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Crystallization and foaming of coagent-modified polypropylene: Nucleation effects of cross-linked nanoparticles

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ABSTRACT

The radical-mediated addition of trimethylolpropane trimethacrylate (TMPTMA) to linear, isotactic polypropylene (PP) yields graft-modified derivatives that contain coagent-rich, cross-linked particles with sub-micron dimensions. The presence of this dispersed phase in coagent-modified polypropylene (CM-PP) is shown to increase the crystallization temperature and crystallization rate, owing to an enhanced heterogeneous nucleation mechanism. Analogous enhancements in nucleation are also demonstrated for a batch foaming process, wherein N_2 is used as a physical blowing agent.

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1. Introduction

The chemical modification of linear, isotactic PP (L-PP) by peroxide-initiated grafting of coagents can provide long-chain branched derivatives with improved melt elasticity and extensional viscosity [1]. These solvent-free processes involve simultaneous chain scission and cross-linking, the balance of which controls the product's molecular weight and branching distributions [2,3]. In general, products derived from coagents bearing multiple acrylate, allylic or styrenic groups are comprised of a linear chain population of relatively low molecular weight, and a high molecular weight chain population containing a disproportionate amount of long chain branching.

The effect of these microstructure changes on melt-state rheological properties is well documented, with several groups reporting losses in complex viscosity as well as enhanced elasticity and strain hardening characteristics [4–7]. However, only recently has the generation of cross-linked particles within coagent modified PP (CM-PP) been identified [8]. These nanoparticles are produced by a precipitation polymerization mechanism wherein coagent oligomerization yields adducts that are insoluble in the polymer melt, leading to the separation of a coagent-rich phase

that cross-links to a very high extent [9]. As a result, CM-PP samples prepared by this chemistry can contain small, rigid particles that are well-dispersed throughout the polymer matrix.

A prime motivation for preparing CM-PP is to develop the extensional strain hardening characteristics needed to suppress cell coalescence during melt foaming processes. When compared to L-PP materials, CM-PP derivatives provide higher volume expansion ratios and more uniform cell sizes [4,10]. These improvements to foam properties have, to date, been attributed to the melt state rheology, while the potential of coagent-rich nano-particles to affect the foaming of CM-PP has been overlooked. Similarly, significant differences in the crystallization behaviour of linear and coagent-modified PP samples have been observed [4,11,12]. Whereas branching in homogeneous polyethylenes is usually associated with lower crystallization rates and crystallinities [13,14], CM-PP materials are reported to crystallize at higher temperatures. Knowledge of the origin of these differences is currently incomplete.

The present work involves the comparison of an isotactic L-PP with two of its derivatives: peroxide degraded PP (DCP-PP), and CM-PP modified with trimethylolpropane trimethacrylate (TMPTMA, Scheme 1) [11]. These materials are subjected to standard characterization techniques including molecular weight distribution as well as oscillatory shear and extensional rheometry. CM-PP is subjected to further analysis by FT-IR to confirm TMPTMA graft content, as well as SEM studies of the sub-micron particles dispersed throughout the sample. Careful studies of

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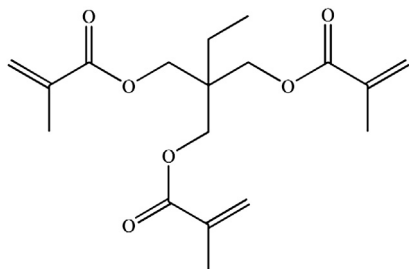
Scheme 1. Molecular structure of TMPTMA.

CM-PP crystallization and foaming are presented, with the objective of discerning the effect of coagent-rich nano-particles on phase nucleation phenomena. Further insight is gained through studies of L-PP compounds containing small amounts of independently synthesized coagent nano-particles.

2. Experimental

2.1. Materials and reactive modification

Trimethylolpropane trimethacrylate (TMPTMA, 98%) and dicumyl peroxide (DCP, 98%) were used as received from Sigma–Aldrich. ESCORENE™ PP 1042, an isotactic linear polypropylene homopolymer (L-PP) (MFR = 1.9 g/10 min), with a number average molecular weight (M_n) of 96 kg/mol and a weight average molecular weight (M_w), of 460 kg/mol, as determined by triple detector gel permeation chromatography (GPC), was obtained from ExxonMobil.

Peroxide-degraded PP (DCP-PP) was prepared by coating ground L-PP powder (40 g) with an acetone solution containing DCP (0.08 g, 296 μmole) and allowing the solvent to evaporate. The resulting mixture was charged to a Haake Polylab R600 internal batch mixer at 180 °C at 60 rpm for 10 min, yielding DCP-PP with a M_n = 63.1 kg/mol and a M_w = 159 kg/mol.

Coagent-modified PP (CM-PP) was synthesized as described for DCP-PP from a mixture of L-PP (40 g), DCP (0.08 g, 296 μmole) and TMPTMA (2.4 g, 7.1 mmole). The product had a M_n = 77.5 kg/mol and a M_w = 209 kg/mol.

Gel content analysis was conducted by extraction into boiling xylenes from a 120 mesh stainless steel sieve for 6 h, according to ASTM D 2765. Residual polymer was dried to constant weight, with gel contents reported as a weight percentage of unextracted material.

Isolation of particles from CM-PP was accomplished by hot xylenes extraction of the polymer from Soxhlet cellulose thimbles. Solvent was replaced every 3 h, and after 10 h no residual polymer could be recovered by precipitation from acetone. The thimble was cut into pieces, soaked in acetone and sonicated. The resulting dispersion was deposited onto glass slides, and coated with gold after solvent evaporation. A JEOL JSM-840 scanning electron microscope (SEM) instrument was used to view the isolated particles.

Cross-linked particles were prepared according to the method proposed by Wu et al. [9]. A homogeneous solution of dodecane (49.3 g, 290.3 mmol), TMPTMA (0.5 g, 1.5 mmol) and DCP (0.05 g, 0.2 mmol) was heated at 170 °C for 10 min, cooled to room temperature and left standing for 12 h to allow particles to settle. Residual liquid was decanted carefully from a minimal volume of suspended solids, a portion of which was deposited on a glass slide and dried under vacuum at 100 °C for 12 h prior to SEM characterization. The total particle yield was 0.2 g (40% based on TMPTMA).

An L-PP based compound containing 1 wt.% TMPTMA particles was prepared as follows. L-PP (1 g) was dissolved in boiling xylenes (20 mL) before adding to a suspension of particles (0.2 g) in dodecane (10 mL). Residual dodecane and xylene were removed under vacuum at 100 °C for 12 h, and the resulting masterbatch mixture (0.2 g) was mixed further with L-PP (2.8 g) using a DSM 5 mL microcompounder, equipped with co-rotating screws, and operating at 230 °C and 150 rpm for 5 min.

2.2. Characterization

Molecular weight distributions were measured using a triple detector GPC (GPCIR by PolymerChar) at 145 °C, employing 1,2,4-trichlorobenzene (TCB) as the mobile phase. Polymer samples were dissolved in TCB at a concentration of 1 mg mL^{-1} and held at 150 °C for 60 min. Samples with an injection volume of 200 μL were eluted through three linear Polymer Laboratories columns which were operated at a flow rate of 1 mL min^{-1}. The light scattering (LS) detector at 15° from the incident beam was used for molecular weight determinations.

FT-IR measurements were carried out in transmittance mode with an Avatar 360 FT-IR ESP spectrometer. Samples were purified by dissolving in boiling xylene and precipitating from acetone prior to drying under vacuum and melt pressing into thin films.

A controlled stress rheometer (ViscoTech by Reologica) with parallel plate fixtures was used in the oscillatory mode at 180 °C with a gap of 1 mm under a nitrogen purge. Stress sweeps were used to ensure that measurements were made within the linear viscoelasticity region. Samples were further characterized in uniaxial extension using an SER-2 universal testing platform from Xpansion Instruments hosted on an MCR-501 Anton Paar rheometer [15]. Measurements were conducted at 170 °C at extension rates ranging from 0.010 to 10 s^{-1} under nitrogen purge.

Differential scanning calorimetry (DSC) was conducted using a DSC Q 100 by TA Instruments. Samples were scanned between −30 and 210 °C at a heating rate of 5 °C/min. After the first heating, each sample was held isothermally at 210 °C for 3 min before cooling at 5 °C/min, to determine the crystallization onset and peak temperatures according to ASTM D3418.

Isothermal crystallization experiments were performed using a Linkam CSS 450 hot stage mounted on an Olympus BX51 optical microscope. Thin films were first heated to 200 °C at a rate of 30 °C/min and held for 10 min to eliminate their heat history. The melt was then cooled to 140 °C at 30 °C/min and the temperature was kept constant for 1 h. The crystallization process was recorded using a Sony ExwaveHAD 3 CCD digital recorder.

2.3. Foaming visualization

Foaming visualization experiments, using N_2 as the blowing agent, were conducted using a batch foaming simulation system, consisting of a pressurized chamber equipped with a sapphire glass window, and a high speed camera/imaging system, at 180 °C at 203 MPa of N_2 [16]. Disks (7 mm diameter × 200 μm thickness) were heated to 180 °C at 203 MPa of N_2. The temperature and pressure in the simulation chamber were regulated using a thermostat and a syringe pump, respectively. A program based on Labview® was used to open the solenoid valve and record the pressure decay after the pressure within the chamber had been maintained for 30 min of saturation, while simultaneously, a high speed camera recorded the cell growth and collapse phenomena at 500 hundred frames per second. For each sample, at least three separate experiments were run, and the images were extracted using the Sigma Scan Pro Plus 6.0® image analysis software.