Polymer Bulletin 42, 353–356 (1999)

Polymer Bulletin

Thermo-mechanical properties of the blend syndiotactic/atactic polystyrene after crystallization of the syndiotactic polystyrene

Martin Bonnet, Maren Buhk, Jurgen Petermann

Department of Chemical Engineering, Institute of Material Science,
University of Dortmund, Emil-Figge-Strasse 66, D-44221 Dortmund, Germany

Received: 20 October 1998/Revised version: 5 January 1999/Accepted: 3 February 1999

Summary

The thermo-mechanical properties of the blend syndiotactic polystyrene (sPS)/ atactic polystyrene (aPS) are characterized by studying the concentration depending softening behavior with thermo-mechanical analysis (TMA) and the temperature depending Young's modulus for different concentrations with dynamic mechanical analysis (DMA).

Introduction

Many polymer systems exhibit incompatibility in the melt or glassy state, and only in a few systems complete compatibility is found (for example PPE/aPS, PMMA/PVDF) (1-5). Compatible polymer systems are important for desired mechanical, thermal and optical properties, which can be adjusted within the property ranges of the pure materials.

For the system sPS/aPS, a compatibility in the melt was concluded from isothermal c_p-measurements, investigations of the enthalpy relaxation at T_g and from the crystallization kinetics (6). The mechanical properties of sPS and aPS are very similar but they differ in their optical and thermal (and therefore thermo-mechanical) properties. aPS is transparent and has a softening point of about 90°C, sPS is opaque and has a melting point of 270°C. Due to the compatibility of the system both, optical and thermal properties can be adjusted between the properties of the pure materials by varying the concentration of the components.

Experimental

Materials and sample preparation

The sPS, kindly supplied by Idemitsu Kosan Ltd. (Japan), has a tacticity of 98%, a molecular weight of M_w = 22,6*10^4, a glass transition temperature, T_g = 92°C, and a melting point of 270°C. The aPS (Polystyrol 143 E, melt index: 9 g/10 min), kindly supplied by BASF-Company (Germany), has a glass transition temperature, T_g = 100°C.

The mixtures were prepared by coextrusion in a DSM double screw miniextruder 97024. The samples of about 5 g were mixed at 290°C with 25 rpm until the torque reached a constant level. The so prepared blends were injection molded into the appropriate dimension in a DSM micro-injection molding machine with a melt temperature of 290°C and a mold temperature of 65°C. After preparation the samples were crystallized at 170°C for 30 min.

Thermo-mechanical analysis (TAM)

The device used was a Thermo-Mechanical Analyser (TMA) 2940-system from TA-Instruments coupled with a TA-Thermal Analyst 2000 control system. The softening behavior of the blends was characterized by the temperature dependent dimension change

using the penetration mode, in which a small force is put on pin, and the dimensional change either caused by the thermal expansion versus temperature or the penetration of the pin into the sample is registered, depending on the state of the sample (solid or viscous).

All measurements were performed with heating rates of 3 K/min and sample dimensions of 10* 10* 2 mm^3 (2 mm height).

Dynamic-mechanical analysis (DMA)

The device used was a Dynamic Mechanical Analyser (DMA) 2980-system from TA-Instruments coupled with a TA-Thermal Analyst 2000 control system. The softening behavior of the samples was characterized by the temperature depending dynamic Young's modulus using the resonant mode. All measurements were performed with heating rates of 3 K/min and sample dimensions of 15·10·2 mm^3.

Results and discussion

In a previous paper it was shown (6) and later confirmed by other authors (7), that the system sPS/aPS is completely compatible in the molten state over the whole concentration range. After the heat treatments (annealing 30 min. at 170°C) of the samples, a crystallization of the sPS component occurs, leading to a demixing of parts of both the components, because only the sPS can crystallize.

When interpreting the following experimental results one has to keep in mind, that the samples now consist out of a crystalline sPS phase (melting temperature of app. 270°C) and an amorphous aPS/sPS phase (glass transition temperature of app. 95°C).

Thermo-mechanical analysis

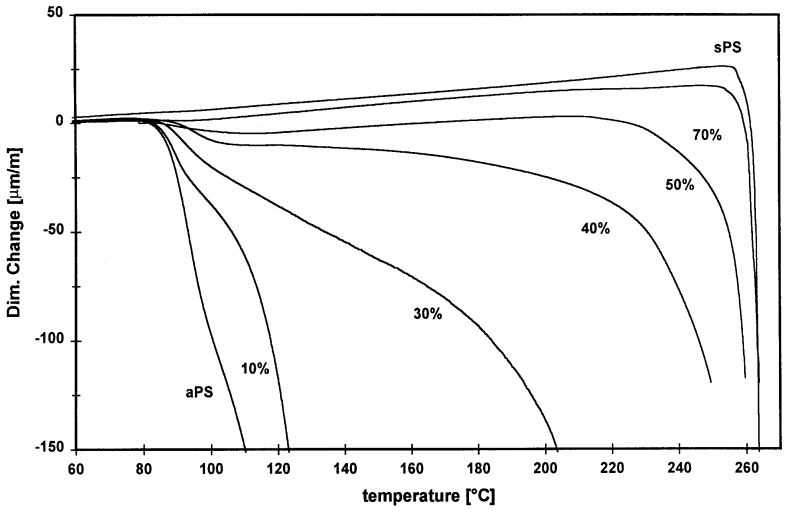

Figure 1. Dimension change versus temperature for aPS, sPS and blends with different sPS concentrations.

The measurements were conducted in a temperature region of 60 to 270°C. In Fig. 1, the dimension change in µm/m is plotted against the temperature for the pure materials

and blends with compositions of 10/90, 30/70, 40/60, 50/50, and 70/30 (sPS/aPS), respectively.

The pure sPS exhibits a positive dimension change to about 250°C, meaning that only thermal expansion determines the measurements and negligible penetration of the pin occurs (no softening). The pure aPS softens at its glass transition temperature (100°C) and mainly the penetration of the pin into the sample is recorded. To a sample concentration of 40% sPS, a softening at T_g occurs, but still over a wide temperature range, a rather stable dimension is maintained (plateau range). Penetration of the pin and therefore viscous behavior characterizes the measurements of the blends below 30% sPS.

Dynamic mechanical analysis

The DMA measurements were performed in a temperature range between 50 to 270°C. Fig. 2 shows the temperature depending dynamic Young's modulus (storage modulus E') for aPS, sPS and blends with compositions of 10/90, 30/70, 40/60, 50/50, 70/30 and 90/10 (sPS/aPS), respectively.

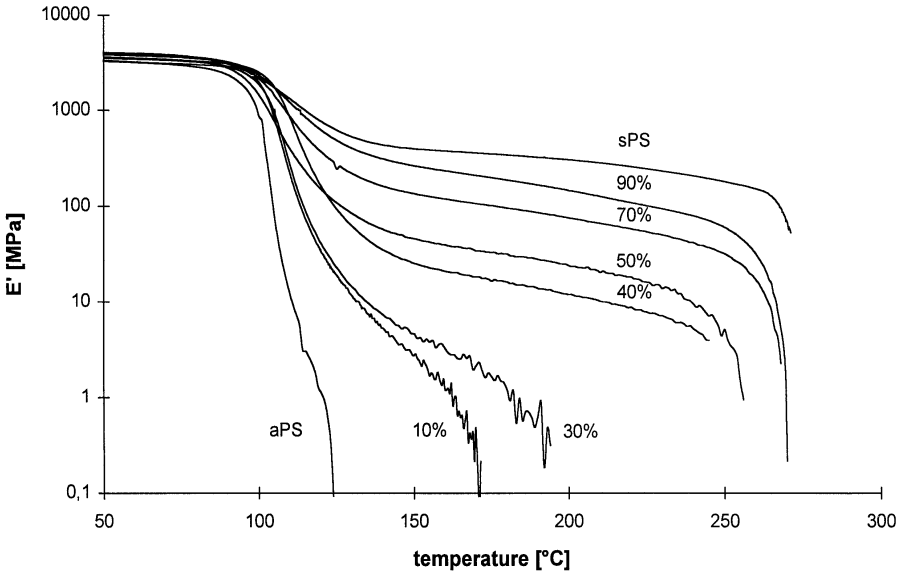

Figure 2. Young's modulus versus temperature for aPS, sPS and blends with different sPS concentrations.

A similar behavior as in the dimension change is observed: a decrease of E' at the glass transition temperature. The decrease above T_g is as more pronounced as higher the content of aPS is in the samples. But similar to the penetration measurements, a plateau range with nearly constant E' over a wide temperature range exists till a composition of 40% sPS. Below this concentration, the storage modulus decreases steeply and steadily with temperature.

From both the measurements, dimension change and DMA it can be concluded, that the stiffness of the samples versus temperature decreases with aPS content, but a plateau with rather constant behavior over a temperature range from 110°C to 250°C exists. This

leads to the suggestion, that a continuous matrix of the crystalline sPS exists to a minimum concentration of 40% sPS. The morphologies of these blends may exist of a continuous crystalline sPS matrix and amorphous aPS inclusions at higher sPS concentrations, and a bi-continuous morphology at lower concentrations. Below 40% of sPS, the amorphous aPS component is the only continuous phase. Because aPS and sPS are very difficult to be separated in optical contrast by imaging in the electron microscopes (SEM, TEM), no direct visual proof for our suggestion can be presented at the moment. Especially, it is not known till now, if the amorphous component (aPS) is dissolved in the interlamellar phase, or forms larger domains. Additional work is necessary, in order to investigate the morphologies of the blends. Nevertheless, with the sPS/aPS blends a polymer alloy system becomes available, which may eventually reach similar importance as the Noryl products (5), which are composed out of the compatible components aPS and PPE (polyphenylene-ether).

Acknowledgment

The financial support of the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

References

1. Guerra G, De Rosa C, Vitagliano VM, Petraccone V, Corradini P (1991) Polym. Comm. 32: 30.
2. Guerra G, De Rosa C, Vitagliano VM, Petraccone V, Corradini P (1991) J. Polym. Sci.: Part B: Polym. Phys. 29: 265.
3. Siqueira DF, Galembeck F, Nunes SP (1991) Polymer 32: 990.
4. Liu Y, Donovan JA (1995) Polymer 36: 4797.
5. Paul DR, Newman S (1978) Polymer Blends, Academic Press, New York.
6. Bonnet M, Buhk M, Trogner G, Rogausch KD, Petermann J (1998) Acta Polymerica 49: 174.
7. Hong BK, Jo WH, Kim J (1998) Polymer 39: 3753