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# Reactive Processing of Syndiotactic Polystyrene with an Epoxy/Amine Solvent System

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**Summary:** Syndiotactic polystyrene (sPS) is a new semi-crystalline thermoplastic which is believed to fill the price-performance gap between engineering and commodity plastics. In order to reduce the high processing temperature of sPS (>290°C), an epoxy-amine model system was used as a reactive solvent. Such a processing aid can be used to achieve a 50 to 500 fold lowering of the melt viscosity. When initially homogeneous solutions of sPS in a stoechiometric epoxy-amine mixture are thermally cured, Reaction Induced Phase Separation (RIPS) takes place, leading to phase separated thermoplastic-thermoset polymer blends. We focus our study on low (wt% sPS < 20%) and high concentration blends (wt% sPS > 60%) prepared by two processing techniques (mechanical stirring in a laboratory reactor or internal mixer/ reactive extrusion respectively). These blends have different potential interests. Low concentration blends (sPS domains in an epoxy-amine matrix) are prepared to create new, tunable blend morphologies by choosing the nature of the phase separation process, i.e. either crystallisation followed by polymerization or polymerization followed crystallisation. High concentration blends (sPS matrix containing dispersed epoxy-amine particles after RIPS) are prepared to facilitate the extrusion of sPS. In this case, the epoxy amine model system served as a reactive solvent. The time to the onset of RIPS is in the order of 7-9 min for low concentration blends, while it increases to 20-45 min for high concentration samples, as the reaction rates are substantially slowed down due to lower epoxy and amine concentrations. During the curing reaction the melting temperature of sPS in the reactive solvent mixture evolves back from a depressed value to the level of pure sPS. This indicates a change in the composition of the sPS phase, caused by (complete) phase separation upon reaction. We conclude that our epoxy amine system is suited for reactive processing of sPS, where final properties depend strongly on composition and processing conditions.

**Keywords:** reaction induced phase separation (RIPS); reactive processing; syndiotactic polystyrene; thermoset-thermoplastic blends

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## 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 processability), sPS has a very good solvent, chemical and steam resistance, a high modulus of elasticity, high heat resistance and good dimensional stability. These properties originate from its semi-crystallinity, which can be between 15 to 60%. As it crystallises about two orders of magnitude faster than iPS (which has not been commercialised due to its low rate of crystallisation), it is therefore expected to fill the price-performance gap that currently exists between performance and commodity plastics. sPS has been commercialised by Dow Chemical Co. (as Questra$^{TM}$) and Idemitsu (as Xarec$^{TM}$). However, sPS has to be processed at temperatures exceeding 290°C, due to its high melting point, causing degradation of the polymer. This could be prevented by lowering the process temperature.

The goal of this study is therefore 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 by using the crystallisation of sPS as a variable parameter during the crosslinking of the epoxy/amine monomers. As the sPS-Epoxy/Amine system is as yet unexplored we also turned our attention to blends containing less than 20wt% sPS (yielding an epoxy resin continuous phase). Here the concept of reactive processing is of course no longer applicable, but one can obtain useful additional information about the crystallisation and phase separation behaviour of the system by studying these blends.

Pursuing the first objective will lead to an sPS matrix filled with epoxy-amine particles as the dispersed phase, while the second objective will give an epoxy-amine matrix filled with sPS particles as the dispersed phase.

When a homogeneous solution of a polymer in a mixture of monomers is thermally cured, the polymer will phase separate during the curing reaction as a consequence of the changing solvent nature (cause primarily by the increasing molecular weight but also by a changing Flory-Huggins interaction parameter [$\chi$]). This so called "Reaction Induced Phase Separation" (RIPS)[2,3] leads to a phase separated thermoplastic-thermoset polymer blend. In a previous study[4] we found a depression of the crystallisation temperature of syndiotactic polystyrene by some 20-50 K in non-reactive blends of sPS with the epoxy monomer Diglycidylether of Bisphenol-A (DGEBA). From comparison with literature data on the shape of the phase diagram, we concluded that DGEBA was considered to be a poor solvent for sPS (where the word poor is used in its usual polymer physical meaning of a solvent that dissolves a polymer, however without the extensive swelling of the coiled chains that a good solvent would cause). The present study is concentrating on the experimental methods used for processing sPS with a DGEBA/MCDEA reactive solvent, and the characterisation of some important processing parameters such as melt viscosity, onset of phase separation, as well as the final morphology of the cured blend.

## Experimental

Syndiotactic polystyrene (Questra QA 101™, kindly donated by Dow Chemical Co.), denoted sPS, of more than 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 reactive system was based on a stoichiometric mixture of diglycidylether of bisphenol-A (Dow DER 330™, $n = 0.15$, $M = 383.1$ g mol$^{-1}$, purchased from Dow Chemical Co.), denoted DGEBA, and the aromatic diamine 4,4'-methylenebis(3-chloro-2,6-diethylaniline) (Lonzacure M-CDEA™, 98%, $M = 379.4$ g mol$^{-1}$, purchased from Lonza) denoted MCDEA. 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 DGEBA and heated in a Wood's metal bath to 290°C to ensure complete dissolution within 10 min. This reactive mixture was then quickly transferred (minimising heat loss to prevent premature crystallisation) to small, preheated microtubes for turbidity measurements.

Blends containing 60 to 100 wt% sPS were prepared in a Haake internal mixer or a Clextral co-rotating twin-screw extruder, due to their high viscosities. Figure 1 shows the reactive extrusion set-up. The screw dimensions were as follows: diameter: 25 mm, length: 900 mm (l/d = 36), distance between screws: 21 mm. The temperature of the first zone was deliberately chosen very high (290°C, the advised extrusion temperature of pure sPS) in order to ensure fast and complete dissolution of the sPS in the DGEBA monomer. DGEBA at 80°C was injected just after the first counter flow element to ensure low counter pressure from the melt in the extruder barrel. At the same point the zone temperature was lowered to 280°C. The sPS/DGEBA mixture passed through a kneader zone for intense mixing followed by a transport zone. After this the temperature was further lowered to 240°C. MCDEA powder (at 20°C) was then added into the melt by a computer controlled vibrating funnel (feeder). Both the DGEBA pump container and the MCDEA funnel/container were placed on a balance in order to control and regulate the material flux into the extruder screw. The cure reaction started when MCDEA liquified and was mixed intimately with the melt by a second kneader followed by a counterflow element in order to ensure an appropriate residence time in the kneader zone. Upon exiting the extruder die the reacting melt (at low reaction conversion) was either captured in the hot, homogeneous state in a 35 mm test tube (which was kept at 240°C in a Wood's metal bath) *and subsequently cured in this tube* (giving RIPS morphology), or it was captured in a cold test tube and allowed to cool to room temperature causing thermal precrystallisation before being cured at 220°C (i.e. the sample underwent CIPS, Crystallisation Induced Phase Separation prior to curing), without remelting the sPS. Cloud point measurements were performed on an in house built apparatus, which consists of a temperature regulated and insulated oven in which a small test tube (8 mm internal diameter) is placed. Light emitted from a white lamp is guided through the sample by glass fibres and then to a photomultiplier and a photocell. The measured voltage is a measure of the relative turbidity of the sample. Rheological measurements were made on a Rheometrics Dynamic Analyser RDA II using a parallel plate geometry (2cm diameter plates, 3mm gap). Frequency scan rate was 1 Hz, temperature scan rate 2.2K min$^{-1}$. 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 crystallisation scans.

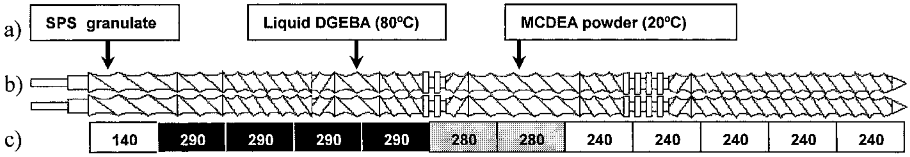

Fig. 1. The reactive extrusion process. a) The injection points of the 3 components; b) Transport, counterflow and kneading elements on the screws; c) Temperatures of heating zones.

## Results

### Non-reactive Systems

The phase diagram (crystallisation temperature vs. concentration) of the non-reactive sPS-DGEBA system as established by DSC is reported elsewhere.[4] It was found that 220°C is the minimum temperature at which low concentration blends (<40 wt% sPS) could be processed in homogeneous conditions, i.e. without premature crystallisation. On the other hand the minimum temperature needed for the reactive extrusion of high concentration blends (>60 wt% sPS) is 230-250°C. To investigate the effect of DGEBA on the melt viscosity of sPS, a number of blends were analysed by rheometry. Figure 2 shows the viscosity of several sPS/DGEBA blends in their molten states. More specifically, the plateau value of the viscosity in the melt of the mixture in question, i.e. the constant value of the viscosity from $T = T_c + 10$ K to $T = T_c + 30$ K (where $T_c$ is the crystallisation temperature) during a crystallisation scan from 300 down to 80°C at -2.2 K $min^{-1}$. One can observe a large decrease in the melt viscosity upon addition of DGEBA: compared to pure sPS a 20-fold decrease from 100 to 4.8Pa s can be seen upon adding 50 wt% DGEBA, while adding 70 wt% DGEBA even causes a 500 fold decrease down to 0.2 Pa s. The latter viscosity is however too low to be processed with an extruder.

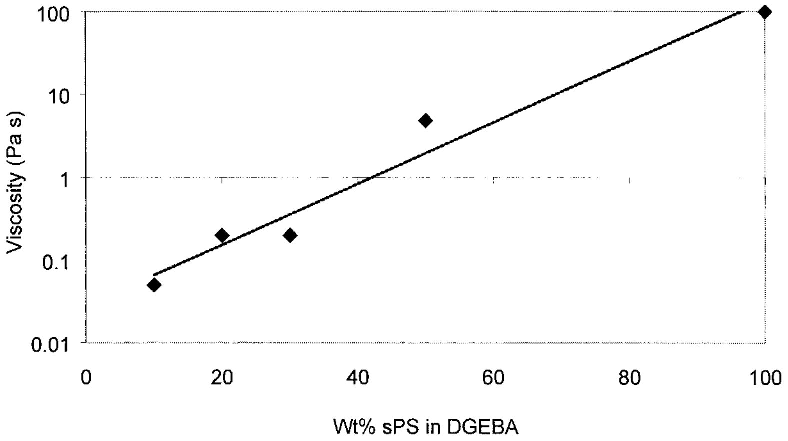

Fig. 2. Melt viscosity vs composition of syndiotactic polystyrene-DGEBA solutions above their crystallisation temperature ($T = T_c + 10$ K, scan frequency 1 Hz).

From the afore mentioned phase diagram and these rheological data, we conclude that DGEBA is a suitable reactive solvent for syndiotactic polystyrene.

**Reactive Systems**

The next step was to cure sPS/DGEBA blends with MCDEA diamine curing agent and follow the cure reaction by monitoring the Reaction Induced Phase Separation (RIPS). Figure 3 shows the phase separation process by following the turbidity of several low concentration, reactive sPS-DGEBA/MCDEA solution during isothermal curing at 220°C. Blends with concentrations above 25 wt% sPS were almost impossible to prepare in test tubes (due to their high viscosity) and contained too many air bubbles to be analysed by turbidity measurements.

After introduction of the sample in the device (after about 2 min reaction time), light transmission was stable at a plateau value for about 5-7 min (i.e. 7-9 min reaction time). After 7 to 9 min one can observe a decrease of the transmitted light intensity in all samples due to the appearance of a dispersed phase (the sample becomes opaque). This is the onset of RIPS, which takes place quite fast due to the high reaction temperature and high epoxy-amine concentrations. After a certain time the intensity falls to almost zero, indicating the end of the RIPS.

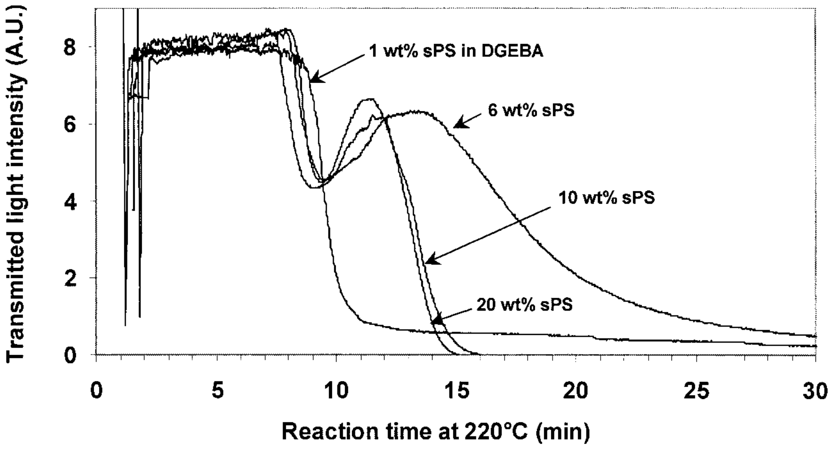

Fig. 3. Turbidity of low concentration sPS-DGEBA/MCDEA blends during cure at 220°C as a function of reaction time.

The cure reaction itself continues and samples are left to cure for 2 h.

The unexpected peak in the intensity after 11 to 15 min for the 6, 10 and 20 wt% samples is most probably caused by a crossing of the refractive index values of the two phases due to their continuous composition change during curing. The phase separation process ends after 12, 15, 16, and 30 min for the 1, 20, 10, and 6wt% sPS samples respectively, observed as a levelling off to a constant value of the observed intensities.

At the time of writing it is yet unresolved if the phase separation of sPS from the epoxy mixture consists of an initial liquid-liquid phase separation followed by crystallisation (liquid to crystalline phase transition) of the sPS component, ór if it is a transition of the dissolved sPS directly into its crystalline state. Literature on the system sPS-decalin suggests that crystallisation takes places directly out of a homogeneous solution, while liquid-liquid phase separation occurs at much lower temperatures.[5] More information on this topic is however scarce.

Although the time to RIPS is very short in the case of these low sPS content blends, the cure kinetics of the epoxy-amine reaction are substantially slowed down in samples with 60 wt% sPS or more. This dilution effect can be observed visually in the mixing chamber as an opacity of the melt in samples prepared in an internal mixer. Figure 4 shows the time to onset of turbidity vs blend composition for both high and low concentration blends.

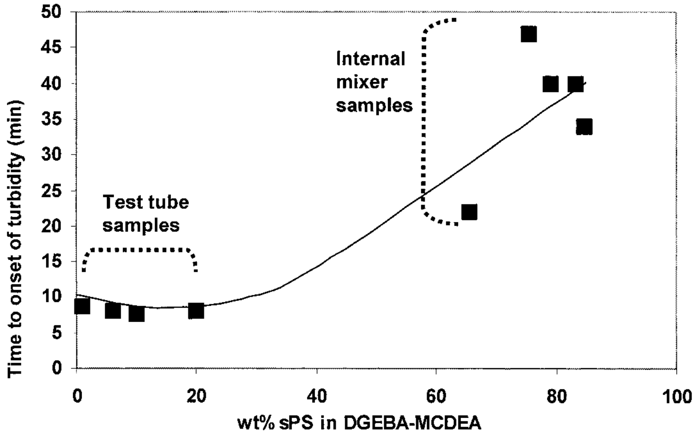

Fig. 4. Time to onset of turbidity in sPS/DGEBA-MCDEA blends during isothermal curing at 220°C as a function of their composition.

It can be seen that time to RIPS for the high concentration blends is now of the order of 20-45 min. DGEBA/MCDEA is therefore well suited for reactive extrusion (without premature phase separation), where the typical mean residence times is 3 to 5 min. Fig 4 reports the cloud point *times* while the correct parameter to characterize the extent of reaction at phase separation would be the cloud point *conversions*. Reaction conversion can generally be obtained by the determination of the residual heat of polymerization, which unfortunately proved to be impossible as explained later in the text We thus used time instead of conversion, which leads to cloud points having the same time corresponding to different reaction extents.

The next step was to investigate the feasibility of processing syndiotactic polystyrene in a co-rotating twin-screw extruder with DGEBA-MCDEA as a reactive solvent. Blends of sPS in DGEBA-MCDEA with compositions ranging from 60 to 90 wt% sPS were reactively extruded. The obtained extrudate was either captured directly from the extruder die into a preheated test tube at 220°C and subsequently cured in this tube (giving RIPS morphology), or it was captured into a cold test tube and allow to cool to room temperature to be precrystallised prior to curing at 220°C (CIPS morphology). The two routes have been found to give rise to very different morphologies. Both the blend morphology at different compositions as well as the tailoring of these morphologies by using the crystallisation ability of sPS as a parameter – yielding a range of interesting morphologies – will be discussed in more detail elsewhere.[6] Figure 5 shows the morphology of pure (beta) sPS and a 64wt% sPS/DGEBA-MCDEA reactively extruded sample. Pure sPS (*5a*) shows a rough fracture surface with no specific morphology, while a 64 wt% sPS/DGEBA-MCDEA blend (*5b*) shows 1-2 μm spherical particles of cured epoxy resin in an sPS matrix. This morphology is well known and characteristic for immiscible polymer blends[7,8] it therefore only serves to give a first impression of the morphologies of our system.

To check the advancement of the cure reaction, we intended to determine the residual heat of polymerisation of samples from the internal mixer taken at regular intervals during curing. To our surprise no residual reaction exotherm could be detected in DSC, which is probably caused by shielding of this exotherm by the melting endotherm of the sPS. We therefore turned our attention to the evolution of the melting temperature of sPS during the curing reaction.

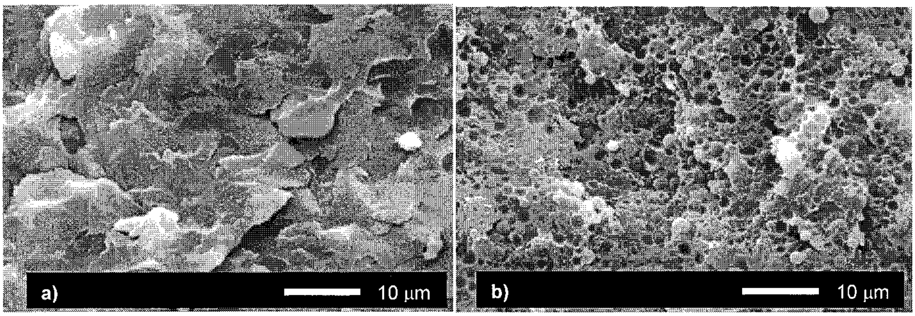

Fig. 5. SEM micrographs showing the morphology of: a) pure sPS (β form), b) 64 wt% sPS reactively extruded with DGEBA/MCDEA, cured at 250°C.

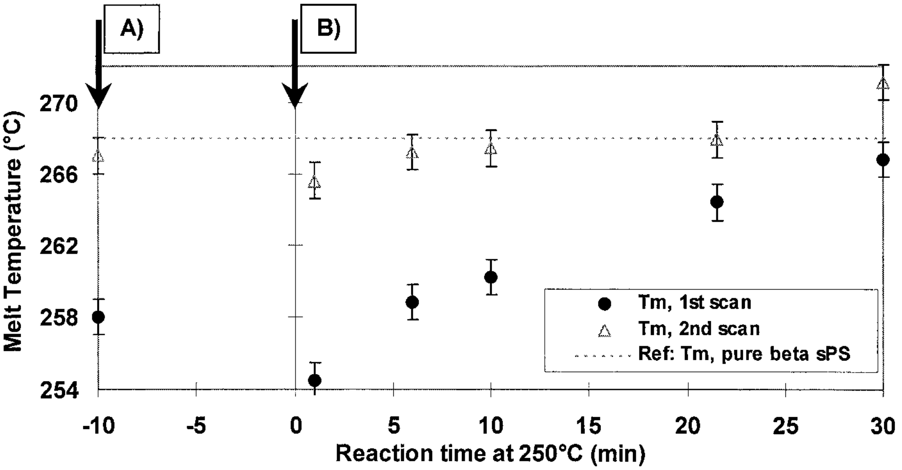

Fig. 6. The evolution of the melting temperature of sPS in sPS/DGEBA-MCDEA blends during reactive processing in an internal mixer at 250°C. A) Non reactive 85 wt% sPS/DGEBA blend. B) Cure reaction starts by adding MCDEA (resulting in a 80 wt% sPS/DGEBA-MCDEA blend).

Figure 6 shows the melting point evolution of an sPS/Epoxy-amine blend during cure, reflecting the effects of Reaction Induced Phase Separation. At point A) a non-reactive 85 wt% sPS/DGEBA blend is homogenised in the mixer for 10 min. At point B) (t=0) the MCDEA diamine curing agent is added to the melt, starting the reaction and changing the overall composition to 85 wt% sPS in DGEBA-MCDEA. One can observe an additional 3-4 °C drop of the melting temperature due to a further decrease of the sPS concentration. Once the cure reaction has started one sees a levelling off with time of the sPS melting point back to the value of pure sPS (268°C) beyond 30 min, indicating that complete phase separation into a pure sPS and a pure epoxy-amine phase has taken place during reaction.

## Conclusions

Despite the poor solvent nature of DGEBA epoxy monomer for syndiotactic polystyrene, it decreases the melt viscosity of sPS 50 to 500-fold. When initially homogeneous blends of sPS and DGEBA-MCDEA are thermally cured, Reaction Induced Phase Separation (RIPS) takes place, leading to completely phase separated blends. The time to the onset of RIPS is in the order of 7-9 min for the 1 to 20 wt% sPS samples. The reaction kinetics of higher concentrated samples prepared in an internal mixer are substantially slowed down due to the lower epoxy and amine concentrations, time to RIPS is now in the order of 20-45 min. Together with a previously found melting point depression this leads us to conclude that DGEBA-MCDEA is a suitable reactive solvent to be used in the reactive processing of sPS. SEM shows 1-2μm cured epoxy resin spherical particles in an sPS matrix. Using DSC no residual cure exotherm could be detected in partially cured samples. We therefore monitored the evolution of the melting temperature during the course of the reaction. After the curing reaction started we observed a levelling off of the sPS melting point back to the value of pure sPS (268°C) with reaction time, indicating complete phase separation. We are currently studying the phase separation and crystallisation by WAXS/SAXS, and measuring the mechanical properties of the cured blends at different compositions and thermal histories. This will lead to an improved insight into the structure-properties relationship for these blends.

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