zett.*, **7**, 1276 (1988).
5. U. W. Gedde, *Prog. Coll. Polym. Sci.*, **87**, 8 (1992).
6. H.-K. Chiang and C. D. Han, *J. Appl. Polym. Sci.*, **29**, 2205 (1984).
7. V. Balsamo and A. Müller, *J. Mat. Sci. Zett.*, **9**, 46 (1990).
8. M. Grigorova and M. Michailov, *Eur. Poly. J.*, **31**, 621 (1995).
9. S. K. Bhateje and E. Andrwes, *Poly. Eng. Sci.*, **23**, 888 (1983).
10. T. Kyn and P. Vadhar, *J. Appl. Polym. Sci.*, **32**, 5575 (1986).
11. M. Matuso and R. S. J. Manley, *Macromolecules*, **16**, 1500 (1983).
12. K. Furuhashi, T. Yokokawa, C. Seoul, and K. Miyasaka, *J. Polym. Sci., Polym. Phys. Ed.*, **24**, 59 (1986).
13. M. Grigorova and M. Michailov, *Angew. Macromol. Chem.*, **217**, 43 (1994).
14. P. Vadhar and T. Kyu, *Polym. Eng. Sci.*, **27**, 202 (1987).
15. M. Grigorova, I. Mladenov, and M. Michailov, *Plaste Kautsch.*, **35**, 86 (1988).
16. M. Grigorova, I. Mladenov, and M. Michailov, *Proc. 31th IUPAC MACRO*, Prague, 1989.

Received November 6, 1995

Accepted March 18, 1996