Melting behavior of PET with sulfonated polypropylene wax

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Abstract. The effects of sulfonate group and composition of sulfonateionomer (SPSN) with low molecular mass on the morphologies, non-isothermal crystallization and melting behaviors of poly(ethylene terephthalate) (PET) in PET/SPSN blends are investigated by thermogravimetric analysis (TG). Sulfonateionomer (SPSN) is synthesized from polypropylene wax by two steps, and at 300°C the mass loss of SPSN is only 1wt % with a good thermal stability. The result shows that sulfonateionomer could be an effective nucleating agent.

1. Introduction
There is a special class of polymers with a relatively small concentration of ionic groups (i.e. carboxylate, phosphate or sulfonate) in the hydrophobic backbone chains [1,2]. Such materials are classified as ionomers, and exhibit an original microstructure made of ionic aggregates (ionic multiplets, also called ionic clusters), which act as effective physical cross-links through both intramolecular and intermolecular interactions. Ionic groups of ionomers have a strong effect on their mechanical and physical properties such as glass transition temperature, and melt viscosity by interactions include hydrogen bonding, ion-dipole interactions, acid-base interactions, or transition metal complexation [3-7].

Indeed, ionomers are known to be used in a variety of applications, including thermal stabilizers [8], compatibilizing agents [9-11], and specially nucleating agent [12]. Poly (ethylene terephthalate) (PET) has been widely used as engineering plastics with excellent thermal and mechanical properties [13]. However, because of its slow rate of crystallization, its applications in engineering material are limited. Ionomers have been commercially recognized as the most effective nucleating agents for PET. In most ionomers micro-phase-separated aggregates rich in the ionic species form due to the strong attractive interactions that occur between the ionic monomer units. The ionic clusters of the polymer chains can act as nucleating sites to initiate heterogeneous nucleation and accelerate the crystallization rate of polymers. A note by Kalfoglou examined the compatibility behaviour of mixtures of poly(ethylene terephthalate) with the sodium ionomer of poly(ethylene-co-methacrylic acid), showed that the presence of the ionomer enhanced PET crystallinity acting as a nucleating agent for PET [11]. Surlyn was a metal salt of a copolymer of ethylene and methacrylic acid produced by DuPont, and an effective nucleating agent for accelerating the crystallization of PET as it promoted both nucleation and molecular motion [14]. AClyn(ethylene–sodium acrylate) has a similar composition to Surlyn, however, it has been found to display different nucleation mechanisms for both PET/AClyn and PET/Surlyn samples [15], and have been commercially recognized as the most effective nucleating agents for PET. Tang et al. reported that the styrene–sodium acrylate ionomers also enhance the crystallization rate of PET with heterogeneous nucleation, and the structure of ionomer affected the
crystallization behaviors of PET/ionomer, whereas other workers have found that the styrene–sodium acrylate ionomers (SAA–Na) induced the formation of PET nuclei like AClyn in the PET/ionomer \[^{16}\].

Generally speaking, the more polarizable sulfonate species have stronger aggregation comparisons of the degree of aggregation of carboxylate and sulfonate ionomers. Exploitation of these stronger interactions has been formally reported including thermoplastic elastomer, stable foams and solution properties \[^{17}\]. In this paper, we considered modification of PPw by grafting styrene as a precursor (PPS) through radical polymerization. Subsequently sulfonation of the grafted polystyrene chains was used to produce PPw with sulfonic acid groups (SPPS). The sulfonate ionomers (SPSN) was obtained by 100% neutralization of SPPS. Structural effects of sulfonate ionomers on the morphology, crystallization and melting behaviors of PET/ionomers were investigated.

2. Experimental

2.1. Materials

Poly (ethylene terephthalate) with intrinsic viscosity of 0.67 dLg\(^{-1}\) in phenol/tetrachloroethane mixture (1:1 by mass, 30°C) was kindly supplied by Hainan Shengzhiye Hi-Tech Company Limited, China. Polypropylene wax was obtained from Guangzhou Long stone Import & Export Trade Company Limited. The series of sulfonate ionomers with different graftions of styrene and different sulfonation were synthesized using a two-step reaction method according to the route as following, and benzoyl peroxide (BPO) was used as the initiator.

2.2. Graft copolymerization

Dried, and weighed PP wax was dissolved in known volume of toluene (50 mL) in a flask placed in the oil bath maintained at constant temperature (80-90°C) with a continuous flow of nitrogen over the period of reaction. To this added a definite amount of the styrene dissolved in toluene and the initiator (BPO, 0.200–3.000 g) under constant stirring. After the stipulated time period, the flask was removed from the oil bath and the contents filtered. The residue was washed with alcohol to remove unreacted BPO and was extracted with ethyl acetate for 48 h by Soxhlet extraction to remove polystyrene. The left over product was dried at till constant mass and PPS was obtained.

2.3. Sulfonation of copolymer

Sulfonate copolymer (SPPS) were prepared from PPw grafted styrene (PPS) in 1,2-dichloroethane at 50°C using acetyl sulfate as the sulfonating reagent. The sodium salts (SPPN) were prepared by titrating the resulting SPPS with excess sodium hydroxide.\[^{18}\]

2.4. Blend preparation

Blends of PET and SPSN were prepared by melt mixing in a Mixer at 280 °C for 5 min to achieve equilibrium. Before use, PET was dried at 120°C for 8 h and SPSN was dried at 65 °C for 8 h under vacuum. The content of SPSN was varied from 0.5 to 4.0 wt%. For comparison, the neat PET was also subjected to the same procedure. Corresponding to the type and content of ionomer, samples were named as neat PET and S series, as shown in Table 1.

| Ionomer | St/PPw \(^a\) (mol/mol) | Sulfonation \(^b\) (SO\(_3\)×10\(^{-3}\)mol/g) | Mn(×10\(^3\)) | Mw(×10\(^3\)) | PDI | T\(_d\) (°C) |
|---------|-----------------|-----------------|-----------------|-----------------|-----|-----------------|
| SPSN1   | 3:10            | 0.32            | 7.3             | 9.9             | 1.4 | 444             |
| SPSN2   | 5:10            | 0.34            | 8.3             | 21.9            | 2.6 | 454             |
| SPSN3   | 5:10            | 0.46            | 8.1             | 20.2            | 2.5 | 452             |
| SPSN4   | 5:10            | 0.82            | 8.1             | 20.3            | 2.5 | 454             |

\(^a\) raw ratio of styrene and PPw.  
\(^b\) sulfonic group concentration calculated by chemical titration.  
T\(_d\). maximum thermal decomposition temperature.
3. Characterization
FTIR measurements are carried out on a BRUKER TENSOR27 Fourier transform infrared (FT-IR) spectrometer to determine the copolymer composition. All samples were prepared by mixing the polymer with dry KBr and analyzed with 32 scans with 2 cm^{-1} resolution.

Thermogravimetric analysis (TG) experiments were conducted on a Netzsch TG209F3 thermogravimeter at a heating rate of 10°C min^{-1} under a nitrogen flow rate of 40 mL min^{-1} from 50–600°C.

4. Results and Discussion
The chemical analysis of the modified PP wax was carried out by FTIR spectroscopy. A series of spectra of samples is shown in Figure 1.

![Figure 1. FT-IR spectroscopy of PP wax and their derivatives](attachment:figure1.png)

Apart from the peaks for PP wax, the new characteristic peak in the IR spectra of grafted PP wax (PPS1) appears between 1601 cm^{-1} and 1453 cm^{-1} corresponding to the aromatic rings, and significant band at 688 cm^{-1} for C-H bending vibration of benzene ring. Upon sulfonation, the IR spectrum changes significantly and shows new strong bands peaks at 1220 cm^{-1} due to S=O (asymmetric stretching), 1043 cm^{-1} due to S=O (symmetric stretching), 630 cm^{-1} due to S—O (stretching), which are absent in the spectrum of the unsulfonate PPS. Moreover, these vibrational bands at 1125–1250 cm^{-1} become wider by titrating the sulfonate copolymer (SPPS) with excess sodium hydroxide. However, a new band attributed to the symmetric stretching vibration of the sulfonic acid group appears as a distinct shoulder at 1175 cm^{-1} due to the low concentrations (<10 mol%) of sulfonic acid groups in these ionomers. As reported in the literature [19], this shoulder band became more prominent with an increase in the degree of sulfonation.

![Figure 2. Thermal gravimetric analysis thermogram of PP wax and their derivatives](attachment:figure2.png)
The thermal gravimetric analysis (TG) thermograms of PP wax derivatives are presented in Figure 2 respectively. It is observed from the TG curves that decomposition of PP grafted styrene (PPS) takes in single stage and at a fast rate with maximum thermal decomposition temperature \( T_d \) at 415 °C. However, the \( T_d \) of sulfonate copolymer (SPPS) is 460 °C, while that of ionomer SPSN is smaller, but higher than that of PPS with two decomposition peak \( (T_{d1} = 417 °C, \ T_{d2} = 444 °C) \). It meant that ionomer SPSN has part crosslinking. Moreover, the loss of SPSN at 300°C is only 1wt% with a good thermal stability.

5. Conclusions
PET composites with low molecular mass sulfonated ionomers (SPSN) from polypropylene wax are prepared by melting mixing. However, as the composition of styrene graft or sulfonation was increased, the crystallization rate of PET was slightly decreased. Probably it is the result that the higher viscosity and decrease in molecular mobility with benzene ring or the sulfonate group, which hinders the crystallization.

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