

Properties of the Polyethylene/Poly(2,6-dimethyl-1,4-phenylene ether)/Polystyrene System in the Presence of SEPS Block Copolymers

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Received 23 July 1996; accepted 19 November 1996

ABSTRACT: An immiscible polymer system of polyethylene (HDPE)/poly(2,6-dimethyl-1,4-phenylene ether)/polystyrene was compatibilized in the presence of a specific formulated compatibilizer and the properties of this system were studied, in particular, as a function of the poly(phenylene ether) and polystyrene content in the blend with polyethylene and as a function of compatibilizer concentration. The compatibilizer used was a hydrogenated styrene/isoprene/styrene triblock copolymer (SEPS) which also contained quantities of polypropylene and paraffin oil. Selected thermal, mechanical, and processing properties were investigated and their special features are discussed. In relation to specific properties like the modulus of elasticity and notched Izod impact strength, the polymer system with a hydrogenated SEPS triblock copolymer investigated seems to be a better compatibilized system than other blends described. The phase behavior of the polymer system was characterized using DSC and showed three general polymer phases: a partially crystalline polyethylene phase, an amorphous mixed phase of miscible poly(phenylene ether) and polystyrene, as well as a preferred isotactic crystalline polypropylene phase. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1835–1842, 1997

Key words: polymer blends; polyethylene/poly(phenylene ether)polystyrene; hydrogenated styrene/isoprene/styrene triblock copolymer; phase behavior

INTRODUCTION

To achieve good thermal, mechanical, and processing properties of polymer blends of incompatible polymer components, a compatibilization of the individual components is frequently implemented by improving the phase adhesion between the particles.¹ In the incompatible polyethylene/polystyrene system, the polymer components can be made compatible by both the modification of the polymer components, e.g., with oxazoline groups and carboxyl groups and subsequent reaction,² and the addition of special polymeric com-

patibilizers such as hydrogenated styrene/butadiene block copolymers.³ Such systems have shown a low water vapor permeability and an enhanced processability and led to interesting applications in the packaging industry, etc.⁴

The poly(phenylene ether)/polystyrene system^{1,5} is one of the relatively few compatible polymer systems. Here, by varying the composition of the two components, the heat resistance of the homogeneous mixture, e.g., can easily be adjusted.

A combination of the mentioned components of the polyethylene/poly(phenylene ether)/polystyrene system without compatibilization will not result in good mechanical properties of this mixture

as the fracture behavior showed, which was examined under an electron microscope by investigations of the fracture surfaces of such systems modified with polybutadiene.⁶ Low molecular polyolefins in such systems can improve the processing characteristics without affecting the mechanical and thermal properties, when using styrene/butadiene triblock copolymers.⁷

For a system consisting of polyethylene, polystyrene, and a polyether copolymer of 2,6-dimethyl-1,4-phenylene ether with 5% trimethylphenol as a co-component and a hydrogenated styrene/butadiene/styrene (SEBS) triblock copolymer as a compatibilizer, the morphology of the blends was studied and the deformation behavior was measured through volume dilatation as a function of the composition.

Also determined were the tensile test properties and the toughness of selected samples.^{8–10} In such a heterogeneous mixture, the polyethylene forms a single phase, while the compatible mixture of polystyrene and poly(phenylene ether) forms the other, glasslike phase of different compositions. The block copolymer is expected to be situated as an interphase at the interface between the polyolefin and the glasslike phase and provides the interfacial adhesion in the solid state as well as the phase stability during the processing of the melt.

The purpose of this article was the investigation of a new formulated compatibilized HDPE/PPE/PS system on the basis of polystyrene and poly(2,6-dimethyl-1,4-phenylene ether) without a co-component and of defined molecular weights in contrast to the literature. Here, the selected specific compatibilizer is based on a hydrogenated styrene/isoprene/styrene (SEPS) triblock copolymer in contrast to a hydrogenated styrene/butadiene/styrene triblock copolymer in Refs. 8–10. Besides the tensile and impact properties examined in the literature system,¹⁰ new properties like density, flow characteristics, thermal behavior, shrinkage, and flexural test results have also been investigated, particularly in dependence on the HDPE/(PPE/PS) composition and the compatibilizer concentration, and will be discussed in context with the literature mentioned above. Finally, the phase behavior was investigated and is discussed on the basis of DSC measurements.

EXPERIMENTAL

The polyethylene used was HDPE with the properties given in Table I. Poly(2,6-dimethyl-1,4-phenylene ether) with a weight-average molecular weight of 61,000 g/mol was used as the poly(phenylene ether). A styrene polymer with a weight-average molecular weight of 198,000 g/mol was the polystyrene utilized. The SEPS triblock copolymer compatibilizer contained the hydrogenated SEPS triblock copolymer with 30% by weight of styrene and, in addition, 9% by weight of polypropylene with a melt flow index of 5.0 g/10 min (190°C, 21.2N) and 25% by weight of paraffin oil.

The components were homogenized and pelletized in a Berstorff double-screw extruder ZE 25 with a screw diameter of 25 mm. The screw length : screw diameter ratio L/D was 32; the number of screw rotations, 400 rpm, and the feeding velocity, 10 kg/h. The average melt temperature was 220°C. The specimens were prepared in accordance with DIN 16776 and taken from pressed sheets. The flexural modulus and the flexural stress were determined at an outer fiber strain of 3.5% in accordance with ISO 178 and DIN 53452, respectively. The tensile modulus of elasticity and the yield stress were measured according to ISO 527, and the notched Izod impact strength, according to ISO 180. The ball indentation hardness (132 N, 30 s) was determined according to ISO 2039; the Vicat softening temperature (B, 50N), according to ISO 306, and the heat-deflection temperature (HDT), according to DIN 53461. The determination of the melt flow index and density was based on ISO 1133 and ISO 1183, respectively, and the determination of the molding shrinkage of the injection-molded test plates of the size 60 × 60 × 2 mm, on DIN 53464. The thermal properties were examined through differential scanning calorimetry by a Perkin-Elmer DSC-2C and at a heating rate of 10 K/min under argon by a repeated run.

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RESULTS AND DISCUSSION

To investigate the properties of the complex polyethylene/poly(phenylene ether)/polystyrene system, the effect of concentration of a block copolymer as well as the influence of weight ratio of polyethylene and poly(phenylene ether)/polystyrene at a constant block copolymer content was studied in the presence of a hydrogenated SEPS triblock polymer.

The effect of the block copolymer concentration already containing the constant quantity of paraffin oil and polypropylene within a range of up to

Table I Properties of the HDPE

Property	Method	Value
Weight-average molecular weight, \overline{M}_w	SEC	205,000 g/mol
Number-average molecular weight, \overline{M}_n	SEC	7300 g/mol
Density	ISO 1183	0.943 g/cm ³
Degree of branching	FTIR	0.48 CH ₃ /100 CH ₂

14% by weight on the properties of the polymer blend at a constant weight ratio of polyethylene : poly(phenylene ether) : polystyrene of 50 : 27.5 : 22.5 is shown in Table II. Because of the expected brittleness of such blends,¹⁰ the investigation of the pure polyethylene/poly(phenylene ether)/polystyrene system without the block copolymer was excluded. From the table, it can be seen that the toughness of the polymer mixture also considerably increases with an increasing concentration of the block copolymer at lower temperatures. This is a result of the successful incorporation of the elastomeric block copolymer in the polyethylene/poly(phenylene ether)/polystyrene system. The stiffness determined in both the tensile strength and the flexural test decreases significantly, which is often accompanied by improvements of toughness in polymeric blend systems. Also, the hardness and the thermal properties such as the heat deflection temperature and Vicat

softening temperature decrease, whereas the drop in both temperatures is unexpectedly low with regard to the high difference in the block copolymer concentration. Here, a location of the block copolymer at the interface between the polyethylene and poly(phenylene ether)/polystyrene phases is expected, leading to a better phase adhesion with an enhanced block copolymer concentration and, therefore, to a better flexibility and to a lower decrease of Vicat softening and heat-deflection temperatures of this polymer system. With regard to the tensile and impact tests at 23°C, a similar relationship dependent on the block copolymer concentration and their contrary trend was also found with another system using a hydrogenated styrene/butadiene/styrene triblock copolymer as the compatibilizer.¹⁰

For the investigations on the dependence of the poly(phenylene ether) and polystyrene quantity in the blend on polyethylene, the constant amount

Table II Properties of Polyethylene/Poly(phenylene ether)/Polystyrene System (Weight Ratio 50 : 27.5 : 22.5) as a Function of the Block Copolymer Concentration

Property	Unit	Block Copolymer Concentration (% by Weight)	
		7	14
Density	g/cm ³	0.985	0.978
Notched Izod impact strength			
23°C	kJ/m ²	3.8	12.5
-20°C	kJ/m ²	3.7	9.2
Flexural modulus	MPa	800	450
Flexural stress	MPa	19.7	12.3
Tensile modulus of elasticity	MPa	874	453
Yield stress	MPa	12.9	12.1
Ball indentation hardness	N/mm ²	31	23
Vicat softening temperature	°C	129	127
Heat deflection temperature	°C	54	51

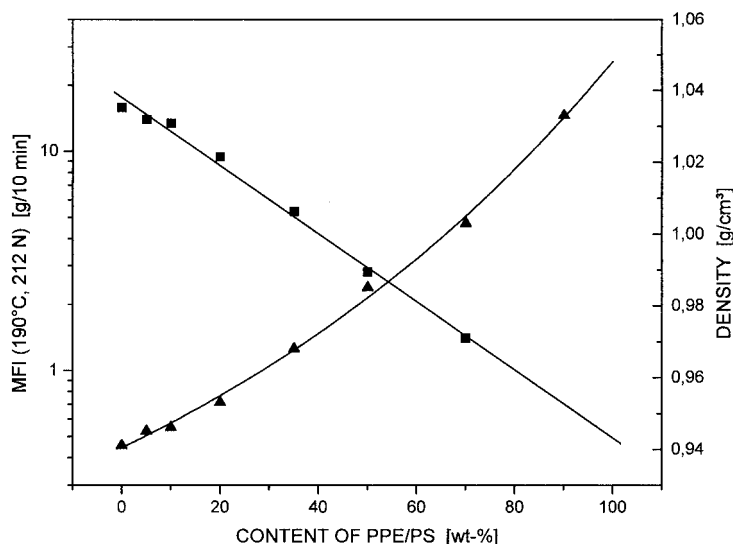


Figure 1 Dependence of (■) melt flow index (MFI) and (▲) density on the poly(phenylene ether) and polystyrene content in the mixture with polyethylene.

of the block copolymer selected was 7% by weight related to the total system. At this amount of the compatibilizer, the polymer system has a sufficient stiffness and enough toughness to examine the system for practical purposes in contrast to 14% by weight. The poly(phenylene ether)/polystyrene weight ratio of 55 : 45 was always maintained.

The melt flow index and density as a function of poly(phenylene ether) and polystyrene content are shown in Figure 1. As can be seen, the melt flow index linearly decreases with increasing poly(phenylene ether) and polystyrene content in a semilogarithmic scale, as is usual for mixtures of ideal polymers. However, the density increases with an increasing amount of poly(phenylene ether) and polystyrene, showing unexpected negative deviations in favor of smaller densities, in particular, in the medium range of composition, if compared to linearity.

The mechanical properties of the polymer system investigated by tensile and flexural tests are plotted in Figures 2 and 3. Figure 2 shows the relationship between the tensile modulus of elasticity as well as yield stress and the poly(phenylene ether) and polystyrene content. While the polyethylene content in the polymer system decreases, the tensile modulus of elasticity increases only slightly at first, but for quantities below 50% by weight of polyethylene, it is considerably strong. The yield stress slightly decreases with a falling HDPE quantity, passes a minimum of

about 30% by weight of HDPE, and increases then significantly. The block copolymer itself reduces the tensile modulus of elasticity of only the polyethylene from 838 to 561 MPa and the yield strength from 22.3 to 20.6 MPa. Contrary to this relationship, for another polyethylene/polyether copolymer/polystyrene system with a hydrogenated styrene/butadiene/styrene triblock copolymer as the compatibilizer, a tensile modulus of the elasticity minimum is expected with about 50% by weight of polyethylene and no minimum of the yield stress for a similar composition provided.¹⁰ Thus, the polymer system with the hydrogenated SEPS triblock copolymer investigated here seems to be a better compatibilized system in relation to a higher modulus without a minimum than is the system with the poly(phenylene ether) copolymer described in Ref. 10.

The flexural modulus and the flexural stress as a function of the composition of the polymer system are plotted in Figure 3. While the flexural modulus curve confirms that of the tensile modulus of elasticity and the discussion there, the flexural stress slightly increases with increasing poly(phenylene ether) and polystyrene content, passes a minimum at about 70% by weight, and then shows a significant increase. The flexural modulus of only the polyethylene is reduced by the addition of the block copolymer from 750 to 480 MPa and the flexural stress is reduced from 18.5 to 13 MPa.

Here, the phase adhesion between the poly-

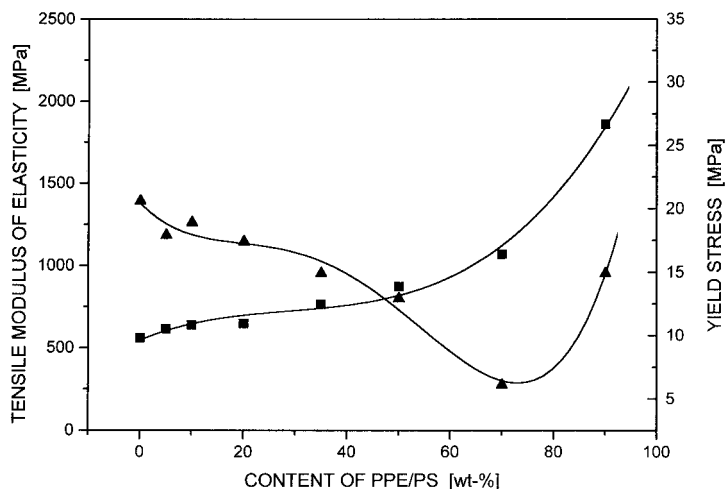


Figure 2 Relationship between (■) tensile modulus of elasticity and (▲) yield stress and the poly(phenylene ether) and polystyrene content in the mixture with polyethylene.

(phenylene ether)/polystyrene phase and the polyethylene phase as the main phases of the polymer system arranged by the block copolymer leads to a good flexibility of the blends over a large range of composition. Only at high concentrations of poly(phenylene ether)/polystyrene does the stiffness of the polymer system increase exponentially.

Figure 4 shows the relationship between the notched Izod impact strength and the poly(phenylene ether) and polystyrene content in the mixture with polyethylene. At both temperatures of 23 and -20°C , a notched impact strength mini-

mum is found for about 30–50% by weight of poly(phenylene ether) and polystyrene.

A similar minimum also exists in the polyethylene/polyether copolymer/polystyrene/SEBS block copolymer system, but for significantly higher block copolymer concentrations of about 20% by weight.¹⁰ At comparable amounts of the block copolymer of 5%, by weight, there is only a strong decrease in notched Izod impact strength with reduced polyethylene content from the highest value of polyethylene to the lowest of the pure poly(phenylene ether) copolymer/polystyrene component in contrast to the relation indicated in Figure 4.

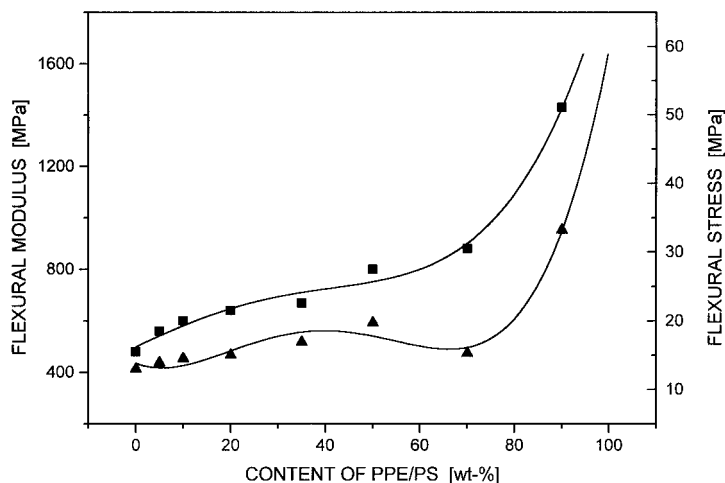


Figure 3 Dependence of (■) flexural modulus and (▲) flexural stress on the poly(phenylene ether) and polystyrene content in the system with polyethylene.

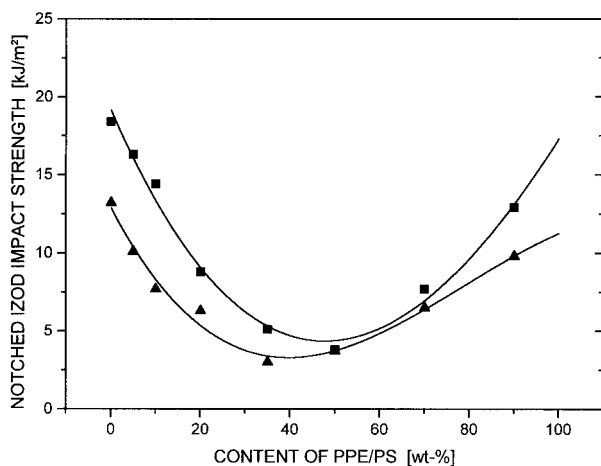


Figure 4 Effect of poly(phenylene ether) and polystyrene content in the system with polyethylene on the notched Izod impact strength at temperatures of (■) 23°C and (▲) -20°C.

The strong increase in notched Izod impact strength in Figure 4 at both temperatures, 23 and -20°C, with decreasing HDPE concentration below about 50% by weight already at such low block copolymer amounts is obviously a result of a more efficient elastification of the PPE/PS mixture by the SEPS copolymer and therefore a better compatibilization of the polymer phases by the selected block copolymer system in opposition to the system in Ref. 10. In agreement with the results of tensile modulus measurements, this SEPS block copolymer system is superior as a compatibilizer for the HDPE/PPE/PS blends than is SEBS for the HDPE/PEC/PS blends.⁸ The block copolymer itself causes an increase in the notched Izod impact strength of only the polyethylene from 11.8 to 18.4 kJ/m² at a temperature of 23°C and from 8.6 to 13.2 kJ/m² at -20°C.

Not only the mechanical properties but also the thermal characteristics are influenced by the composition of the polyethylene/poly(phenylene ether)/polystyrene system. In Figure 5, these dependencies for the Vicat softening temperatures and the heat-deflection temperatures are shown. At low contents of poly(phenylene ether) and polystyrene, the two parameters increase only weakly. For a polyethylene content of less than 50% by weight, however, they indicate a considerable increase. This trend is in agreement with observations on a polyethylene/poly(phenylene ether) copolymer/polystyrene system and with SEBS as the compatibilizer with high amounts of a poly(phenylene ether) copolymer⁸ and should be caused by a change in the phase morphology to the effect that a phase

inversion occurs at approximately 50% by weight from the continuous polyethylene phase at higher polyethylene concentrations to a continuous poly(phenylene ether)/polystyrene phase at lower polyethylene amounts. With regard to the processing properties of the polyethylene/poly(phenylene ether)/polystyrene system, the molding shrinkage was examined in addition to the melt flow index.

The relationship between the poly(phenylene ether) and polystyrene content in the mixture with polyethylene and the shrinkage is shown in Figure 6. While the molding shrinkage only slightly reduces with decreasing polyethylene content in the transverse direction to the flow, a small poly(phenylene ether)/polystyrene content of up to about 50% by weight enormously reduces the molding shrinkage in parallel to the flow direction. The addition of the block copolymer to only the polyethylene slightly increases the molding shrinkage from 4.6 to 4.7% in parallel to the flow direction and from 1.6 to 1.7% in the transverse direction to the flow. So, the molding shrinkage of polyethylene can be considerably reduced by the addition of low amounts of poly(phenylene ether)/polystyrene blends.

Also shown in Figure 6 is the ball indentation hardness as a mechanical property. Up to a content of about 60% by weight of poly(phenylene ether) and polystyrene, it grows slightly. With a higher content, it significantly increases. This tendency should be a result of the different continuous phases at variable polyethylene concentrations as already discussed in connection with the thermal properties. The addition of the block copolymer itself to only the polyethylene causes a clear decrease in the ball indentation hardness from 35 to 27 N/mm².

To characterize the phase behavior of the polyethylene/poly(phenylene ether)/polystyrene system in the presence of a hydrogenated SEPS triblock copolymer containing a low quantity of polypropylene in more detail, DSC investigations were carried out. The results are plotted in Figure 7 as a function of the poly(phenylene ether) and polystyrene content in the mixture with polyethylene. Mainly, three general phases were observed: The melt peak at 127°C can be assigned to the crystalline content of the partially crystalline polyethylene phase. It decreases with increasing poly(phenylene ether) and polystyrene amount to about 122°C at 90% by weight of both. From about 10% by weight of poly(phenylene ether) and polystyrene in the mixture with the polyethylene, the

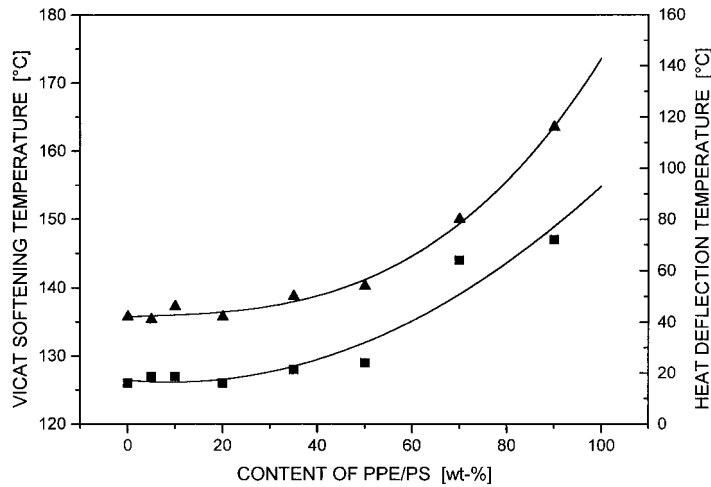


Figure 5 Relationship between (■) Vicat softening temperature and (▲) heat-deflection temperature and the poly(phenylene ether) and polystyrene content in the mixture with polyethylene.

common glass transition temperature of the compatible amorphous poly(phenylene ether) and polystyrene phase becomes visible. This glass transition temperature rapidly increases with an increasing poly(phenylene ether) and polystyrene content and slowly decreases with a content of more than 20% by weight. The third visible conversion temperature at 160°C is the melting temperature of the crystalline polypropylene, which according to the content forms only a very small phase. A glass transition temperature of the rubber phase expected for the sole SEPS block copolymer at about -50°C was not observed in the poly-

mer system because of the possibly low concentration. The effect of the amount of the added block copolymer showed that the increase of this quantity from 7 to 14% by weight at a polyethylene : poly(phenylene ether) : polystyrene quantity ratio of 50 : 27.5 : 22.5 resulted in an insignificant decrease in the glass transition temperature of the poly(phenylene ether)/polystyrene phase from 143.0 to 141.8°C and in the melting temperature of the polyethylene from 126.1 to 125.1°C at a constant melting temperature of the polypropylene of 160°C.

Therefore, in the special polypropylene con-

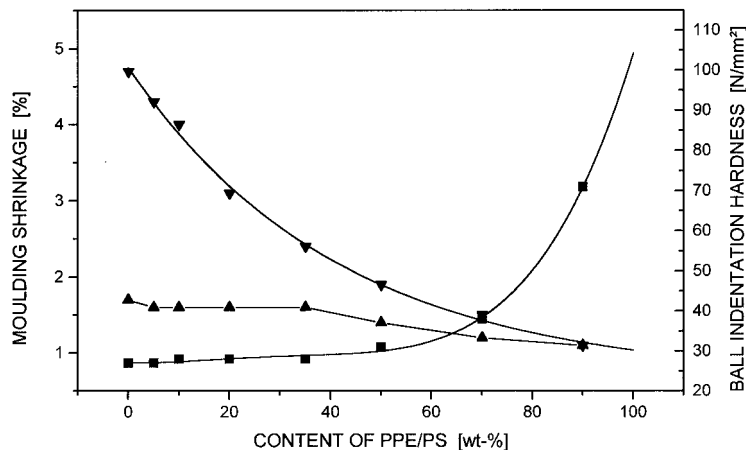


Figure 6 Effect of the poly(phenylene ether) and polystyrene content in the mixture with polyethylene on the moulding shrinkage (▼) parallel to the flow direction, (▲) in the transverse direction to the flow, and (■) on the ball indentation hardness.

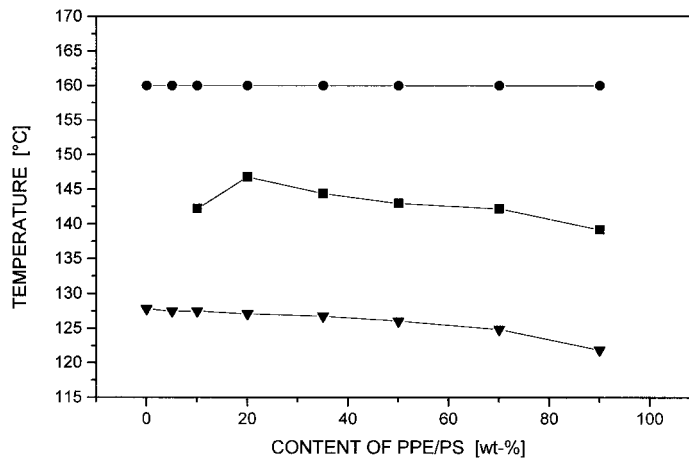


Figure 7 Dependence of the thermal conversion temperatures on the poly(phenylene ether) and polystyrene content in the mixture with polyethylene (DSC measurement): (▼) melting temperature of the polyethylene; (■) glass transition temperature of the compatible mixture of poly(phenylene ether) and polystyrene; (●) melting temperature of polypropylene.

taining and SEPS compatibilized system of polyethylene/poly(phenylene ether)/polystyrene, the existence of three general phases could be proved: a partially crystalline polyethylene phase, an amorphous over the full composition range miscible poly(phenylene ether)/polystyrene phase, and a preferred isotactic crystalline polypropylene phase.

REFERENCES

1. L. A. Utracki, *Polymer Alloys and Blends*, Hanser, Munich, Vienna, New York, 1990.
2. W. E. Baker and M. Saleem, *Polymer*, **28**, 2057 (1987).
3. C. R. Lindsey, D. R. Paul, and J. W. Barlow, *J. Appl. Polym. Sci.*, **26**, 1 (1981).
4. H. Hönl, *Kunststoffe*, **80**, 706 (1990).
5. L. Bottenbruch, *Technische Polymer-Blends, Kunststoff-Handbuch*, Bd. 3/2, Carl Hanser Verlag, Munich, Wien, 1993.
6. C. M. Rimmnac, R. W. Hertzberg, and J. A. Manson, *Polymer*, **23**, 1977 (1982).
7. Q. Zhang, Y. X. Shi, H. P. Wang, and Y. T. Cheng, in *C-MRS International Symposium Proceedings 1990*, North-Holland, Amsterdam, 1991, Vol. 3, p. 73.
8. M. C. Schwarz, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **37**, 403 (1989).
9. M. C. Schwarz, H. Keskulla, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **35**, 653 (1988).
10. M. C. Schwarz, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **35**, 2053 (1988).