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An Investigation of sPS/Epoxy Blends by Means of X-Ray Scattering Techniques

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Summary: SPS is a fast crystallisable polymer that possesses a number of interesting properties due to its semicrystalline nature. However, one major problem is the necessity of applying high temperature for processing sPS (above 290°C), as its melting point is approximately 270°C, and its degradation threshold is at 310-320°C A possible solution to the processing problem may be blending of the sPS with another polymer to lower the viscosity, and subsequently, the processing temperature. SPS, however, exhibits polymorphism like many other semicrystalline polymers. Due to its polymorphism it is necessary to investigate the crystallisation of sPS in sPS blends. Such an investigation is conducted in the present study for the system sPS/epoxy by means of x-ray scattering techniques. The results from WAXS revealed that the degree of crystallinity increases by decreasing the sPS content in the sPS/DGEBA blends. Investigations by means of SAXS revealed a trend of increasing the long period by decreasing the sPS content in the blends.

Keywords: blends, crystallisation, SAXS, syndiotactic polystyrene, WAXS

Introduction

Syndiotactic polystyrene (sPS) is a relatively new engineering thermoplastic that has been introduced by Ishihara et al. in 1986.[1] In contrast to the other two polystyrenes, the commonly used atactic one and the isotactic one, sPS crystallises very fast, at rates comparable to the ones for polyolefines.[2,3] Furthermore, sPS like many other semicrystalline polymers exhibits polymorphism and four distinct crystal forms have been reported until today. The first two crystal modifications are the α and β crystal forms and are the most common ones. In both these forms, sPS chains have an all-trans planar zigzag conformation.[4] The α crystal phase is the

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kinetically stable crystal form for sPS, i.e. it forms upon fast cooling of sPS from the melt, and possesses a hexagonal structure.[4] On the other hand, the β crystal phase is the thermodynamically stable crystal form of sPS, i.e it forms mostly under slow cooling and isothermal crystallisation conditions, and possesses an orthorhombic structure[4]. The other two crystal forms of sPS are the δ and γ phases, which are usually formed upon crystallisation of sPS from solution and are also termed as 'clathrate'[5,6]. Both the δ and γ phases posses a helical symmetry and crystallise in the monoclinic system.[5,6]

As may be expected the sPS has properties that are very different from the commonly used atactic PS, due to its high crystallinity. However, even though many of the sPS properties make it very attractive for use in certain applications (e.g. high chemical resistance, high stiffness, high heat deflection point), it is not totally free of problems. In particular, sPS due to its semicrystalline structure has a high melting point (≈275°C), which creates many problems in terms of processing as high temperatures need to be applied to lower the viscosity of the melt. The situation becomes more complicated by the fact that sPS being a styrenic polymer degrades very fast at temperatures above 300°C. One method to improve the processability of sPS is to blend it with another polymer. Very recently, our team has studied the system sPS/epoxy resin and a notable depression of the melting point of about 40-50°C was observed.[7] The present study focuses on a preliminary investigation of the sPS crystallinity in the presence of epoxy resin, conducted by means of wide angle x-ray scattering (WAXS) and small angle x-ray scattering (SAXS).

Experimental

Syndiotactic polystyrene (Questra QA 101™), supplied by Dow Chemical Co., of minimum 99% syndiotacicity (^{1}H and ^{13}C-NMR), with a number average polar mass of 94,100 g/mol, and weight average molar mass of 192,000 g/mol was used. The epoxy resin used was a diglycidylether of bisphenol-A (DER 330™), purchased by Dow Chemical Co., with n=0.15, and molecular weight of 383.1 g/mol. The aromatic diamine (MCDEA) used as a hardener was 4,4-methylenebis(3-chloro-2,6-diethylaniline) (Lonzacure M-CDEA™, 98%) was kindly supplied by Lonza Co., Germany.

The low content sPS blends (below 30wt% sPS) were prepared in test tubes in the following manner. sPS was added to the epoxy resin (DGEBA) at 290°C and stirring was employed for 10 min to ensure full dissolution. The DGEBA had been previously degassed in a vacuum oven. Subsequently, the sPS/DGEBA unreacted blend was mixed with MCDEA at 220°C and the ternary blend was left to cure at the same temperature. Five different concentration (sPS) blends were prepared (5, 8, 15, 20, 26 wt% sPS). The higher content sPS blend (64wt%) due to its high viscosity was prepared in a Clextral co-rotating twin screw extruder at temperatures between 240 and 290°C. sPS plates were prepared through injection moulding at 290°C and the moulded specimens were air-cooled to room temperature. Afterwards, thin slices (approximately 1mm) of the cured blends were cut and were used for the scattering experiments.

WAXS (wide angle x-ray scattering) experiments were performed on a four circle diffractometer (SIEMENS Kalsruhe, now BRUCKER AXS Kalsruhe) operated at 40 mV and 30 mA, with CuKα radiation (λ=1.542 Å). The primary x-ray beam was monochromatised by the use of a graphite crystal. The scattering range measured was: $2\theta = 1.5 \ldots 40.0°$ in transmission by area gas detection system HiStar / GADDS. The beam at the detector pin hole had a diameter of 0.5 mm (distance sample-to-detector 12 cm), and data were obtained at measuring times of Δt = 1800 s (accumulation). The SAXS experiments were performed on a three pinhole camera with CuKα radiation ((λ=1.542 Å) generated from a 18kW Rigaku rotating anode, operating at 40 mV and 100mA. The primary x-ray beam was monochromatised by the use of a multilayer focusing mirror. The sizes of the first and second pinholes were 0.9 and 0.1 mm, respectively, and the size of the guard pinhole before the sample was 0.6 mm. The scattered x-rays were collected by a two-dimensional position-sensitive gas detector HiStar/GADDS (20x20cm^2) with approximately 1-mm resolution. The sample to detector distance was 1.76m. The data were corrected for background and detector response and then azimuthally averaged to one dimensional form of intensity (I) vs. the scattering wavevector ($q=(4\pi/\lambda)\sin(\theta)$). All scattering measurements were performed at room temperature. All calculated degrees of crystallinity are normalised to the sPS content in the blends, and do not refer to the whole specimens.

Results and Discussion

In Figure 1 the WAXS patterns for pure sPS and four sPS/DGEBA blends are shown.

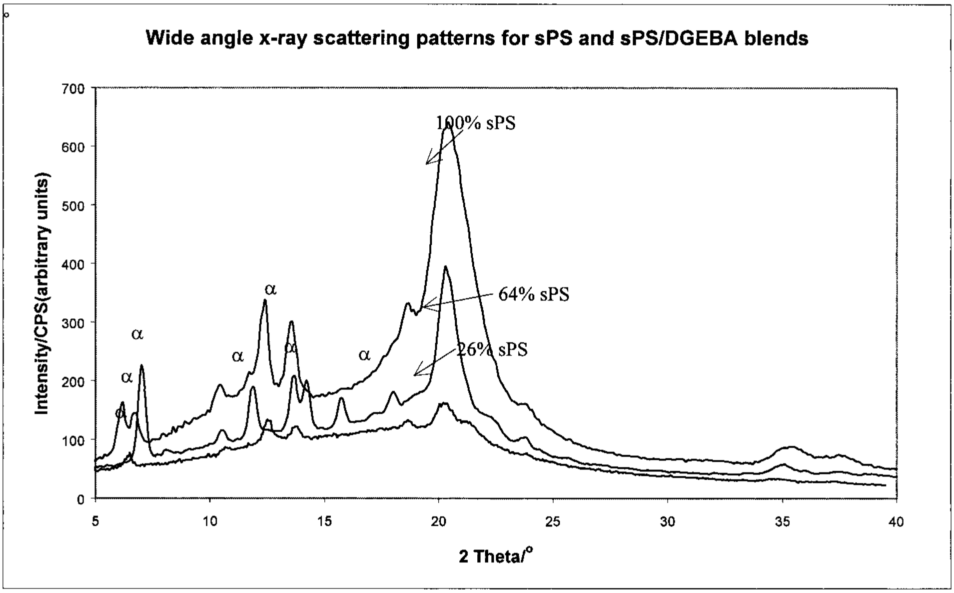

Figure 1. WAXS patterns for sPS and sPS/DGEBA blends.

From the WAXS pattern one can see that the low sPS blends (15, 20, 26wt% sPS) are mostly dominated by the β crystal form of sPS, which is the thermodynamically stable crystal form. Only for the 26wt% sPS blend one peak at 6.5° 2θ appears. On the other hand, the high sPS content blend (64wt% sPS) and the pure sPS exhibit a mixture of α and β crystal forms. It is recalled that the α crystal form is the kinetically stable crystal form of sPS. The difference of the crystal forms between the low sPS content and the high sPS content blends, as well as the pure sPS is probably due to the processing route, rather than the presence of the DGEBA resin. In fact, for the low sPS content blends, crystallisation took place at 220°C, while curing of DGEBA was carried out. Hence, the thermodynamically stable β crystal form was allowed to develop. On the other hand, sPS crystallised under air-cooling for the cases of the injection moulded 100% sPS and the 64wt% sPS/DGEBA blend. Under air cooling the kinetically stable α crystal form is more favoured to develop. The absence of the δ and γ crystal forms, which have been reported in the literature to form in gels of sPS with good solvents[8] indicates that the blend is fully phase separated after curing and little, if any, DGEBA may be found in the sPS rich areas of the blend. It should also be noted that for the 8wt% sPS blend (not shown in Figure 2) only two very weak peaks were located, and for the 5wt% sPS blend, no crystalline material was detected. For the 8wt% sPS blend it was possible to subtract the amorphous scattering (and also the incoherent scattering) from the crystalline scattering curves, but such an operation was not successful for the 5wt% sPS blend. It should similarly be noted that the width of the crystalline peaks does not significantly change fore different concentrations. It, thus, can be concluded that a nearly perfect phase separation occurs and that the DGEBA compound is mostly expelled from the crystalline sPS phase.

It is interesting to investigate the effect of the presence of DGEBA on the overall degree of crystallinity of sPS. In Figure 2 the overall degree of sPS crystallinty (x_c) is shown.

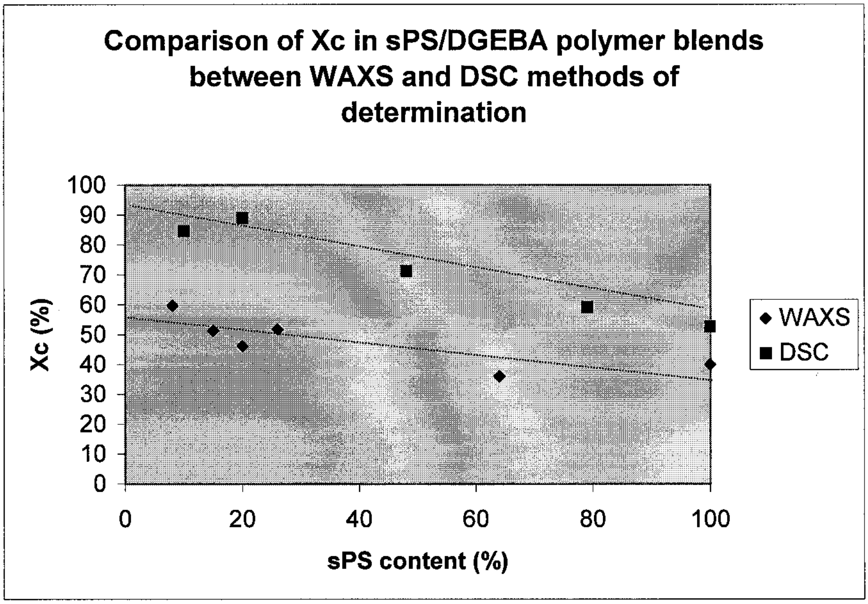

Figure 2. Comparison of x_c in sPS/DGEBA polymer blends between WAXS and DSC methods of determination.

The surprising result is that the degree of sPS crystallinity shows a trend of increasing with increasing the DGEBA content. This trend has also been found after examination of sPS/DGEBA blends by means of DSC as is also shown in Figure 2. At this stage it is rather difficult to explain, but one possible explanation may be that during phase separation the sPS chains are more extended at smaller concentrations, and the conditions are more favourable for a higher degree of crystallisation to develop. This is also supported by the increase in the long period, as is explained below, with decreasing concentrations. Another more trivial explanation might be just the different undercooling at different concentration, since the crystallisation of sPS start at 270°C and for the blends at 220°C only. Crystallinity and the long period are known to be dependent on crystallisation temperature. More research is currently ongoing in an attempt to shed more light on this interesting behaviour. It should also be noted at this point that the calculations concerning the degree of crystallinity were performed for the sPS part of the blend (i.e. the calculated x_c values are for the sPS only and not for the whole blend). The overall degree of crystallinity of the whole blend, is obviously reduced as the content of DGEBA increases.

The SAXS experiments have also revealed an interesting behaviour for the low content sPS blends. In Figure 3 the $\log(I^*q^2)$ vs. q is shown for the low sPS content blends. Note that the SAXS intensity profiles were corrected by the subtraction of the background intensity arising from the thermal density fluctuation (I_b) by the use of the Porod-Ruland model:[9]

$$I(q) = K\frac{e^{-\sigma^2 q^2}}{q^4} + I_b \qquad (1)$$

were K is the Porod constant and σ is related to the thickness of crystalline/amorphous interphases. The values of K, σ and I_b may be calculated by curve fitting the intensity at high q range.

As seen in Figure 4 for the 5 and 8wt% sPS content blends no long period was detected. However, for the other three blends, a broad peak is seen at q values between 0.3 and 0.5 nm^{-1}. These peaks are quite broad and denote the long period of the semicrystalline sPS. The long period can be calculated from Bragg's law as $L=2\pi/q^*$, were q^* is the peak position. In Table 1 the calculated values for the log period is given.

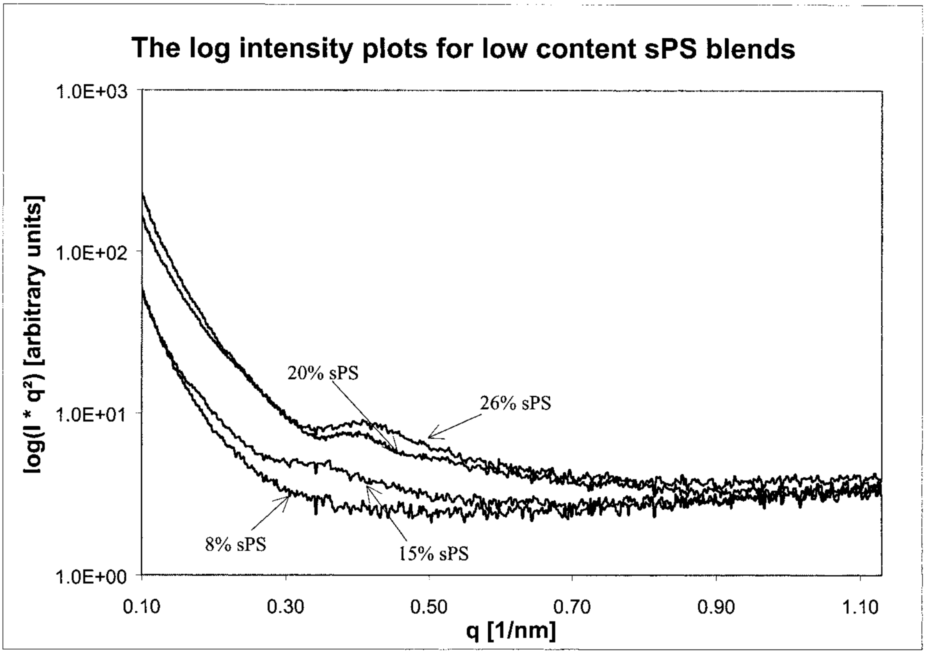

Figure 3. The logarithmic intensity plot for the low sPS content blends.

Table 1. Calculated values for the long period.

Grade of Material	Long period (L) (nm)
15 wt% sPS blend	17.6 ±1.1
20 wt% sPS blend	16.2 ±0.9
26 wt% sPS blend	14.9 ±0.8
100% sPS	15.2 ±0.9

It is interesting to note that that the long period appears to increase by decreasing the sPS content. This increase again may be due to an extended chain conformation of sPS at low concentrations as mentioned before. SAXS data, however, also indicate strong phase separation between sPS and DGEBA giving rise to crystallisation of sPS. SAXS experiments are also ongoing for the high sPS content blends. It should also be noted that for all the tested blends, extensive scattering at small q was found, which may be attributed to the phase separated sPS domains.

Conclusions

The investigation of sPS/DGEBA blends by means of WAXS revealed that the low sPS content blends are mostly dominated by the β crystal form of sPS, which is the most thermodynamically stable form. On the other hand, the high sPS content blend and the pure sPS were found to have both the β and α crystal forms. However, the non-existence of the α crystal form in the low sPS content blends is probably due to the processing route followed to prepare the samples, rather than to the presence of DGEBA. The occurrence of the largely unperturbed crystalline phase is, however, a strong indication that nearly perfect phase separation between sPS and DGEBA takes place. The calculation of the degree of crystallinity for the sPS domains, revealed that sPS becomes more crystalline with increasing of the DGEBA content. This result has also been found by the calculation of the degree of crystallinity for the blends by means of DSC. The examination of the low sPS content revealed that the long period is shifting to higher values by increasing the DGEBA content. The higher crystallinity and increase of the long period at small concentrations of sPS might be explained by two effects: the decreased undercooling due to the decrease of the crystallisation temperature and a possible change in chain conformation at different concentrations. The reasons for this shift of the long period to higher values is also at the moment unknown. More research is currently underway in an attempt to shed more light to the mechanisms of sPS crystallisation involved during phase separation. Synchrotron x-ray scattering experiments will be performed in the future to study the crystallisation of sPS during phase separation in real time.

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