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SHORT COMMUNICATION

S.-P. Rwei
F.-H. Ku

The dispersion of pigment slurries via incorporation with water-soluble sulfonate poly(ethylene terephthalate)

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S.-P. Rwei (✉) · F.-H. Ku
Institute of Organic and Polymeric
Materials, National Taipei University
of Technology, Taipei, Taiwan
e-mail: f10714@ntut.edu.tw
Tel.: +886-2-27712171 ext. 2432
Fax: +886-2-27317174

Abstract A water-soluble sulfonate poly(ethylene terephthalate) copolymer has been synthesized and identified as a high-temperature endurable surfactant. The glass-transition temperature and the storage modulus increase in correlation to the increase in sulfonate content. Various characterization studies were performed, including light scattering, zeta-potential measurement and a sedimentation test. The results suggest that at equal numbers of sulfonate units in a solution, a low concentration of a dispersant of high sulfonate content is more effective than a high concentration of a dispersant of low sulfonate content.

Key words Water-soluble poly(ethylene terephthalate) · Sulfonate content · Thermoplastic dispersant · Thermal degradation · Dispersion stability

Introduction

Water-soluble polymers have many industrial applications, including detergents, textile finishing, oil production and mineral processing [1]. The most common usage is in the coating industry [2], where they serve as stabilizers for colloidal dispersions. The water-soluble polymer functions as a surfactant to decrease the interfacial tensions as well as to stabilize the particles against reagglomeration. Notably, the polymers in the previously mentioned applications have relatively low molecular weights. The polymer typically possesses a maximum weight not exceeding 3000, with a constant degradation temperature of less than 200 °C. Many new applications relate to coating, where the surfactant-treated slurries are dried first and are then subjected to further high-temperature processes. These include melt extrusion or thermal fusion, and they require a dispersant with high molecular weight (normally exceeding 10,000) to endure severe thermal conditions. Applications using these polymers include pigment compounding, toner processes and high-temperature painting. The water-soluble polymer wrapped around the particle surface works as a dispersion stabilizer and as a lubricant for compounded additives in a molten matrix. To date, this field has received limited attention by academics, with the majority of results being published in patents [3–5].

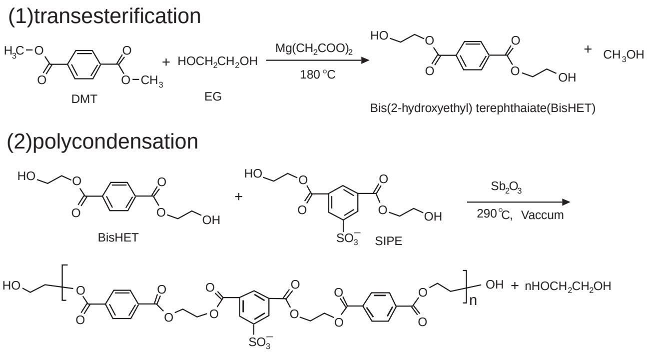
Recently, to further explore this field there have been attempts to discover novel polymers. Unfortunately, most water-soluble polymers are derived from natural sources and are easily degraded or cross-linked at high temperature. Synthesizing both a thermoplastic and a water-soluble polymer was therefore the preferable approach. One of the most promising candidates is the water-soluble polyester. A review of the literature concerning the modifications of polyester for improved water-solubility reveals three categories: sulfonate polyester [6–9], phosphorus polyesters [10, 11], carboxyl-functional polyester [12]. The specific alkyl or phenyl monomers combined with sulfonate, phosphorus or pendant carboxylic groups react with the diol and diacid monomers to form copolymers. The sulfonate, phosphorus or carboxylic groups function not only as hydrophilic elements that dissolve in water, but also as a source of repulsive charge for stabilizing the particle dispersion.

For the purpose of this study, water-soluble poly(ethylene terephthalate) (PET) was synthesized by adding sulfonate groups to a polymerization process. The polymer dissolved in water and blended with 10% by weight of pigments. Subsequently, tests for polymer identification, thermal analysis and slurry stability characterizations were conducted.

Experimental

Materials

It is well known that a commercial grade of cationic dyeable polyester for spinning fiber is one type of sulfonate PET, which is polymerized by one-step polycondensation of terephthalic acid (TPA), ethylene glycol (EG) and a small amount (approximately 3% by weight) of 5-sulfoisophthalic acid (SIP). If the weight percent of SIP is increased to 10%, the PET can be dissolved in water. This reaction, however, yields high levels of undesired diethylene glycol (DEG) or triethylene glycol (TEG) compounds grafted in the main chain. The DEG or TEG may suppress the degree of polymerization and seriously reduce both the glass-transition temperature, T_g, and thermal endurability of the copolymer. In this work, applying a two-step polymerization process with dimethyl terephthalate (DMT) and EG as well as replacing SIP with diethanol 5-sulfoisophthalate (SIPE) resolved this difficulty. Detailed reactions can be represented as follows.



Phthalocyanine green (Phth. Green) was the pigment selected for this study. Since Phth. Green is very difficult to disperse in water or in a polymeric matrix, an attempt was made to enwrap its surface with a synthesized polymer to stabilize the dispersion. Ten percent by weight of Phth. Green (BASF K-9360) was dispersed in solutions containing various concentrations of water-soluble PET. A glass-bead tumbler then milled the slurries for 3 days before further carrying out light scattering tests.

Methods

After polymerization, polymer characterization employing various analytical tools was conducted. The sulfonate group was identified from the IR spectrum by employing the "Spectrum gx FTIR" from Perkin-Elmer. The molecular weight was measured in a gel permeation chromatography (GPC) setup from Waters. Chloroform/*m*-cresol (3/1) was employed as a solvent for the injection of the sample. The T_g, was determined by employing a differential scanning calorimeter (DSC) (Perkin-Elmer DSC 7). The scanning temperature ranged from 25 to 280 °C at a heating rate of 10 °C/min. A thermogravimetric analyzer (TGA) from TA Instrument (TGA 51) was used to detect the thermal degradation. Rheological measurements of the polymer melt were performed in a parallel disk with na SR-5 Rheometer from Rheometric Scientific.

The particle size analysis for the Phth. Green slurry was performed in a Zeta Plus quasielastic light scattering instrument from Brookhaven Instrument Company (BIC). The Zeta Plus was used to measure the scattered light as a function of time at an angle of 90°. The device was fitted with a focused helium–neon laser beam with a wavelength of 670 nm. The mean particle size was calculated through the autocorrelation function of the scattered light using particle size software from BIC. The same instrument was also used to measure the zeta potential of the particle's surface. To initiate the mobility of the charged particle an additional electrode was inserted into the slurry. The scattering angle of the probe for detecting particle movement was approximately 15°. After the moving velocity had been measured, the calculation of the zeta potential of the charged particle was conducted using BIC zeta potential software, based on Smoluchowski's equation. In addition, a conventional settlement experiment [13] was conducted to confirm the dispersion quality of Path. Green.

Results and discussion

Characterization of sulfonate PET

Water-soluble PET containing different amounts of SIPE was prepared based on the polycondensation reaction expressed in Eq. (1). Various tools were then employed to characterize the synthesized samples. IR spectra of the samples are displayed in Fig. 1. The peak of approximately 753 $\mathrm{cm^{-1}}$ represents the ring-bending

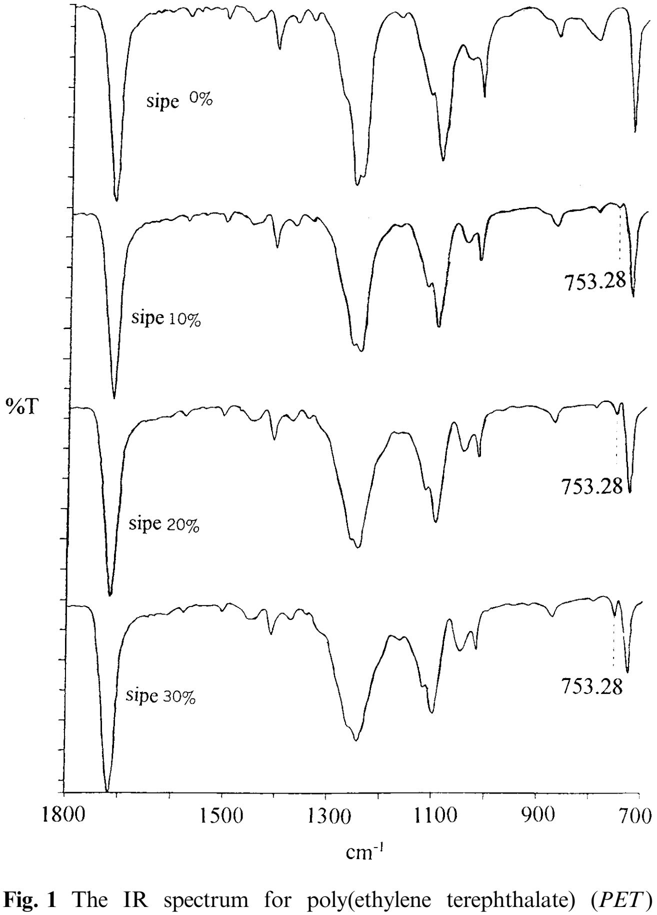


Fig. 1 The IR spectrum for poly(ethylene terephthalate) (*PET*) containing various weight percents of diethanol 5-sulfoisophthalate (*SIPE*)

mode of trisubstituted benzene [14]. This peak identifies the existence of SIPE in the PET copolymer's backbone. Figure 1 reveals that the peak intensity is qualitatively proportional to the SIPE content, but is not sufficient for further quantitative analysis. The average molar mass was determined by GPC and is tabulated in Table 1. The molar mass appears to be controlled at approximately 15000 g/mol.

The weight loss by thermal degradation from the TGA measurement and the T_g observation from the DSC measurement are displayed in Figs. 2 and 3 respectively. Figure 2 demonstrates that a water-soluble PET with high sulfonate content leads to higher thermal degradation. However, a small amount of weight loss (about 6%) was detected for a PET with 30% of SIPE after 2 h in a cell at 300 °C. In an actual compounding process whose residence time is usually shorter than 20 min, the weight loss is insignificant and can therefore be neglected. This result confirms that the water-soluble PET synthesized in this work is able to endure temperatures between 200 and 300 °C. Figure 3 illustrates the DSC thermograms of PET copolymers. No melting temperature is detected should the sulfonate content exceed 10%. The result indicates that the sulfonate benzene in the backbone serves as a hindrance effect to suppress the polymer's crystallization. The high-sulfonate PET is a completely amorphous rather than a semicrystalline polymer. The hindrance effect can also be adopted to explain the reasons why the T_g value increased as the sulfonate content increased. In general, for a system with a bulky side-chain polymer compared to the original, e.g. polystyrene versus polyethylene or polypropylene versus polyethylene, the hindrance effect caused by the bulky side chain will lead to a higher T_g. Figure 3 indicates that the hindrance effect caused by the segment of sulfonate benzene will slow down the chain movement and it results in a higher T_g value.

Table 1 Weight-average molecular weight (M_w) by gel permeation chromatography measurement for different contents of diethanol 5-sulfoisophthalate (SIPE)

SIPE content (%)	M_w	Polydispersity
SIPE-10	1.57×10^4	1.90
SIPE-15	1.74×10^4	2.20
SIPE-20	1.79×10^4	1.91
SIPE-30	1.53×10^4	2.01

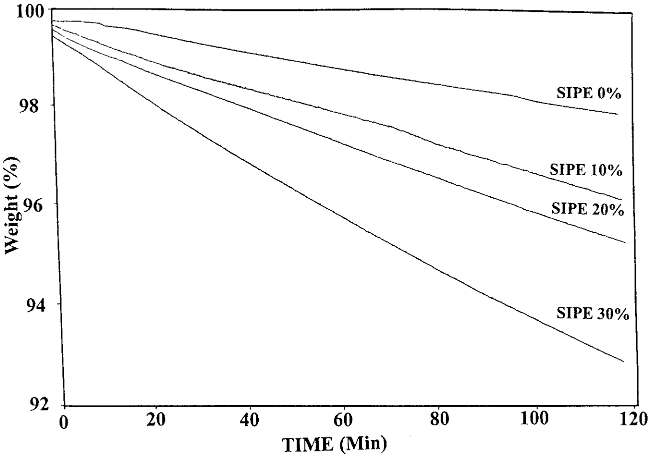


Fig. 2 The thermogravimetric analysis for PET containing various weight percents of SIPE

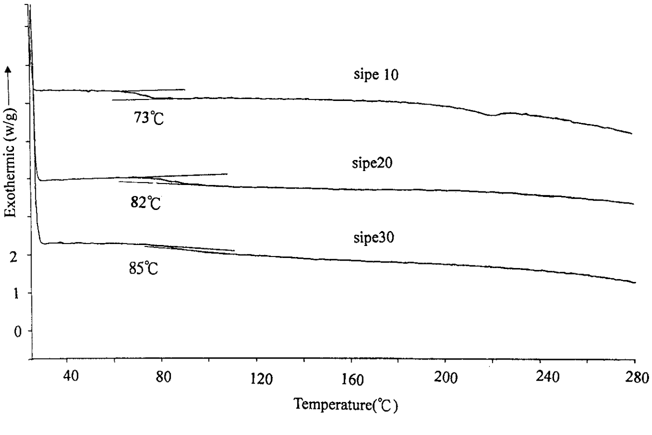


Fig. 3 The differential scanning calorimetry analysis for PET containing various weight percents of SIPE

The storage modulus, G', of the copolymer's melt is plotted against the oscillation frequency, ω, in Fig. 4. Since the dynamic measurement at a frequency ω is qualitatively equivalent to that of a transient one at $t = 1/\omega$, the graph is approximately a mirror image for the relaxation modulus, $G(t)$. Figure 4 also reveals that PET with a higher SIPE content leads to a higher magnitude of $G'(\omega)$, proving that the backbone containing sulfonate benzene will take a long period of time

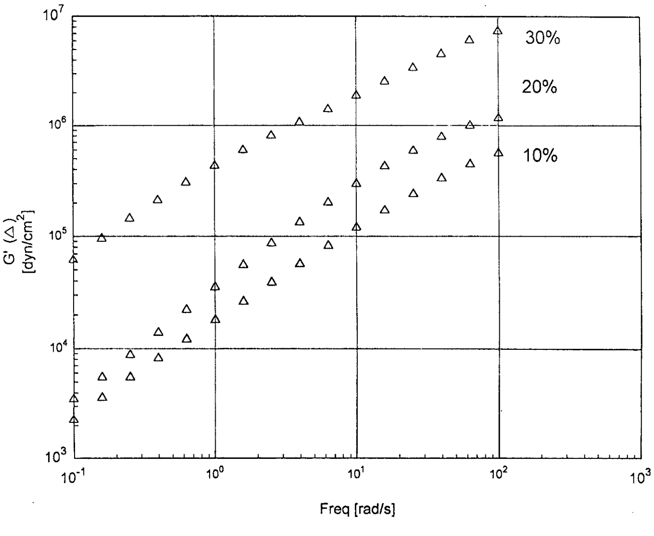


Fig. 4 Storage modulus versus frequency for PET containing various weight percents of SIPE (temperature: 220 °C; gap between two plates: 2 mm)

for contour rearrangement or chain relaxation [15]. The SIPE effect is similar to another well-known case in which the higher molecular weight leads to a higher $G(t)$ in the viscoelastic region of a master curve [16].

Characterization of slurry stability

Phth. Green (10% by weight) was dispersed into aqueous solutions containing various amounts of SIPE10. Here, the PET copolymer with 10% of SIPE is denoted as SIPE10. The same notation is applied for SIPE15, SIPE20 and SIPE30. The size of a dispersed particle is plotted against the dispersion time in Fig. 5. Once the particle had recoagulated and grew to 10 μm, our measurement was terminated in response to the accuracy limit of the light scattering instrument. Figure 5 reveals that the suspension containing 5% of SIPE10 instantly reagglomerates; however, the other two suspensions, with higher SIPE concentration, remained stabile for a longer period of time. The plot also demonstrates that the higher concentration of SIPE results in a dispersion with a smaller particle size. These results confirm that with a higher SIPE concentration more repulsive charges of the sulfonate group could be provided to surround the particles and to stabilize the suspension.

Figure 6 depicts the dispersion stability for a solution where the total concentration of SIPE units is maintained (approximately 1.5%), however the dispersant concentration is varied according to the SIPE value of a given PET copolymer. This plot illustrates that an ideal dispersion could be obtained when a system dissolves a high-sulfonate PET, such as SIPE30, at a low concentration. In contrast, a poor dispersion is found for a solution dissolving a low-sulfonate PET, such as SIPE10, at a high concentration. The particle size of the pigment slurry dispersed in 10% of SIPE15 and 15% of SIPE10 demonstrated a considerable difference by a factor of 1–2 orders of magnitude. In addition, the particle size distribution (which is marked as an error bar in the figure) represents a narrower distribution range for the solution with high-sulfonate PET at a low concentration. Moreover, Fig. 6 can elucidate the dispersion mechanism regarding the different dispersion forces. In general, there are two primary forces in an aqueous solution to stabilize the dispersion. These are the electrostatic forces from the "double layers of electric charges" and the steric force by the overlapping of the coating polymers. Therefore, the solution with 15% of SIPE10 will dissolve 3 times the polymer by volume when compared to 5% of SIPE30. Clearly, the former one would have a better steric effect than thelatter. However, when given equal charges in the solution, the former coated with a thicker shell would have less "charge density" and exhibit a weaker

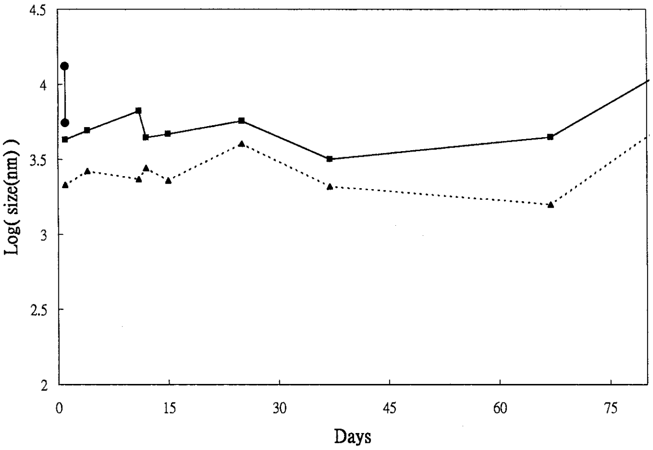


Fig. 5 Mean particle size versus shelf time for phthalocyanine green (*Phth. Green*) slurries incorporated with various concentrations of PET-SIPE 10 dispersant. (SIPE10-5%: –●–, SIPE10-10%: –■–, SIPE10-15%: –▲–)

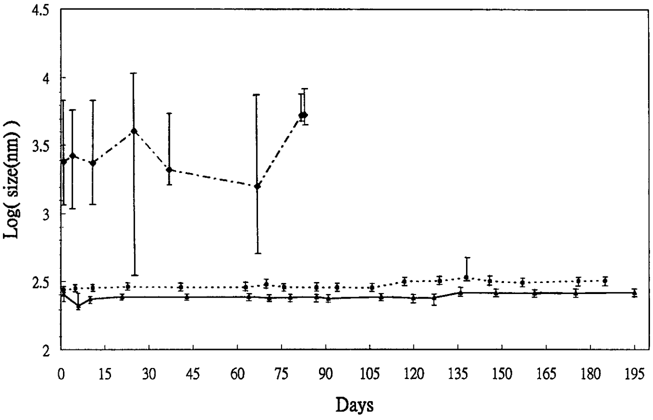


Fig. 6 Mean particle size versus shelf time for Phth. Green slurries. Dispersants with three SIPE values from 10 to 30 were applied; however, the total SIPE units for each solution were maintained at 1.5%. (SIPE10-15%: –◆–, SIPE15-10%: –●–, SIPE30-5%: –▲–)

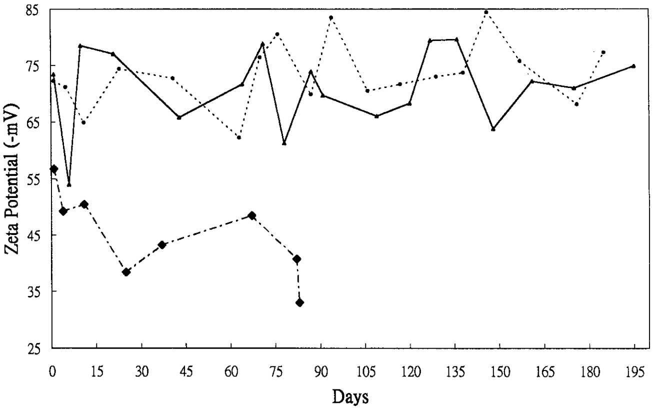
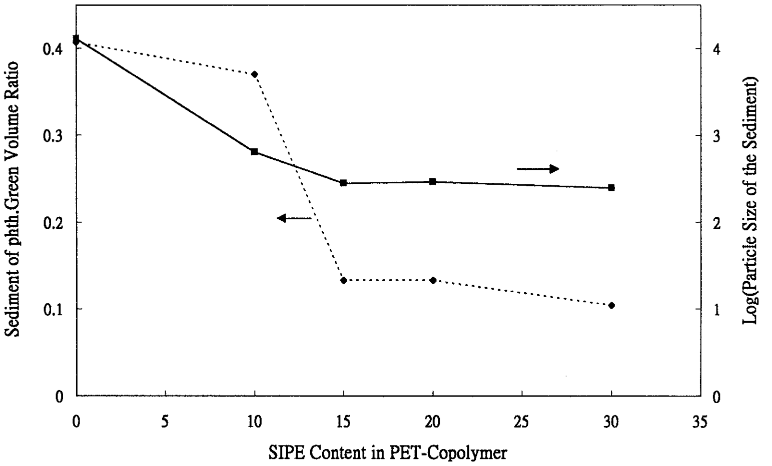


Fig. 7 Zeta potential versus shelf time for the dispersion conditions corresponding to Fig. 6. (SIPE10-15%: –◆–, SIPE15-10%: –●–, SIPE30- 5%: –▲–)

Fig. 8 Volume and mean particle size of Phth. Green sediment after a settling time of 30 days as a function of the SIPE grafting content in the PET copolymer. The total SIPE units in each solution were maintained at 1% except for the dispersant-free condition



electrostatic repulsion. The experimental result expressing a poor dispersion for the 15% of SIPE10 indicates that the electrostatic effect is more effective than the steric effect for the pigment dispersion.

The zeta potential is a parameter that characterizes the strength of an electrostatically stabilized dispersion. Although it is not a direct measurement of surface charge density, it changes in relation to the surface charge density. Reaching electrostatic stabilization in a colloidal system usually requires a value of the zeta potential higher than 40 mV. The zeta potential versus time for Phth. Green powder enwrapped with different SIPE copolymers is displayed in Fig. 7. The figure reveals that a solution with SIPE10 copolymer possesses a zeta value lower than 40 and this indicates a poor dispersion. This result is consistent with our previous finding from Fig. 6.

The sediment volume patterns given by the Phth. Green particle settlement experiments are displayed in Fig. 8 as a function of dispersant content. The particle size of the sediment was measured after redispersion. When the total concentration of the SIPE units in the solution is maintained (approximately 1 % of SIPE), both the volumes and the particle sizes in the sediment are large for a dispersant-free suspension and decrease as the coplymer's SIPE content increases. This reconfirms the previous finding.

Conclusions

To conclude, the following points have been determined.

1. A water-soluble PET resin composed of TPA, EG and SIPE was synthesized in this work. The resin was identified as a thermoplastic and could endure a process temperature higher than 200 °C. The thermal degradation increased as the sulfonate content increased, and only a slight loss was detected for the copolymer with the highest SIPE content (30/70 SIPE/PET). Subsequently, the T_g and G' increased as the sulfonate content increased.
2. From numerous tests, including light scattering, zeta-potential measurement and a sedimentation test, it can be concluded that for equal numbers of SIPE units, a low concentration of a dispersant of high sulfonate content is more effective than a high concentration of a dispersant of low sulfonate content.

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