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Material properties

Effects of toughening propylene/ethylene graft copolymer on the crystallization behavior and mechanical properties of polypropylene random-copolymerized with a small amount of ethylene

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ABSTRACT

Linear low-density polyethylene (LLDPE) was grafted onto the backbone chains of isotactic polypropylene (iPP) during reactive melt-extrusion to produce a novel toughening modifier, propylene/ethylene graft copolymer (PEGC), to improve the properties of iPP random(-copolymerized with a small amount of ethylene) (PPR). The crystallization behavior as well as the non-isothermal crystallization kinetics of the PEGC modified PPRs were investigated via differential scanning calorimetry (DSC), polarized optical microscopy (POM) and wide-angle X-ray diffraction (WAXD). The fractured surface topography was characterized using scanning electron microscopy (SEM), and the mechanical properties through notched impact and tensile testing as well as dynamic mechanical thermal analysis (DMTA). The results show that, at a PEGC content of 8 wt%, notched impact strength of the PEGC modified PPR increased by 30.6% at low temperature (−25 °C). As regards crystalline morphology, the PEGC, as an effective heterogeneous nucleating agent, fostered nucleation of the PPR to elevate its crystallization temperature as well as rate of crystallization, thus refining the PPR (iPP) spherulites and improving the interfacial structure between iPP spherulites. The Jeziorny approach was unsatisfactory for simulation of the non-isothermal crystallization process of the PEGC modified PPRs; however, the Mo method described consistently the crystallization kinetics over the entire isothermal process.

1. Introduction

Isotactic polypropylene (iPP) random(-copolymerized with a small amount of ethylene) (PPR) is made up of iPP backbone chains along which 3–5 wt% of a second ethylene monomer unit are randomly interspaced. Compared with iPP homopolymer, PPR has lower rigidity and melting temperature but relatively higher impact, heat-aging and compression resistance, which finds it important applications in plumbing. However, PPR is so brittle at low temperatures (5 to −10 °C) that it is readily prone to stress-induced cracking, which must be resolved for installation and maintenance of PPR pipes [1–3]. To address this issue, engineers usually have to employ ethylene–propylene–diene monomer (EPDM) rubber [4–6] or ethylene–propylene rubber (EPR) [7–9] at a relatively high loading level to effectively toughen PPR; this leads to steep decreases in its rigidity, heat and compression resistance, and thus failure to meet the standard properties requirements for plumbing materials.

In the present work, linear low-density polyethylene (LLDPE) has been grafted onto the backbone chains of iPP

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via melt-extrusion grafting to obtain a propylene/ethylene graft copolymer (PEGC) as the toughening agent, a small amount of which has subsequently been melt-blended with PPR to prepare PEGC modified PPR. Its crystallization behavior, non-isothermal crystallization kinetics as well as mechanical properties are investigated against those of neat (unmodified) PPR, with the aim of contributing to the knowledge on cryogenic toughening of PPR pipes.

2. Experimental

2.1. Materials

Polypropylene random (PPR) (RP2400) with a melt flow rate of 0.35 g/10 min (230 °C, 2.16 Kg) was obtained from Korea National Oil Corporation (KNOC). Isotactic polypropylene (iPP) (S1003) was purchased from Dushanzi Petrochemical, PetroChina. Linear low-density polyethylene (LLDPE) (DFDA-7042N) was kindly supplied by Lanzhou Petrochemical, PetroChina.

Toughening agent, PEGC pellets, with density of 0.92 g/cm^3, melt flow rate of 0.545 g/10 min (230 °C, 2.16 Kg), M_w of 16.6 × 10^4 g/mol, and M_w/M_n of 5.44, was prepared independently in our laboratory through reactive melt extrusion (CTE-35, Coperion Keya Machinery (Nanjing, China)) of the above iPP and LLDPE at a mass ratio of 1:1 at 220 °C and in the presence of 0.8 wt% of dicumyl peroxide (DCP) as initiator, followed by pelletization.

2.2. Sample preparation

The PPR-resin pellets were tumble-mixed at room temperature with variable amounts (0, 6, 8 and 10 wt%) of the toughening agent, PEGC pellets, to form PPR/PEGC physical blends, which were then melt-blended at 220 °C for 5 min in an internal mixer (RM-200A, Hapro Electric, Harbin, China) at a rotor speed of 30 rpm, followed by grinding and, finally, injection molding (TY-200, Dayu Machinery, Hangzhou, China) at 190–220 °C into standard mechanical specimens for the PEGC-modified PPR.

2.3. Tensile and impact measurements

Tensile tests were performed with a universal tensile tester (GDXA 40/150, MTS Industrial Systems (China)) on injection molded dumbbell shaped specimens at ambient temperature and a crosshead speed of 50 mm/min according to GB/T 1040.2-2006 (China National Standard). V-notched impact properties of the specimens were tested on a Charpy impact test machine (XJJ-50, Chengde Test Machinery, China) according to GB 1093; the dimensions of each injection molded impact specimen were 80 mm × 10 mm × 4 mm. For both the tensile and impact tests, each composition of PEGC-modified PPR was tested using 5 specimens, the median result being taken as the property value.

2.4. Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (DMTA) was carried out using a dynamic mechanical thermal analyzer (Q800, TA Instruments). The single-cantilever beam mode was used for rectangular shaped specimens with dimensions of 25 mm × 10 mm × 2 mm, which were cut from larger sheets prepared via melt pressing. Measurements were conducted from −50 to 120 °C at a heating rate of 3 °C/min with an oscillatory frequency of 1 Hz and a deformation amplitude of 15 μm. Cooling was achieved by pumping liquid nitrogen through the accessories provided by the DMTA instrument.

2.5. Thermogravimetric analysis

Thermogravimetric analysis (TGA) traces of PEGC-modified PPR samples were obtained on a thermogravimetric analyzer (DTAS-1A, Yuanbo Instruments, China) with nitrogen atmosphere as the purge gas. Scans were run from 30 to 600 °C at a heating rate of 10 °C/min; sample weight used for analysis was ca. 8 mg, cut from a melt-pressed sheet of ca. 1 mm in thickness.

2.6. Differential scanning calorimetry (DSC)

The thermal transition behavior of the PEGC-modified PPR was examined using a differential scanning calorimeter (DSC8000, Perkin Elmer) with nitrogen-gas atmosphere at a flow rate of 20 ml/min. A small amount (ca. 8 mg) of 1 mm thick sample was encapsulated in an aluminum pan, which was then placed in the DSC cell, heated to 210 °C at a rate of 20 °C/min, and held there for 3 min to eliminate any effect(s) of previous thermal history prior to testing. The sample was subsequently cooled from 210 to 30 °C, and, finally, heated again to 210 °C to record any crystallization and melting transitions. The cooling rate was varied from 5 to 40 °C/min while the heating rate was fixed at 10 °C/min. Normalized heat flow (W/g) was plotted against temperature (°C). The peak point (°C) and the peak area (J/g) across any melt crystallization (or melting) peak were taken as the melt crystallization (or melting) temperature and the crystallization (or melting) enthalpy.

2.7. Wide-angle X-ray diffraction (WAXD)

In order to study the crystalline structure of PPR modified with PEGC, an X-ray diffractometer (D/MAX-RB, Rigaku, Japan) was employed to probe the wide angle X-ray diffraction (scattering) (WAXS) properties of the PEGC modified PPRs. WAXS patterns were obtained by using an area detector and a rotating anode X-ray generator equipped with a graphite monochromator (Cu Kα; λ = 1.5406 Å) operating at 40 kV and 50 mA. The scanning angle ranged continuously from 10 to 45° with a scan rate of 4°/min. Disk samples with ca. 10 mm in diameter and 1 mm in thickness were prepared via melt pressing for the WAXD analysis.

2.8. Scanning electron microscopy (SEM)

Cryogenically (at −25 °C) fractured surface topography of the above impacted specimens, sputtered with gold, was observed using a scanning electron microscope (JSM-6390LV, JEOL, Japan). The acceleration voltage was 30 kV, and the magnification was 500.