



Surface modification of polypropylene with poly(methyl methacrylate) initiated by a diethylzinc and 1,10-phenanthroline complex

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ABSTRACT

Methyl methacrylate (MMA) was grafted onto the surface of polypropylene (PP) films and fibers through simple radical polymerization of diethyl(1,10-phenanthroline N^1, N^{10})zinc (Phen-DEZ) and with oxygen molecules as the radical initiator. The grafting yield could be changed by varying the reaction time, temperature, and amount of solvent. The resultant grafted PP films were characterized by Fourier transform infrared spectra, Raman spectra, and X-ray diffraction measurements, as well as thermogravimetric analysis. The surface morphology of the grafted PP film was analyzed using an atomic force microscope. Furthermore, the usual hydrophobic surface behavior of PP film became hydrophilic, as observed from the change in the water contact angle (106.1° to 64.8°), after grafting with PMMA. The scanning electron microscopy images showed that the graft polymerization process did not change the original microstructure of PP fibers. From the results of these analyses, it was proved that MMA could be grafted to the PP films using the novel Phen-DEZ/ O_2 initiator.

1. Introduction

Polyolefins, such as polypropylene and polyethylene, are indispensable materials with many beneficial industrial uses. Their excellent properties, as represented by low specific density, high mechanical strength, high chemical resistance, and good processability, have led to the fabrication of objects for many different appliances. While they have many advantages, polyolefins do not contain polar groups, so they lack dyeability, printability, and adhesiveness unlike other functionalized polymers.

Various methods for the surface pretreatment of polyolefins have been developed with the aim of expanding their applications to high-performance fields; these pretreatment techniques include glow discharge [1], plasma treatment [2,3], corona discharge [4], and acid etching [5]. In addition, graft polymerization is a simple and efficient method for modifying the polymer surface. The surfaces of polyolefins can be modified with various kinds of vinyl monomers, and the products inherit many desirable properties from the monomers. Living graft polymerization is particularly noteworthy because it can precisely control the molecular weight and structure of the grafted chains. Ying et al. prepared multifunctional polyolefin-based elastomers via graft-from anionic living polymerization [6]. Ding et al. successfully synthesized photosensitive graft copolymers by living atom transfer radical polymerization [7]. Ye et al. summarized the recent developments in

the area of Pd-diimine-catalyzed living ethylene polymerization [8].

Various monomers have been used for grafting onto various polyolefin backbones with different initiating systems. Jang et al. reported the UV-initiated radical graft polymerization of polypropylene fabrics. By grafting 2-hydroxyethyl methacrylate (HEMA) onto the polypropylene (PP) surface, the hydrophilic property of PP was significantly improved [9]. Grafting glycidyl methacrylate (GMA) onto the PP surface [10,11] is advantageous for the further modification of PP. The epoxy group of GMA is capable of reacting with many different functional groups, and the reactive compatibilization of PP/polyethylene terephthalate (PET) was improved while, at the same time, the blends exhibited better mechanical properties [12]. The heat distortion temperature and printing properties of PP can be improved by grafting styrene [13] and methyl methacrylate (MMA) [14–16] to the surface. The grafted PP can be used as a compatibilizer to improve the impact strength of its hybrid. However, most graft polymerizations must be carried out at high temperatures (i.e., $> 80^\circ\text{C}$) because the initiator must absorb energy to initiate the reaction. Usually, the use of these initiators is energy intensive, making them less attractive for industrial applications. Herein, we report a more convenient system that can be operated at room temperature for the grafting polymerization of vinyl monomers. Unlike commonly used initiators, diethylzinc (DEZ) shows superior properties for generating free radicals at low temperatures [17–19], which make it a promising initiator for materials that are

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prone to side reactions under high-temperature reaction conditions. This system does not require external stimulation such as corona discharge, plasma, or high temperatures. However, because DEZ is an unstable compound that is spontaneously flammable in air and vigorously hydrolyzed in water, it is challenging to carry out the radical graft polymerization of vinyl monomers using DEZ.

On the other hand, the reaction of DEZ with an N-donor ligand yields a Lewis acid–base complex, so it is expected that the stability of DEZ can be enhanced. Here, a complex of DEZ and 1,10-phenanthroline (Phen–DEZ) was synthesized using 1,10-phenanthroline as the N-donor ligand and the obtained Phen–DEZ complex is relatively stable and safe to handle. In this system, radicals are formed on the deactivated PP surface due to radicals generated from Phen–DEZ and oxygen, thus initiating the radical polymerization of the vinyl monomer and resulting in vinyl monomers grafted on the PP surface. In the present work, we provide a simple method to modify the PP surface by grafting in a one-step reaction under very mild conditions using MMA as the monomer.

2. Materials and experiment

2.1. Materials

The PP film was provided by Toyobo (Pylon Film-CT), washed in refluxing chloroform, and dried under vacuum. PP fiber was provided by Zetta Ltd. Methyl methacrylate (MMA) monomer was purchased from Wako Pure Chemical Industry, Ltd., and the stabilizer was removed by washing with sodium hydroxide (NaOH) solution followed by treatment with magnesium sulfate ($MgSO_4$). Diethylzinc was supplied by Nippon Aluminum Alkyls, Ltd. Hexane, toluene, 1,10-phenanthroline, tetrahydrofuran (THF), chloroform ($CHCl_3$), $MgSO_4$, and NaOH were purchased from Wako Pure Chemical Industry, Ltd.

2.2. Measurements

The Fourier transform infrared spectra (FT-IR) were obtained using a Jasco FT/IR-480 Plus spectrometer. Thermogravimetric analyses (TGA, Hitachi, STA 7200 RV) was carried out to determine the thermal stability of the films. The tests were performed in air from 25 to 550 °C (10 °C/min) at a flow rate of 25 mL min^{-1} . Size-exclusion chromatography (SEC) was performed with a Jasco PU-2080 Plus pump and an RI-2031 Plus Intelligent RI detector. $CHCl_3$ was used as the eluent. X-ray diffraction (XRD) patterns were recorded under ambient conditions with $Cu-K\alpha$ radiation. Raman spectra were obtained on an HR800 Horiba Raman spectrometer. Atomic force microscopy (AFM, Nanoscope II, Digital Instruments) was used to analyze the morphology of the grafted PP films. The contact angle study was analyzed using a portable contact angle analyzer (PGX). Scanning electron microscopy (SEM) images were obtained using a field emission (FE)-SEM (Hitachi SU-8020) microscope.

2.3. Synthesis of Phen–DEZ

The Phen–DEZ complex was synthesized in a 50 mL two-neck flask under the protection of argon gas. First, 1,10-phenanthroline (1080 mg) and hexane (20 mL) were added to the flask, and the mixture was gently stirred while diethyl zinc (0.7 mL) was slowly injected. After stirring the mixture for 24 h at 23 °C, the solution was filtered. The reddish-orange Phen–DEZ complex was treated by vacuum desiccation and the yield of Phen–DEZ complex was 90%.

2.4. Grafting and sample preparation

All the graft polymerization process was performed under an argon atmosphere. Several pieces of PP film (15 mg, 1 × 1 cm, 0.15 mm thickness)/PP fibers (50 mg) were placed in an oven-dried Schlenk flask

fitted with a stopcock. Then, toluene (3 mL) and Phen–DEZ (90 mg, 0.3 mmol) were added to the flask, followed by the monomer (6 mL), and the resulting solution was gently stirred for 24 h under argon. Subsequently, Phen–DEZ was reacted with diffused oxygen to form radicals. In this stage, graft polymerization of the monomer on the surface of PP and self-homopolymerization of the monomer occurred simultaneously. The free homopolymer was removed from the grafted PP by Soxhlet extraction with chloroform for 24 h. The grafting yield was calculated using the integration of FTIR absorbance peak area [20,21]. Different ratio of PP and PMMA were mixed and measured by FTIR. A linear relationship between the ratio of PP/PMMA and the area of reference peaks was obtained. The internal reference peaks at 2720 and 1732 cm^{-1} were used to determine the grafting yield of MMA. The percentage of grafting and homopolymer were estimated as follows:

$$\text{Graft yield (G)} = \frac{\text{Weight of PMMA grafted}}{\text{Weight of PP}} \times 100\%$$

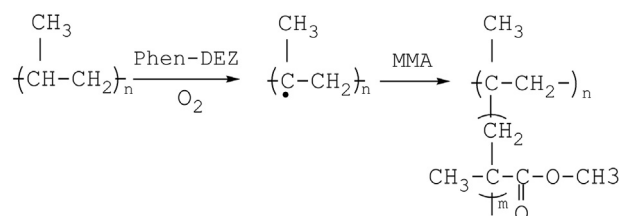
$$\text{Yield(homo)} = \frac{\text{Weight of homo PMMA}}{\text{Weight of MMA charged}} \times 100\%$$

3. Results and discussion

The graft polymerization was carried out in toluene solution and via bulk polymerization. Under both conditions, PP was miscible with the reaction solution. Moreover, weak van der Waals forces between DEZ and toluene result in the absorption of DEZ onto the PP surface. The reaction of DEZ with diffused oxygen produces free radicals, the radicals attacked the PP tertiary carbon atoms and formed active site, thus the MMA could be grafted to the surface of PP successfully. The reaction scheme for the graft polymerization is shown in Scheme 1.

The influences of various reaction conditions on the graft yield (G) were investigated by carrying out a series of graft polymerizations with different reaction times, solvents, and temperatures. Table 1 summarizes the results of graft polymerization obtained under various reaction conditions. Phen–DEZ can initiate graft polymerization at relatively low temperatures compared to commonly used initiators such as azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO), which require high reaction temperatures.

Graft polymerization in toluene solution at 23 °C for 24 h gave a grafting yield of 4.2% (Table 1, entry 1). On increasing the reaction time or temperature, the grafting yield improved to 6.4% and 5.8%, respectively. MMA could be grafted onto PP even by graft polymerization carried out at 0 °C under bulk polymerization conditions. That is, despite the absence of reactive sites on PP polymer chains, Phen–DEZ can also cleave some stable CH bonds at 0 °C and form radicals for the grafting reaction. In addition, the grafting yield was 7.6% at room temperature (23 °C), reaching a maximum (G = 27.0%) at 60 °C in the bulk system. The grafting yield increased with increase in the reaction temperature, and this was also observed for solution graft polymerization. By comparing the G of grafted PP prepared in solution and bulk, we can conclude that the grafting yield was affected by the monomer concentration. The SEC measurements of the homopolymer indicate that the molecular weight (M_w) of the PMMA prepared at 60 °C was 380,000, which is slightly lower than that obtained from the



Scheme 1. Mechanism of grafting polymerization process of MMA onto PP.

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