

Super-tough poly(butylene terephthalate) based blends by modification with core-shell structured polyacrylic nanoparticles



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ABSTRACT

Core-shell structured polyacrylic nanoparticles (named CSPN) impact modifiers consisting of a rubbery poly(*n*-butyl acrylate) core and a rigid poly(methyl methacrylate) shell with a size of about 352 nm were synthesized by seed emulsion polymerization. The CSPN modifier with core-shell weight ratio 80/20 was used to toughen poly(butylene terephthalate) (PBT) by melt blending. With an increase in CSPN content, the impact strength and the elongation at break of PBT/CSPN blends increased significantly compared with those of PBT; however, the tensile strength decreased. It was found that the polymerization had a very high instantaneous conversion (>93%) and overall conversion (99%). The core-shell structure of CSPN was examined by means of transmission electron microscope. Scanning electron microscope was used to observe the morphology of CSPN particle and fractured surfaces of the blends. The dynamic mechanical analyses of PBT/CSPN blends showed two merged transition peaks of PBT matrix, with the presence of CSPN modifier, which was responsible for the improvement of PBT toughness. The results indicated that the notched impact strength of PBT/CSPN blend with a weight ratio of 80/20 was 8.61 times greater than that of pure PBT where the brittle-ductile transition point appeared.

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1. Introduction

Poly(butylene terephthalate) (PBT) is one of the most promising and universal thermoplastic polymers that is widely used as an engineering plastic [1–6]. Recently, PBT has attracted more attention of researchers, and the production and application of polymeric materials based on PBT have increased dramatically. The reasons for this are various that PBT and its products have a number of profitable properties, such as increased mechanical characteristics, good resistance to chemicals and water, and fine processability, etc. The unnotched impact strength of PBT is acceptable; however, pure PBT is high notch-sensitive, and commonly breaks in a brittle fashion when the notched specimens are tested. These disadvantages significantly limit the application of PBT. In order to overcome this drawback, elastomeric particles have been employed to modify PBT, resulting in blends of high toughness [7,8]. The toughening methodology includes copolymerization strategy, plasticization with a miscible component, and blending with a block copolymer or a rubbery component [9,10]. As a solution to this problem, core-shell rubber (CSR) type fillers are commonly used for polymer toughening. For other rubbers, the domain sizes are hard to control, because they are process-dependent [11–20]. The core-shell particles typically have a core of crosslinked butadiene or acrylic rubber and

a shell of grafted chains. These polymer chains may physically or chemically interact with the PBT matrix to ensure desired dispersion and coupling, such as ethylene propylene diene rubber grafted with glycidyl methacrylate (EPDM-g-GMA) [19], styrene-acrylonitrile copolymer (SAN-g-GMA) [20], CSR with methacrylic acid (MA) [21], and ABS particles [22]. To the best of our knowledge, there are few reports on the core-shell particles that the shell surface does not contain any functional monomers and on the effective toughening modifier of PBT to get high toughness.

In this study, we report the synthesis of core-shell structured polyacrylic nanoparticles (CSPN) by seed emulsion polymerization with redox initiator system. The modifier is a latex particle with a predetermined size (Fig. 1) and was used to modify the mechanical properties of PBT. The rubbery core phase of CSPN is poly(butyl acrylate) [Poly(BA)] and the shell phase is methyl methacrylate [Poly(MMA)]. The rubbery core should provide resistance to impact, whereas the glassy shell may provide rigidity and compatibility to the PBT matrix. Addition of small amounts of CSPN to the PBT matrix may improve the impact strength of PBT/CSPN blends significantly. The CSPN modifiers and PBT matrix were blended with weight ratios of 95/5, 90/10, 85/15, 80/20, 75/25, 70/30 and 65/35. Moreover, the effects of CSPN content on the rheological and mechanical properties of PBT blends were evaluated, and the structure and morphology of the modifiers and the PBT blends were characterized by transmission electron microscope (TEM) and scanning electron microscope (SEM). Dynamic

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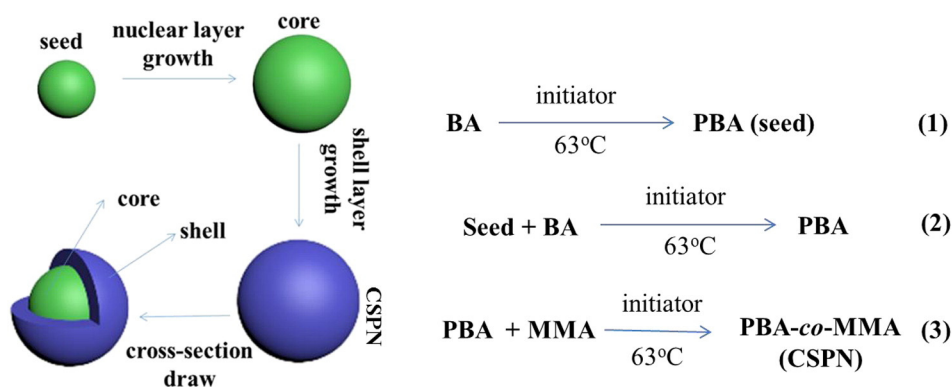


Fig. 1. The schematic representation for the seed emulsion polymerization process of the CSPN latex.

mechanical analysis (DMA) was also used to explore the molecular movement of PBT/CSPN blends.

2. Experimental

2.1. Materials

The initiator potassium persulfate (KPS) and sodium hydrogen sulfite (NaHSO_3) were purchased from Tianjin Chemical Agent Co. (Tianjin City, China), the anionic surfactant (Aerosol MA Series) from Cytec (Heavens City, The Netherlands), and hydroquinone and 1,4-butanediol diacrylate (BDDA) from Tianjiao Chemical of China (Tianjin City, China). Those materials were used without further purification. PBT resin (1100–211 M) was provided by Changchun Industry (Taiwan, ROC). *n*-Butyl acrylate (BA) and methyl methacrylate (MMA) were purchased from Beijing Dongfang Chemical Co. (Beijing City, China). To free the BA monomer of inhibitor, it was washed with a 2 wt.% of NaOH solution until the filtrated water was neutral, dried with CaCl_2 overnight, and distilled under reduced pressure. The MMA monomer was purified by distillation under reduced pressure just before use. Deionized water was used throughout this work.

2.2. Semicontinuous emulsion polymerization

Core-shell structured latexes were synthesized as 50% of solid latexes via a two-stage semicontinuous emulsion polymerization. The surfactant (0.3 g), KPS (0.27 g) and water (140 g) were added to a 0.5-L flanged reaction flask under nitrogen, and heated at about 63 °C for 30 min. The seed-stage BA monomer (10.0 g, 5 wt.% of total monomer) was added to the surfactant solution and stirred for 10 min. A solution of 0.013 g NaHSO_3 in 5 g water was added and repeated after 30 min. The growth stage involved three layers of pre-emulsified monomers: a) 150 g BA and 1.35 g BDDA with 1.875 g surfactant, b) 10 g MMA with 0.125 g surfactant and c) **30 g MMA with 0.375 g surfactant**. Pre-emulsified monomers of the first two layers were gradually poured into the flask at a constant rate over 1.5 h. At the same time, 0.104 g NaHSO_3 in 40.0 g water was added to the reaction flask at the same rate. The third layer of pre-emulsified monomers and 0.026 g NaHSO_3 in 10.0 g water were added to the reaction flask at a constant rate for 15 min. The core-shell weight ratio of CSPN particle was 80/20. After 60 min, the latex was cooled down to room temperature and filtered through a 53- μm sieve to obtain the coagulated products. The modifier sample was obtained by freeze-thaw cycling and washed with water several times.

2.3. Blends preparation

The PBT and the CSPN modifier were sufficiently dried in a vacuum oven at 120 °C and 40 °C, respectively. A TE-34 twin screw extruder of

L/D = 28 (Nanjing Institute of Extrusion Machinery, China) was used to prepare PBT/CSPN blends with the weight ratios of 95/5 (5%), 90/10 (10%), 85/15 (15%), 80/20 (20%), 75/25 (25%), 70/30 (30%) and 65/35 (35%) at a screw speed of 65 rpm and barrel temperatures of 227, 235, 245, 240 °C. The pelletized materials were dried and molded in an injection-molding machine (JPH-30, Guangdong Hongli Machine China) at 240 °C.

2.4. Characterization

Emulsion polymerizations of CSPN latexes were carried out with a KPS/ NaHSO_3 redox initiator system at a temperature of 63 °C. At 30-min intervals, 10-mL samples of the latex were transferred into preweighed vials containing 1 mL of hydroquinone solution (2 wt.%) to prevent further polymerization. The vials were cooled down with ice to quench the polymerization and analyzed gravimetrically to determine the instantaneous conversion and overall conversion. Instantaneous and overall conversions were calculated from a mass balance of the reagents in the polymerization with the percentage solid content measured at each sampling time [21]:

$$\text{Instantaneous conversion (\%)} = \frac{[\text{Mass of polymer formed} / \text{mass of monomer added}]}{\times 100} \quad (1)$$

where the mass of monomer added is the sum of the monomer at the seed stage and any monomer that has been added at each sampling time during the growth stage.

$$\text{Overall conversion (\%)} = \frac{[\text{Mass of polymer formed} / \text{mass of monomer added}]}{\times 100} \quad (2)$$

where, the total mass of monomer is the sum of the monomers in the seed stage and the monomers added during the growth stage.

Particle size was measured online with a fixed 90° scattering angle and dynamic light scattering (DLS) on a Malvern Zetasizer NANO-ZS90 (Worcestershire, UK), while the cell temperature was kept at 25 ± 0.1 °C. The particle diameters are reported as the mean values of *z*-average diameters (d_{zs}) calculated by cumulate method.

Transmission electron microscope (TEM, JEM-2100) was used to study the final CSPN latex structure. To characterize the latex, it was dispersed in sufficient water with ultrasonic waves, followed by casting one drop of diluted solution onto a carbon-coated copper grid. A field emission scanning electron microscope (FE-SEM, Nova NanoSEM 450, FEI) was used to examine the CSPN latex morphology and the morphology of the notched Charpy impact-fractured surfaces of PBT/CSPN blends. The modifier surface was coated with gold before examination.

Tensile strength was tested with CMT-6104 machine (Shenzhen, China) according to ASTM D-638 and impact strength was

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