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Microwave-assisted hydrosilylation of polypropylene and its application to in-situ grafted polypropylene/SiO_2 nanocomposites

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ABSTRACT

Grafting end-functionalized polypropylene (PP) to the surfaces of nanoparticles is a promising approach in boosting physical properties of PP-based nanocomposites. In this study, a practical pathway is presented for the fabrication of PP-grafted nanocomposites: Reactive silicon alkoxy groups were introduced through microwave-assisted hydrosilylation of terminal unsaturation of vis-breaking PP. Thus obtained hydrosilylated PP was added as a reactive additive in melt compounding of PP with SiO_2 nanoparticles to implement in-situ grafting. Significant improvements were attained in the dispersion of SiO_2 nanoparticles, the crystallization rate and the tensile strength.

1. Introduction

Polypropylene (PP) nanocomposites have continuously attracted great attention from both academia and industry due to their cost-performance benefits and a wide spectrum of applications [1]. By the definition, at least one of the phase has a dimension smaller than 100 nm [2], thus facilitating extremely large interfacial area to endow a variety of properties. Also, high particle density can interfere with the polymer chain relaxation to alter macroscopic properties such as the glass transition and viscoelastic response [3–5]. However, fabrication of PP nanocomposites in conventional melt mixing is challenging owing to the chemical inertness of PP against inorganic nanoparticles. The addition of a compatibilizer such as maleic anhydride-grafted PP [6], and chemical modification of filler surfaces typically using alkyl amines [7] or a silane coupling agent [8] are typically applied to alleviate the dispersion problem by inserting a compatibilizing layer at the matrix-filler interfaces. Nonetheless, inherently soft or plasticizing interfaces arising from an excessive amount of organic modifiers [9] or multiple contacts of side-chain functionalized PP hamper the hardness of inorganic fillers and consequently make the stress transfer at the interfaces less effective for reinforcement [10], especially for spherical particles possessing the minimal aspect ratio.

Replacing the soft interfacial layer by polymer chains grafted onto filler surfaces at their chain end was reported as a promising strategy to fabricate performant PP nanocomposites [11–17]. The polymer grafting not only improves the dispersion by inserting a compatibilizing interfacial layer, but additional mechanisms such as inter-diffusion and entanglement strengthen the interfacial bonding. Generally, the polymer-grafted nanoparticles can be prepared through either of the "grafting-from" or "grafting-to" method [18]. The former adopts the controlled polymerization techniques such as atom transfer radical polymerization [19], nitroxide-mediated polymerization [20], and reversible-addition-fragmentation chain transfer polymerization [21], where an initiator is introduced onto the surfaces of nanoparticles prior to the polymer growth from the surfaces. Though the grafting-from method facilitates a precise control in the chain length and graft density, it is not applicable for PP which is the ideal graft chain for PP nanocomposites. On the other hand, the grafting-to method allows the utilization of pre-synthesized PP having a terminal reactive group to be coupled with functional groups present on nanoparticle surfaces. The most important advantage of the grafting-to method is at the fact that not only the polymer type, but also its detailed microstructure can be pre-designed in order to maximize the miscibility and the interfacial bonding. Frequently, terminally functionalized PP is synthesized by controlling the chain transfer reaction: Catalyzed propylene polymerization in the presence of appropriate chain transfer agents such as metal alkyl [22,23] and organoborane [24] leads to the formation of metal-terminated PP chains, which can be post-transformed into different types of functional groups. In our previous works, terminally hydroxylated PP chains having different molecular weight were synthesized based on the chain transfer to alkyl aluminum followed by the oxidation and hydrolysis [15,16]. The successful grafting of terminally hydroxylated PP chains to SiO_2 nanoparticles prior to melt mixing afforded several positive consequences, particularly, uniform dispersion up to 10 wt%, crystallization acceleration up to 2–3 folds, and dramatic reinforcement, especially up to 26% increment of the tensile strength

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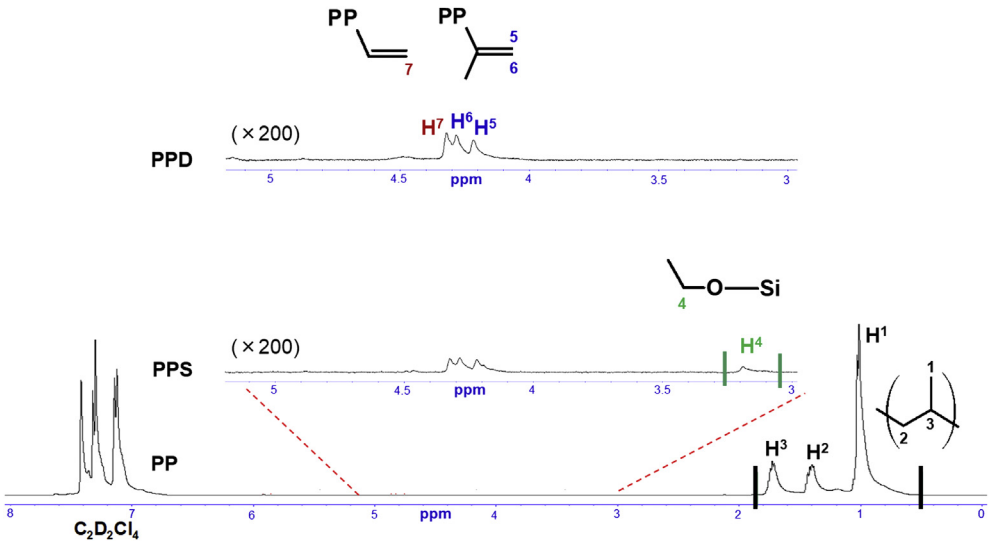

Fig. 1. ^{1}H NMR spectra of PPD before and after hydrosilylation.

due to physical cross-linkage through co-crystallization between the matrix and grafted chains. In addition, we successfully extended the technique to the fabrication of graft-type PP/graphene oxide nanocomposites where grafted PP chains improved the mechanical and electrical properties [17].

In this study, we have addressed synthetic elaborations for the preparation of PP-grafted nanocomposites: The control of the chain transfer reaction during catalyzed polymerization necessitated an extremely low yield operation of a catalyst, and the excessively added chain transfer agent (and its derivatives) needed to be repetitively separated from the product. Hence, a practical pathway for the preparation of graft-type PP/SiO_2 nanocomposites was developed. Starting from commercially available terminally unsaturated PP, silicon alkoxy groups were introduced by microwave-assisted hydrosilylation at the chain end. Thus prepared hydrosilylated PP was used as a reactive additive during melt mixing between the PP matrix and SiO_2 nanoparticles. Positive consequences of the addition of the hydrosilylated PP were investigated on the dispersion of nanoparticles and physical properties of PP/SiO_2 nanocomposites.

2. Material and methods

2.1. Materials

Pristine PP pellet ($M_n = 4.6 \times 10^4$, $M_w/M_n = 5.65$, *mmmm* = 98 mol%) was used as the matrix polymer. Four samples of terminally unsaturated PP (termed as PPD1-4) were provided by IRPC Public Co., Ltd. These samples were prepared via a vis-breaking process using 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane as a vis-breaking agent. The content of terminal double bonds was determined as a total fraction of vinyl and vinylidene groups per monomer unit in ^{1}H NMR, and it was 3.7×10^{-3}, 2.2×10^{-3}, 1.2×10^{-3}, and 5.3×10^{-4} mol/mol for PPD1-4, respectively. Triethoxysilane (TES), platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (known as the Karstedt catalyst), *o*-dichlorobenzene (ODCB), and 1,2,4-trichlorobenzene (TCB) were used as delivered. Toluene was used after dehydration by passing through a column of molecular sieve 4A and bubbling with N_2 for 2 h. Nano-sized SiO_2 powder (average diameter = 26 nm and surface area = 110 m^2/g) was purchased from Kanto Chemical Co., Inc. Octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate (AO-50) was donated by ADEKA Co. and used as a stabilizer.

2.2. Hydrosilylation

PP samples with a reactive silicon alkoxy group at the chain end (PPS) were prepared by hydrosilylation of the terminal double bonds of PPD using TES. A 10 mL glass vial was charged with 1.25 g of a PPD sample, 12 mL of ODCB or TCB as a solvent, 67.5 mmol of TES, and 1.0 μmol of the Karstedt catalyst under N_2 atmosphere. The mixture was subjected to microwave irradiation (Discover SP, CEM) at a constant temperature mode under vigorous stirring for a specified duration. For better understanding, the reaction was also performed without adding TES, without adding the catalyst, or with the addition of 500 mg of SiO_2 nanoparticles. The obtained product was washed with toluene, dried at 50 °C under vacuum, and stored under N_2 at room temperature in order to minimize the hydrolysis of introduced silicon alkoxy groups before melt mixing.

2.3. Preparation of PP/SiO_2 nanocomposites

Nanocomposites were prepared by melt mixing using a two-roll mixer rotated at 20 rpm. 10 g of the PP pellet was kneaded at 185 °C for 5 min in the presence of 0.3 wt% of AO-50, and subsequently melt-mixed with 5.0 wt% of SiO_2 and a specified weight fraction of PPS for additional 10 min. Thus prepared nanocomposites were hot-pressed into films with the thickness of 200 μm at 230 °C and 20 MPa, and then quenched at 100 °C. A series of reference samples were similarly prepared by adding a PPD sample instead of PPS, or by excluding the addition of either PPS or SiO_2 nanoparticles.

2.4. Characterization

^{1}H NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer at 120 °C using 1,1,2,2-tetrachloroethane-d_2 as an internal lock and reference. The contents of double bonds and ethoxy groups were respectively estimated using Eqs. (1) and (2):

$$\text{DB content (mol/mol)} = \frac{(H^5 + H^6)/2 + H^7/2}{(H^1/3 + H^2/2 + H^3)/3} \quad (1)$$

$$\text{OEt content (mol/mol)} = \frac{H^4/2}{(H^1/3 + H^2/2 + H^3)/3} \quad (2)$$

where relevant assignments are presented in typical NMR spectra of a PPD sample before and after hydrosilylation in Fig. 1.

The dispersion of SiO_2 nanoparticles in the PP matrix was observed on a transmission electron microscope (TEM, Hitachi H-7100) operated