



CHAPTER II

LITERATURE REVIEWS

2.1 Syndiotactic Polystyrene

N. Ishihara *et al.* [1] succeeded in obtaining a new polystyrene which has a syndiotactic structure and a high degree of crystallinity. They described the determination of the stereoregularity and some other properties of the newly obtained polystyrene. They polymerized the styrene with their novel catalyst system, containing a titanium compound and an organoaluminum compound, for 2 h at 50 °C, and 20.3 g of polymer was obtained. The crude product was extracted with methyl ethyl ketone (MEK) under reflux for 4 h. A total of 98 wt % of the polymer was insoluble in MEK and its weight-average molecular weight was 82000.

Hew-Der Wu, Shoei-Chin Wu, I-Der Wu, Feng-Chih Chang [4] have used Fourier transform infrared spectroscopy (FTIR) to studied the crystallization characterization of bulk syndiothactic polystyrene (SPS) sample. The WAXD is further used to identify the s-PS crystal formation to confirm the specific absorbance in FTIR spectra. Only the β -form is formed during melt-crystallization, while the both α and β -forms are presented during cold-crystallization. The formation rate of the α -form is significantly higher than that of the β -form because formation of α -form has a lower activation energy. In the cold-crystallization process, the α -form is formed initially because it is kinetically more favorable. Furthermore, the sum of the crystallinities of $\alpha + \beta$ is nearly constant (~ 0.5) during cold-crystallization after 5 min. This observation emphasizes that the β -form is produced from the form through phase transformation process during cold-crystallization, not directly generated from the amorphous phase. This FTIR method provides immediate and precise evidence of the crystallization behavior of the bulk SPS sample.

E. M. Woo, Y. S. Sun and M. L. Lee [5] have used differential scanning calorimetry (DSC) and X-ray diffraction characterize the dominating crystal form(s)

being developed in cold-crystallized syndiotactic polystyrene (SPS) in comparison with melt-crystallized polystyrene. The DSC results revealed that there are three (or fewer depending on the temperature of melt-crystallization) sharp melting peaks (Peak-1, -2, and -3) for the melt-crystallized s-PS samples, but only one peak (broad-based) for the cold-crystallized SPS (when scanned at 10°C/min). The X-ray result suggested that cold-crystallization at higher than 200°C (200, 250°C) produced only α -type crystal (or majority). This is in distinct contrast with melt-crystallization, which produced a combination of α -type (Peak-2 and Peak-3) and β -type (Peak-1) crystals at lower temperatures (240°C or lower), or majority of β -type if at temperatures higher than 260°C.

2.2 Polymer Blends

S. Cimmino, E. Di Pace, E. Martuscelli and C. Silvestre [6] have used differential scanning calorimetry (DSC) and optical microscope (OM) to investigate the crystallization from the melt, the morphology and the miscibility of syndiotactic polystyrene/poly(vinyl methyl ether) (SPS/PVME) blends and syndiotactic polystyrene/poly(2,6-dimethyl-1,4-diphenylene oxide) (SPS/PPO) blends. It was found that the kinetic parameters are strongly altered by the blending and by the crystallization conditions. In particular, the spherulite growth rate of SPS decrease if PPO is added, whereas it increase in the case of SPS/PVME blends. The half-time of crystallization is drastically increased by the presence of both PPO and PVME. The PVME segregated into spherical domains in the SPS intraspherulitic region, whereas there is no microscopic evidence that the PPO forms segregated domains. These results were correlated to the viscosity of the melt and the degree of miscibility of the blends. It was concluded that the SPS/PPO system is completely miscible in the amorphous phase, whereas PVME forms with SPS a two-phase separated system. This conclusion results in agreement with the presence of one T_g , composition-dependent, for the SPS/PPO blend, and of two T_g for the SPS/PVME blends.

C. Wang *et al.* [7] investigated the lamellar morphologies of melt-crystallized blends of syndiotactic polystyrene (sPS, weight-average molecular weight $M_w = 200$ k) and atactic polystyrene (aPS, $M_w = 100$ k) using small-angle X-ray scattering

(SAXS) and transmission electron microscopy (TEM). sPS/aPS blends with various compositions were prepared and crystallized isothermally at 250 °C prior to morphological studies. Due to the proximity in the densities of the crystal and amorphous phases, a weak SAXS reflection associated with lamellar microstructure was obtained at room temperature. In addition, strong diffuse scattering at low scattering vectors was evidently observed and its appearance may obscure the intensity maximum associated with the lamellar features, leading to the difficulties in determining the microstructure of the blends. To enhance the density contrast, SAXS intensities at an elevated temperature of 150 °C were measured as well to deduce the morphological results with better precision. Based on the Debye–Bueche theory, the intensities of the diffuse scattering were estimated and subtracted from the observed intensities to obtain the scattering contribution exclusively from the lamellar microstructure. Morphological parameters of the sPS/aPS blends were derived from the one-dimensional correlation function. On addition of aPS, no significant changes in the lamellar thickness have been found and the derived lamellar thicknesses are in good agreement with TEM measurements. Segregation of rejected aPS components during sPS crystallization was evidently observed from TEM images, which showed aPS pockets located between sPS lamellar stacks and distributed uniformly in the bulk samples, leading to the interfibrillar segregation.

T. K. Mandal and E. M. Woo [8] have used differential scanning calorimetry (DSC), optical microscopy (OM) and scanning electron microscopy (SEM) to investigate the state of miscibility and possible molecular aggregation in blends of semicrystalline syndiotactic polystyrene (SPS) with poly(vinyl methyl ether) (PVME). The results are then directly compared to the classical amorphous PS/PVME blend prepared using exactly the same solvent and procedures. Similar to the classical amorphous APS/PVME, the semicrystalline SPS/PVME exhibit the same scales of various molecular aggregations depending on composition leading to a so-called borderline miscibility, which is thoroughly discussed using the results of T_g -composition relationship and morphology evidence. The behavior of SPS/PVME agrees mostly with that of APS/PVME, indicating that tacticity or crystallinity in SPS does not affect the phase behavior of SPS/PVME in the amorphous domain.

F.-C. Chiu, M.-T. Li [9] have used Differential scanning calorimetry, polarized light microscopy and wide angle X-ray diffraction technique to examine the miscibility, crystallization kinetics, melting behavior and crystal structure of syndiotactic polystyrene (SPS)/poly(styrene-co- α -methyl styrene) blends. The single composition-dependent T_g s of the blends and the melting temperature (T_m) depression of SPS in the blends indicated the miscible characteristic of the blend system at all compositions. Furthermore, the T_g s of the blends could be predicted by either of the Gordon–Taylor equation (with $K = 0.99$) or the Fox equation with a slightly higher deviation. The dynamic and isothermal crystallization abilities of SPS were hindered with the incorporation of the miscible copolymer. Complex melting behavior was observed for melt-crystallized pure SPS and its blends as well. Nevertheless, the blends showed relatively simpler melting curves. Comparing with melt-crystallized samples, the cold-crystallized samples exhibited simpler melting behavior. The equilibrium melting temperature (T_m^0) of β form SPS crystal determined from the conventional extrapolative method is 295.2 °C. The Flory–Huggins interaction parameter, χ , of the blends was estimated to be -0.27. The crystal morphology of SPS was disturbed in the blends. Only underdeveloped granular-like crystalline superstructure of SPS exhibited in cold-crystallized blends. Moreover, the existence of the copolymer in the blends apparently reduced the possibility of forming the less stable form SPS crystals.

A. Siegmann, A. Dagan and S. Kenig [10] prepared the polymer blends of liquid crystalline aromatic copolyester (based on 6-hydroxy-2-naphthanoic acid (HNA) and *p*-hydroxybenzoic acid) and an amorphous polyamide (PA) by melted mixing method. The rheological behavior of the blends was very different from pure component and viscosity of blends significantly changed. Only 5 % by weight of LCP in the blend could reduce the viscosity 20-25 times. The tensile mechanical behavior of the blends was very similar to that of polymeric matrix. The blend of two-phase morphologies was found that be affected by the LCP compositions. The LCP phase changed gradually with increasing LCP content from ellipsoidal particles to rod-like and fibrillar structure

Fang-Chyou Chiu and Chi-Gong Peng [11] investigated aPs/sPs blends are miscible in the amorphous state regardless of the aPS molecular weight. APS with a lower molecular weight caused a decrease in the crystallization rate of sPS. The melting temperature of these blends was lower than those of the parent sPS, and they decreased as the molecular weight of aPS decreased. With the result of the WAXD, the existence of aPS in the blends with lower molecular weight reduced the possibility of forming the less stable α form in sPS crystals.

S. Stack *et al.* [12] used thermogravimetry and differential scanning calorimetry to investigate thermal degradation of blends of sPS and PPE. The three different molecular weight polystyrenes degraded in an identical manner, suggesting that initiation is by random chain scission. The onset of sPS degradation in the blend occurs at higher temperatures than in the pure polymer indicating stabilization of that component, whilst degradation of PPE in the blends is accelerated relative to the pure polymer. IR spectroscopy shows that PPE undergoes structural rearrangement in which the ether link is broken and chain continuity is re-established through the methyl group before any mass loss is apparent.

Seok-Ho Hwang *et al.* [13] investigated mechanical and thermal properties of syndiotactic polystyrene blends with poly(*p*-phenylene sulfide). The thermal and morphological properties show the immiscible binary blend evidences, which have a clear phase separation between the components at all compositions and a lack of adhesion at the interface. From XRD patterns of the blends, the crystalline structure of sPS in the blend is not altered from α form to β form. The result for tensile test, there is no synergism of the modulus of elasticity for sPS/PPs blend system.

2.3 Mechanical Properties

Halimatudahliana, H. Ismail, M. Nasir [14] investigated effect of various compatibilizers on the mechanical properties of polystyrene/polypropylene (PS/PP) blends. The tensile strength, elongation at break, Young's modulus and impact strength of binary and ternary blends were compared. The blends containing SEBS and EVA showed a positive effect on the ductility of the blend. In the presence of Surlyn the strength of the blend increased, whereas 4 ssa.ssh showed a negative effect.

A specimen size of 12*2 cm (length*width) was used for tensile tests (ASTM D 638). The machine was set at a crosshead speed of 50-mm/min and 70 mm gage length while temperature was 25 °C.

M. Kapnistos, A. Hinrichs, D. Vlassopoulos, S. H. Anastasiadis, A. Stammer, and B. A. Wolf [15] investigated the linear viscoelastic behavior of the lower critical solution temperature blend polystyrene/poly(vinyl methyl ether), PS/PVME, as a function of temperature and composition with small amplitude oscillatory shear rheology. At low temperatures, where the mixture is homogeneous, the dependence of the zero shear viscosity (η_0) on concentration is measured and is well described by means of a new mixing rule, based on surface fractions instead of volume fractions. Shift factors from time-temperature superposition (TTS) exhibit a Williams-Landel-Ferry (WLF) behavior. As the macrophase separation temperature is approached (the phase diagram being established by turbidity measurements), the blend exhibits a thermorheologically complex behavior. A failure of TTS is observed at low frequencies, both in the homogeneous pretransitional and in the two-phase regimes. Its origin is attributed to the enhanced concentration fluctuations, which exhibit a critical slowing down near the phase boundary in the homogeneous regime, and in the two-phase morphology inside the phase-separated regime. The anomalous pretransitional behavior can be quantified using a recent mean field theory, yielding the spinodal temperature. Furthermore, in the two-phase region an intermediate region of enhanced moduli at low frequencies is observed, followed by flow at even lower frequencies, which is attributed to the two-phase structure.