Macromol. Symp. **2003**, *198,* 355-362

DGEBA Monomer as a Solvent for Syndiotactic Polystyrene

Jaap Schut,[1,2] *Manfred Stamm,*[2] *Michel Dumon,*[1] *Jean-François Gérard**[1]

[1] National Institute of Applied Sciences, Laboratory of Macromolecular Materials (IMP/LMM), UMR CNRS 5627; 17, Avenue Jean Capelle, 69621 Villeurbanne Cedex, France
E-mail: jfgerard@insa-lyon.fr
[2] Institute of Polymer Research Dresden, Physical Chemistry and Physics of Polymers; Hohe Strasse 6, 01069 Dresden, Germany

Summary: Syndiotactic polystyrene (sPS) has to be processed at high temperatures (i.e. >290°C due to its melting point of 270°C), which approaches its degradation temperature. We aim to facilitate the processing of sPS by lowering its melt temperature and viscosity with a curable epoxy/amine model system as reactive solvent, which will result in a thermoplastic-thermoset polymer blend. As a first step we therefore investigated the melting behaviour of sPS in epoxy monomer, established its phase diagram, and investigated the crystalline form of sPS in these mixtures. DGEBA epoxy monomer is found to be a solvent for syndiotactic polystyrene at temperatures above 220°C. The DGEBA-sPS phase diagram was established by means of DSC, on the basis of crystallization and melting peaks. The form of the curve in the phase diagram indicates that DGEBA is a poor solvent for sPS. In WAXS studies of blends only the β crystalline form was detected, not the δ form, thus no sPS-DGEBA polymer-solvent compounds (clathrates) were detected. However, DGEBA can still serve as a monomer for improved processing as it depresses the crystallization temperature by 20 to 60 K upon addition of 20 to 90 wt% DGEBA respectively, while a 16 to 45 K melting peak depression can be observed by adding 20 to 90 wt % DGEBA.

Keywords: blends, crystallization, phase diagram, reactive solvent, syndiotactic polystyrene

Introduction

Syndiotactic polystyrene (sPS) is a relatively new and promising semi-crystalline engineering thermoplastic with a melting point around 270°C, which was first synthesized in 1985 by Ishihara *et al.* with the use of a titanium metallocene catalyst.[1] In addition to the advantages of atactic polystyrene (attractive price, low specific gravity, low dielectric constant, and good

DOI: 10.1002/masy.200350830

processability), sPS has very good solvent, chemical and steam resistance, high modulus of elasticity, high heat resistance and good dimensional stability, all due to its semi-crystalline nature. Syndisotactic polystyrene crystallizes about two orders of magnitude faster than iPS (which has not been commercialised due to its slow rate of crystallization), and displays a crystallinity between 15 to 60%. sPS is therefore expected to fill the price-performance gap that currently exists between performance and commodity plastics, and has been commercialised by Dow Chemical Co. (Questra^{TM}) and Idemitsu (Xarec^{TM}).

However, due to its high melting point sPS has to be processed at temperatures exceeding 290°C, which approaches its degradation temperature, and is thus a disadvantage.

Our goal in the present study is twofold. Firstly to facilitate the processing of sPS by lowering its melt temperature and viscosity with a curable epoxy/amine model system as reactive solvent, which will result in a thermoplastic-thermoset polymer blend. Secondly we aim to generate new blend morphologies, using the crystallization of sPS as an adjustable parameter during the crosslinking of the epoxy/amine monomers. The present study is concerned with the characterisation of the solvent quality of epoxy monomer for syndiotactic polystyrene. We have therefore investigated the melting behaviour of sPS in epoxy monomer, established its phase diagram, and studied the crystalline form of sPS in these mixtures.

Syndiotactic polystyrene has two stable chain conformations, the all-trans, planar zigzag (or T_4) conformation, and the helical (or T_2G_2) conformation, which give rise to 4 crystalline modifications: α, β, δ, and γ.[2] Fast cooling from the melt leads to the α form crystalline (kinetically stable), while slow cooling leads to the β crystalline form (thermodynamically stable), with sPS having the planar zig-zag conformation in both cases. The δ form is a polymer-solvent complex (clathrate) where sPS is crystallised in its helical conformation and solvent molecules are incorporated in the crystalline unit cell. When the δ form is carefully heated to remove the solvent molecules, the δ_e or γ forms result, which are solvent free forms of sPS in the helical conformation.[3],[4],[5] Figure 1 shows the schematic phase diagrams of sPS in a good and poor solvent,[6] with the superposition of the aPS-good solvent phase diagram for comparison.

Figure 1a shows that upon *slowly cooling* a weakly concentrated, hot solution of sPS in a good solvent (such as chloroform, benzene, toluene, or chlorobenzene) the δ form is generated, which is a stable thermoreversible gel. At higher concentrations ór in the case of a poor solvent (such as decalin, cyclohexane, or cyclohexanol, Figure 1b at the whole concentration range, this gel can only be formed by *rapid quenching* of the hot solution, which now yields a *metastable* thermoreversible gel. However, when these solutions are *slowly cooled*, sPS directly crystallises in the β crystalline form. Heating a stable gel causes it to melt directly to a homogeneous solution, while heating a metastable gel gives first rise to a transition from δ to β -observed as a horizontal line in the phase diagram- followed by a melting of the β crystals to a homogeneous solution.

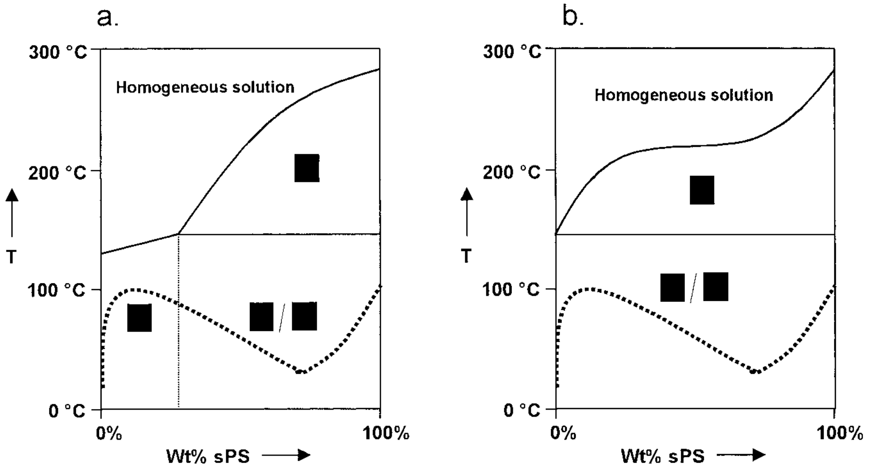

Fig. 1. Schematic temperature-composition diagram of syndiotactic polystyrene and solvent systems. a) Good solvent b) Poor solvent. The dotted curves represent the atactic PS-good solvent phase diagram for comparison.

Compared to pure sPS a melting point depression is observed in sPS-solvent mixtures upon the addition of both a good and a poor solvent. The normal Upper Critical Solution Temperature phase of aPS in a good solvent diagram is "hidden" by the crystallization of the syndiotactic polymer.

Experimental

Syndiotactic polystyrene (Questra QA 101^{TM}, supplied by Dow Chemical Co.), denoted sPS, of 99+% syndiotacticity (^{1}H and ^{13}C-NMR), with a number average molar mass of 94,100 g.mol^{-1}, and weight average molar mass of 192,000 g.mol^{-1} was used. The epoxy resin system used was a diglycidylether of bisphenol-A (Dow DER 330^{TM}, n=0.15, M=383.1 g.mol^{-1}, purchased from Dow chemical Co.), denoted DGEBA.

sPS-DGEBA blends at concentrations below 30 wt% sPS were prepared in a large test tube equipped with a mechanical stirrer. Powdered sPS was added to vacuum degassed (liquid) DGEBA and heated to 290°C in a Wood's metal bath to ensure dissolution within 10 min. Due to their high viscosity, blends containing 60 wt% sPS or above were prepared in a Haake internal mixer or a Clextral co-rotating twin screw extruder at 240-290°C.

DSC measurements were performed on a water-cooled Perkin-Elmer DSC-7 under nitrogen atmosphere at a temperature scan rate of 10 K.min^{-1}. All samples were held for 5 min at 300°C to erase thermal history prior to the crystallization and subsequent melting scans.

Results

Syndiotactic polystyrene was found to be soluble in DGEBA epoxy monomer above 220°C. To establish the temperature-composition diagram of the non-reactive sPS-DGEBA system, DSC was

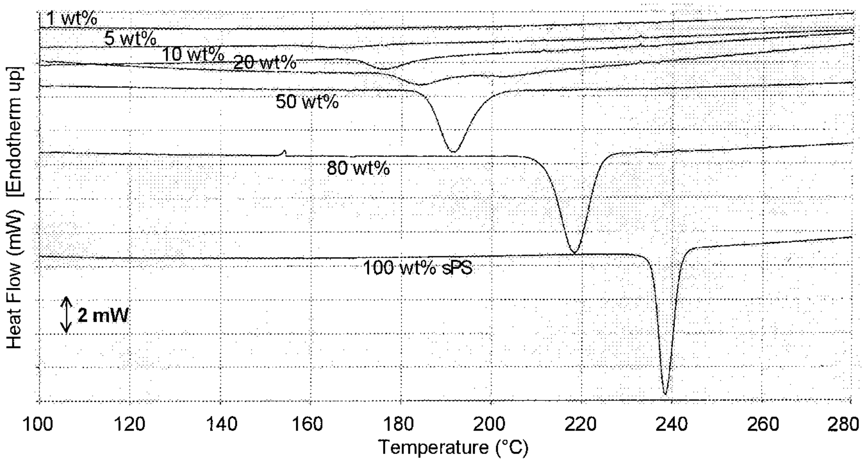

Fig. 2. DSC cooling scans (10 K.min^{-1}) of different sPS-DGEBA mixtures. Samples were held for 5 min at 300°C before cooling.

employed to investigate crystallization and melting behaviour. Figure 2 shows the crystallization scans of several of these blends. The crystallization temperature is depressed by 20 to 60 K upon addition of 20 to 90 wt% DGEBA, respectively.

The melting point depression can be observed from the DSC heating scans in Figure 3. Pure sPS exhibits multiple melting peaks, attributed to melting and re-crystallization of different lamella crystals.[7],[8],[9] While a 16 to 45 K melting peak depression can be observed by adding 20 to 90 wt % DGEBA.

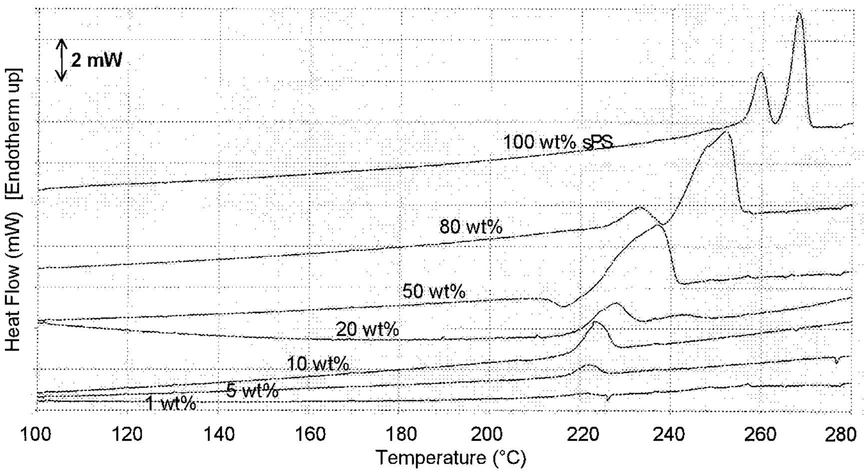

Fig. 3. DSC heating scans (10 K.min^{-1}) of different sPS-DGEBA mixtures. Samples were previously crystallised by cooling from 300°C at 10 K.min^{-1}.

The onset of crystallization and melting peak temperatures were used to construct the phase diagram shown in Figure 4.

Scrutinising the onset of crystallization one may see that 220°C is the minimum temperature at which low concentration blends (<40 wt% sPS) can be safely processed in homogeneous conditions, i.e. without premature crystallization. On the other hand the minimum temperature needed for the reactive extrusion of high concentration blends (>60 wt% sPS) is 230-250°C.

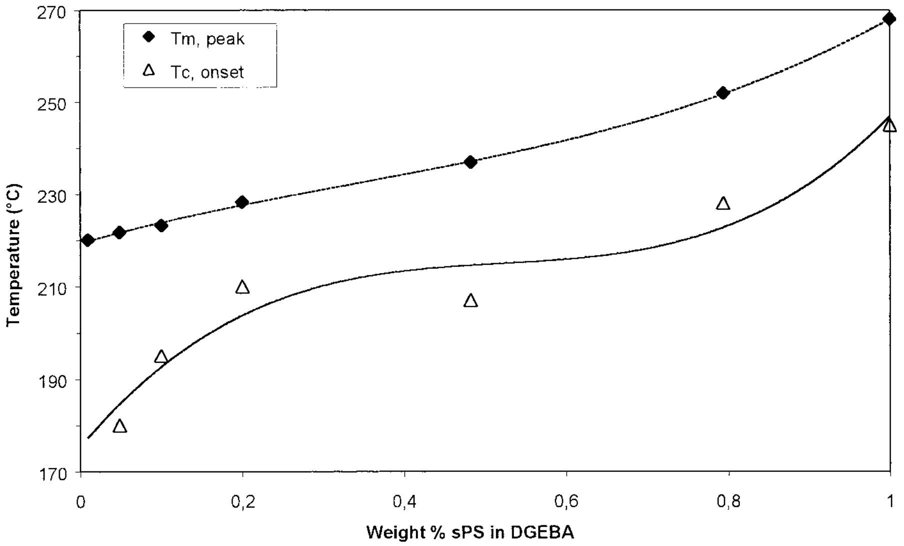

Fig. 4. Temperature-composition diagram of the syndiotactic polystyrene-DGEBA system.

These high temperatures needed to obtain homogenous mixtures of sPS in DGEBA, cause some concern as to the degradation or thermal homopolymeriization of the epoxy monomer. TGA and SEC/GPC however showed that there was no significant degradation or polymeriization even after 6h at 220°C.[10]

The shape of the crystallization curve resembles that of a poor solvent system as shown in Figure 1b. When homogeneous solutions of sPS in DGEBA were quenched into liquid nitrogen no gel formation could be observed, but only crystallization of the sPS into spherulites.

Figure 5 shows the WAXS patterns of pure and slowly crystallised sPS compared to its blends with DGEBA. The pure sPS pattern is characteristic for the β crystalline form, with peaks at 6.3, 7.0, 10.6, 12.5, 13.7, 18.7, 20.4, 24.0, 35.2, and 37.7° (2θ scale).[11]

Although the patterns have a low signal to noise ratio due to the low sPS concentration, the major peaks at 6.3, 12.5, and 20.4° are seen not to shift in the 20, 10, and 3% mixtures, nor do any additional peaks arise when compared to the β form of pure sPS, although the amount crystallinity is low due to low sPS concentrations.

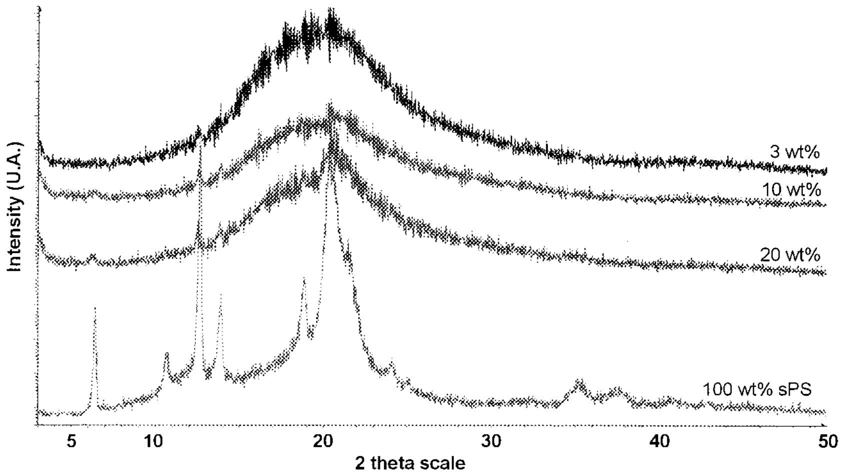

Fig. 5. Wide angle X-ray diffraction patterns of pure (β) sPS and its mixtures with DGEBA monomer.

Conclusions

DGEBA epoxy monomer is found to be a solvent for syndiotactic polystyrene at temperatures above 220°C. Although these are relatively high temperatures for using epoxy resin, no significant degradation or thermal homopolymeriization of DGEBA could be detected by TGA and SEC/GPC. The DGEBA-sPS phase diagram was established by means of DSC. The form of the crystallization curve in the phase diagram indicates that DGEBA is a poor solvent for sPS. This is also supported by the fact that no other crystalline modifications other than β could be detected by WAXS at various concentrations of DGEBA. No sPS-DGEBA polymer-solvent compounds (clathrates) can therefore be detected, and relatively pure sPS and DGEBA phases are formed during phase separation. However, DGEBA can still serve as a monomer for improved processing as it depresses the crystallization temperature by 20 to 60 K upon addition of 20 to 90 wt% DGEBA respectively, while a 16 to 45 K melting peak depression can be observed by adding 20 to 90 wt % DGEBA.

Additional work is in progress on the effect of the presence of DGEBA monomer on the crystallization kinetics of sPS, as well as on ternary blends cured with a diamine hardener processed on laboratory scale and by reactive extrusion. Future work will include the optimisation of the reactive extrusion of sPS with DGEBA/MCDEA, studying the reaction induced phase separation and crystallization by WAXS/SAXS, and relating the mechanical properties of the cured blends to their compositions and thermal histories.

Acknowledgments

This research was funded by the Research Training Networks (RTN) program under the name « PolyNetSet »; contract number HPRN-CT-2000-00146, under auspices of the Directorate-General for Research of the European Commission.

Our thanks go to Mr. Ruben Vera (Claude Bernard University, Villeurbanne) for performing the WAXS measurements, and Dr. Nick Zafeiropoulos for the useful discussions.

[1] N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, *Macromolecules*, **1986**, *19*, 2464-2465.
[2] G. Guerra, V.M. Vitagliano, C. De Rosa, V. Petraccone, P. Corradini, *Macromolecules*, **1990**, *23*, 1539-1544.
[3] S. Moyses, S. Spells, *Polymer*, **1999**, 40(*12*), 3269-3274.
[4] G. Guerra, C. Manfredi, P. Musto, S. Tavone, *Macromolecules*, **1998**, *31*, 1329-1334.
[5] E. Reverchon, G. Guerra, V. Venditto, *J. Appl. Pol. Sc.*, **1999**, *74*, 2077-2082.
[6] S. Rastogi, J.G.P. Goossens, P.J. Lemstra, *Macromolecules*, **1998**, *31*, 2983-2998.
[7] Y .S. Sun, E.M. Woo, *Macromolecules*, **1999**, 32, 7836-7844.
[8] Y .S. Sun, E.M. Woo, *J. Pol. Sci. part B: Pol. Phys.*, **2000**, 38, 3210-3221.
[9] Y .S. Sun, E.M. Woo, *Pol. Mat. Eng.*, **2001**, 84, 551.
[10] Unpublished results.
[11] S. Duff, S. Iwamoto, T. Iwamoto, F. Fujibayashi, C. Birkinshaw, **2001**, 42(3), 991-1000.