A novel preparation method of maleic anhydride grafted syndiotactic polystyrene and its blend performance with nylon6

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Summary

This work is intended to provide a method for the preparation of maleic anhydride grafted syndiotactic polystyrene (sPS-g-MA). In particular, a novel solid reaction method by a radical grafting approach is investigated. The grafting reaction is performed at a solid state, where the syndiotactic polystyrene (sPS) is swollen in solvent at relatively low temperature compared to the conventional melt modification method. The formation of sPS-g-MA is directly confirmed by Fourier transform infrared spectroscopy and by the morphology observation of sPS/polyamide-6 (Nylon6) blends, when sPS-g-MA is used as a reactive compatibilizer.

Introduction

Syndiotactic polystyrene (sPS) was first synthesized using homogeneous organometallic catalytic systems based on titanium compounds and methylaluminoxane [1]. Because of its low specific gravity, low dielectric constant, high modulus and excellent resistance to chemicals, the future of sPS is prospective for a large number of applications such as automotive, electronic and packaging industries. However, sPS suffers from poor compatibilization with most polymers, little adhesion to metals, insufficient impact resistance. Therefore, modification of sPS is necessary. Functionalization or grafting a polar group on the sPS backbone is

believed to be a good way to solve these problems and this is the subject of a number of studies [2-4].

Functionalization of atactic polystyrene (aPS) has been a subject of interest for a long time [5-14]. Xue et al. studied graft copolymerization of acrylonitrile onto polystyrene in methylcyclohexane solution using benzoyl peroxide as an initiator. They drew the conclusion that it is very difficult to graft acrylonitrile onto polystyrene by a radical process because the methine hydrogen may not be removed by the radical [15].

Maleic anhydride (MA) grafting onto a polyolefin backbone by a radical process has been the subject of extensive investigations [16~22] and it is also known as a good example of reactive extrusion widely used in commercial production. Grafting a polar radical or polar polymer onto the sPS backbone with a radical initiator using reactive extrusion can be considerable, though serious problems may arise. A much higher processing temperature (270ºC) than the boiling point of MA (200 ºC) makes it remove before the occurrence of reaction and degradation of sPS in the presence of a radical initiator are expected. As a matter of fact, the later is what occurs in the modification of polyolenfins with MA.

In this study, we present a novel solid method to graft MA onto sPS. Basically, the grafting of MA occurs in the solid state of sPS, which is swollen in toluene. Diffusion of MA and initiator into the swollen sPS and the grafting reaction between MA and sPS take place simultaneously. Due to the low temperature compared to the conventional melt grafting method, our novel solid grafting method overcomes the drawbacks mentioned previously.

Experiments

Materials

Triisobutylaluminium (TIBA) and methyl aluminoxane (MAO) were supplied from Akzo nobel company. Metalocene catalyst (Pentamethylcyclopentadienyltitanium trichloride: Cp^*TiCl_3), maleic anhydride (MA), Azobisisobutyronitrile (AIBN) and dicumylperoxide (DCP) were purchased from Aldrich Chemicals. Nylon6 was supplied from Kolon chemicals (trade name: KN171).

Polymerization of sPS

Syndiotactic polystyrene (Mw: 612,800 g / mol; syndiotactic index checked by NMR: 99.5 %) was prepared in a 1 liter glass reactor equipped with a temperature controller, a mechanical agitator and a rubber septum through which the monomer and catalyst are fed. The reactor was first degasssed and filled up with N_2 gas to replace the air. Subsequently, purified styrene monomer (Samsung General Chemicals) of 200 cc, TIBA of 36 mmol in toluene and MAO of 4.5 mmol in toluene were introduced into the reactor at 70ºC. After the reactor was agitated for

30 minutes, metalocene catalyst (Cp*TiCl₃) of 45 μmol in toluene was injected into the reactor to start the polymerization. During the polymerization step, the reactor was agitated with a specially designed mechanical agitator, which can prevent agglermoration or the formation of lumps of sPS powder, at 400 rpm for 2 hours. The resulting polymer was washed several times with acetone and methanol, respectively, and then vacuum-dried at 80ºC for 6 hours.

Grafting of sPS

Maleation was carried out at 70ºC and 100 ºC for 8 hours in a 2 liter glass reactor equipped with a mechanical agitator. sPS powder of 1kg was introduced into the glass reactor and then purged by nitrogen gas for a few hours. Toluene was poured into the reactor until the sPS powder was completely soaked with toluene. Toluene was used to swell the sPS so that the diffusion of initiator and MA into the sPS solid particle is enhanced. A radical initiator (DCP or AIBN) was then fed to the reactor and the temperature was maintained at 70ºC. The mixture was stirred by the mechanical agitator at 80rpm for one hour. The reactor temperature was elevated to assigned temperature (70ºC or 100ºC) and then MA was added into the reactor and stirred for 8 hours at high speed (about 400 rpm). The products were obtained in this way and were washed twice by methanol and acetone, respectively. Filtration was applied at each washing step. Finally methylethylketone (MEK) was used to extract the remaining MA for several hours. The final product powders were dried at 80ºC for 5 hours.

FTIR analysis

The presence and amount of MA grafted onto sPS was assessed using a Fourier transform infrared spectrometer (FTIR; a Bruker IFS66 Model) at a resolution of $4 cm^{-1}$. Unreacted MA in sPS-g-MA for FTIR analysis was further extracted by MEK in a soxhlet apparatus for 24 hours. sPS and sPS-g-MA samples were compression-molded at 290ºC to obtain thin films of about 15 μm thickness. A series of standard solution containing different ration of atactic polystyrene(aPS) and poly(styrene-*co*-maleic anhydride) (SMA, Melt Index 1.7 g / 10 min (230 ºC / 2.16 Kg), 7wt.% MA content) were prepared by dissolving 200 mg of these materials in 1 mL of THF. By evaporating THF, the standard thin films of SMA and aPS mixture were obtained. A calibration curve was formed to determine the degree of grafting contents of MA in a mixture by plotting the ratio of the peak intensity between a C=O double bond (1780cm-1) of the MA unit and a tertiary carbon (1600cm-1) of styrene unit with known MA concentration in SMA and aPS mixture. In each known MA concentration, we repeated FTIR analysis in five times and average values were shown in Fig. 1.
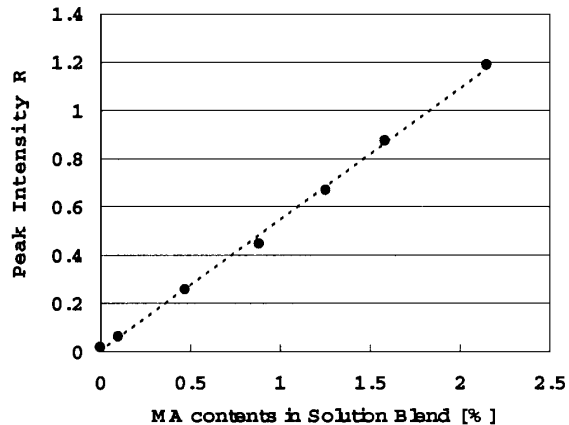
Figure 1. MA contents calibration master curve in SMA / aPS solution blend

Blend preparation

Nylon6, sPS and sPS-g-MA were dried for 24 hr at 80ºC before melt blending. The polymers were melt-mixed for 6 minutes in an internal batch mixer (HAAKE Rheomix 90 mixer with a capacity of 60cc/batch) operated at a rotor speed of 50 rpm and a temperature of 280ºC.

Evaluation of microstructures and mechanical properties in blend samples

Morphology of the blends was observed in a scanning electron microscopy (SEM; Jeol Model 840A). Blended samples were compression-molded into sheets at 30 ton/cm^2 and 280ºC. These molded samples were fractured in liquid nitrogen. The surfaces were coated with a thin film of gold by sputtering method. Izod impact strength of the blend was measured on a Toyoseiki impact tester. Samples were compression-molded into sheets at 280ºC and then cut into pieces of dimension 63 x 13 x 3 mm.

Result and Discussion

Characterization of sPS-g-MA

The maleic anhydride grafted onto a polymer is easily detectable in the infrared. FTIR spectra of sPS and sPS-g-MA are shown in Fig. 2. In the spectrum for sPS-g-MA, new absorption band at 1780 cm^{-1} appears. However, those bands are not observed in the spectrum of sPS. These characteristic bands are assigned to a C=O

double bond stretching of MA group grafted onto sPS main chain. This FTIR spectrum is a clear evidence for the grafting reaction because the remaining MA was removed from the sPS-g-MA.
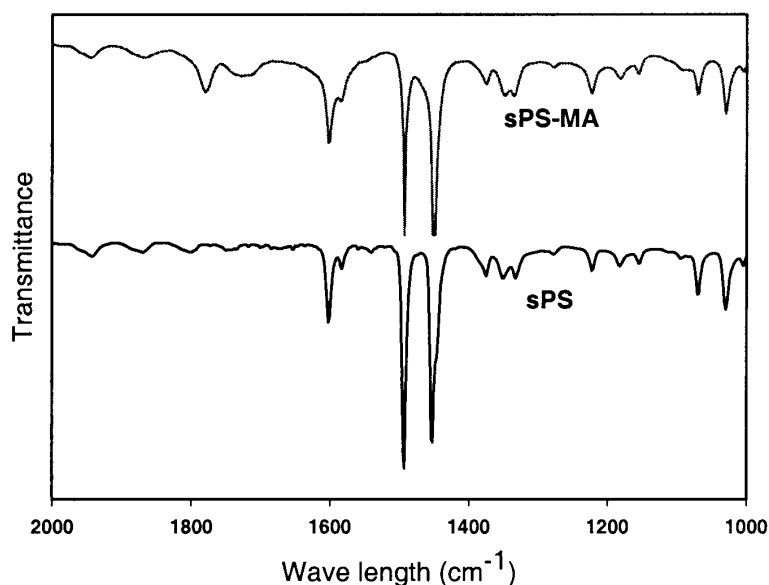

Figure 2. FT-IR spectrums of sPS and sPS-g-MA

In order to find out the amount of MA grafted onto sPS in quick analysis for understanding a trendy experiments, we can get the corresponding value of MA content from a calibration curve (Fig. 1). That is the ratio value between the peak intensity of the maleic anhydride and that of tertiary carbon in SMA and aPS mixture. In the solid line calculated by least square method in Figure 1, all of the ratio value from FTIR analysis is matched to arbitrary MA content. The expected MA contents from our various conditions in sPS-g-MA are obtained is summarized in Table 1.

Table 1. The MA content in the sPS-g-MA prepared at various conditions.

SPS (g	MA (g	DCP (g	AIBN (g	Temperature (	Grafted MA conter (wt.%)
1000	500	30	0	70	1.09
1000	500	30	0	100	1.47
1000	500	0	30	70	0.13
1000	500	0	30	100	0.20

We find that DCP is more efficient as an initiator in the graft reaction of MA onto sPS. The reaction temperature of 100°C produces more amount of the MA grafting. The graft reaction is carried out in the solid state of sPS which is swollen by toluene

at an elevated temperature. The initiator and MA should be diffused into the sPS particle prior to graft reaction. It is most likely that a higher temperature leads to faster diffusion and reaction rate. Consequently, the amount of the MA grafted is expected to be larger at higher reaction temperature. However, it is also possible that the swollen sPS particle becomes more liquid like and aggregates each other at higher temperature. In that case, the surface area of swollen sPS powder aggregates is reduced and the total solid grafting reaction efficiency is decreased. Therefore, optimization control for production conditions is needed and detailed study on the effect of reaction condition including a reaction temperature, concentration of the initiator and the size of sPS particle will be explored in our further scheme.

Morphology and impact property of sPS / sPS-g-MA / Nylon6 blends

The presence of MA in sPS-g-MA can be confirmed when it is used as a reactive compatibilizer in sPS/Nylon6 blends followed by morphology observation. Figure 3 shows the SEM images of the sPS/Nylon6 blends compatibilized with various amounts of sPS-g-MA as a reactive compatibilizer. The blend without sPS-g-MA shows highly incompatible nature as expected (Fig. 3a). The large and non-uniformly distributed Nylon6 domains are clearly seen. The smooth and clear surface of the Nylon6 domains indicates poor interfacial adhesion between two phases. With the addition of sPS-g-MA of 3 wt.%, the size of Nylon6 domain is significantly reduced (Fig. 3b), and the domain size decreases with the further addition of the sPS-g-MA (Fig. 3c and d).

The remarkable reduction of domain size in the compatibilized blends is attributed to the compatibilization effect of the sPS/Nylon6 copolymer formed by a reaction between maleic anhydrides in sPS-g-MA and amine groups in Nylon6 during the mixing process.

Figure 4 shows izod impact strengths versus the amount of sPS-g-MA in the blends. Izod impact strength of the blend increases with amount of sPS-g-MA. Since Nylon6 has better toughness than sPS, the Nylon6 domains can absorb more impact energy than sPS. Therefore, compatibilized sPS/Nylon6 should have better impact strength than sPS.
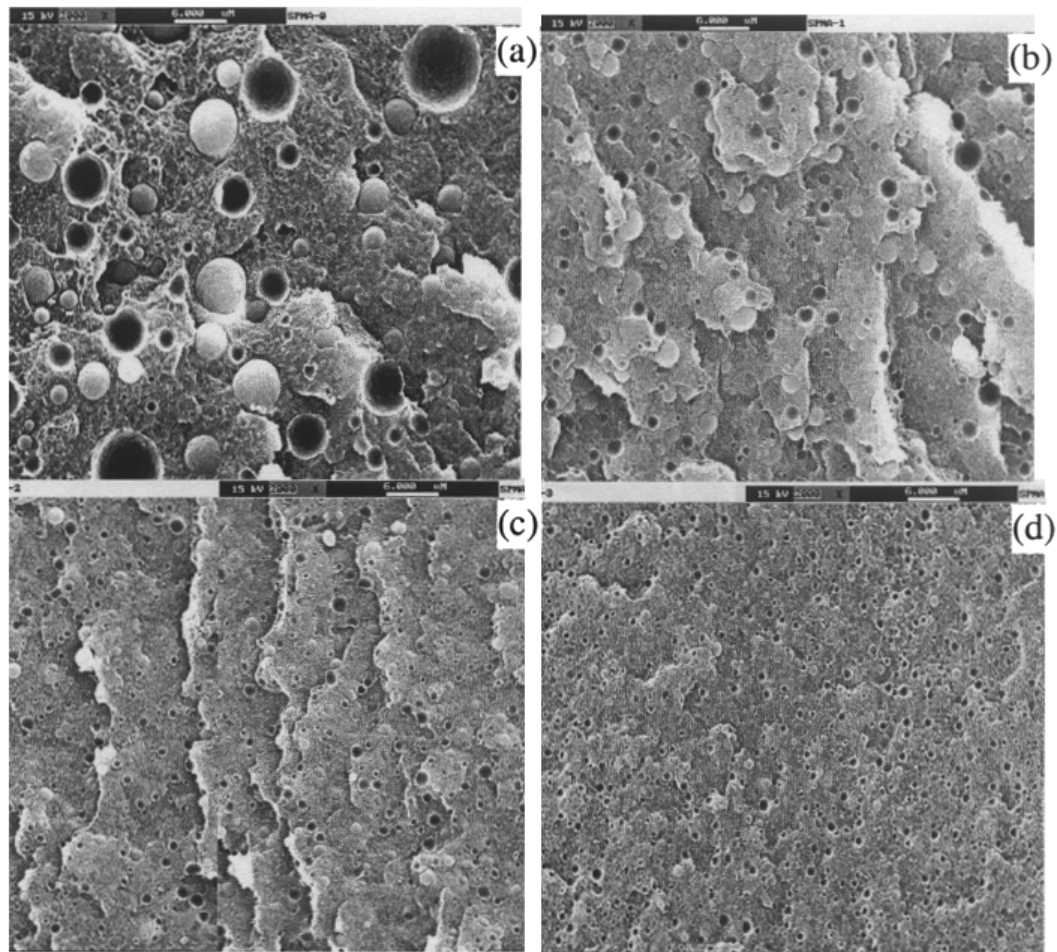
Figure 3. SEM photograph of sPS / sPS-g-MA / Nylon6 blend systems (wt %): (a) sPS / Nylon6 (80/20); sPS / sPS-g-MA / Nylon6 (77/3/20); (c) sPS / sPS-g-MA / Nylon6 (75/5/20); (d) sPS / sPS-g-MA / Nylon6 (70/10/20).

The sPS/Nylon6 without compatibilizer shows very low impact strength due to the weak adhesion between two phases. The increase of izod impact strength with the addition of sPS-g-MA is attributed to the improved adhesion between two phases and increased number of even size domains. In the blend containing the sPS-g-MA of 10 wt%, an uniform domain size seems to be obtained and consequently the blend has maximum impact strength.

Occurrence of the reaction may also be detected rheologically, for example, by measurement of mixing torque during blending. Torque values of the blends when they are melt-mixed in a batch mixer are shown in Fig. 5. With the addition of 10 weight % sPS-g-MA to the blends, the steady-state average torque value between 3 minutes and 7 minutes increases to 90 Nm from 66 Nm of sPS / Nylon6 (80/20).

The formation of in-situ high molecular weight sPS / Nylon6 copolymer can be responsible for the increased torque value of the reactive compatibilized blends.
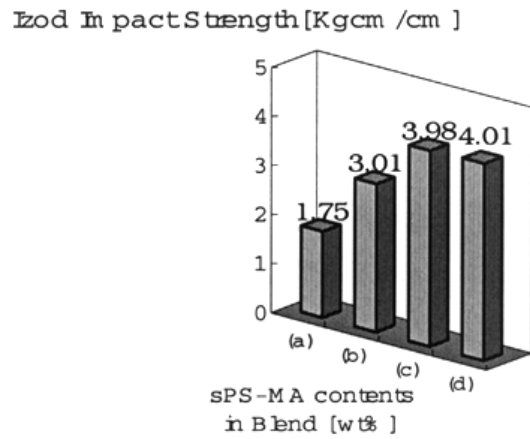

Figure 4. Izod Impact Strength of sPS / sPS-g-MA / Nylon6 blend system (Wt %): (a) sPS / nylon6 (80/20); (b) sPS / sPS-g-MA / Nylon6 (77/3/20); (c) sPS / sPS-g-MA / Nylon6 (75/5/20); (d) sPS / sPS-g-MA / Nylon6 (70/10/20).
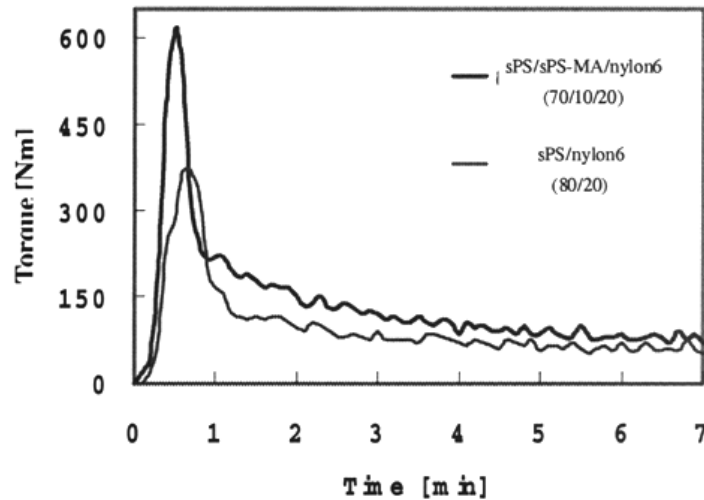

Figure 5. HAAKE mixer torque intensity profile with processing time (a) sPS/sPS-g-MA/Nylon6(70/10/20) (b) sPS/Nylon6(80/20)

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