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AFM study of the morphologic change of HDPE surface photografted with glycidyl methacrylate

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ABSTRACT

The UV-induced grafting of glycidyl methacrylate (GMA) onto high-density polyethylene (HDPE) and the atomic force microscopy (AFM) study of the morphologic change of the grafted surface are reported. The grafting was carried out in GMA acetone solutions with different monomer concentrations. Grafting was much faster in a solution with a higher monomer concentration. FTIR analyses proved that GMA had been successfully grafted onto HDPE. The morphologies of grafted HDPE surfaces changed with UV irradiation time. The monomer concentration had a significant effect on the morphologies of the grafted HDPE surfaces. The HDPE surface grafted in a solution with a higher monomer concentration was much rougher than that grafted in a solution with a lower monomer concentration. The growth models of the grafted granules or clusters are also proposed.

1. Introduction

Most polyolefins are usually difficult to be bonded, coated, painted, colored, laminated and electroplated due to their hydrophobic and chemically inert surfaces. Many polymer surface modification methods have been developed in the last several decades in many fields of application. UV or photo-induced grafting has become a very popular technique for the modification and functionalization of polymeric materials due to its significant advantages [1–3].

Many monomers, such as methacrylic acid (MAA) [4–6], acrylic acid (AAc) [5,6], acrylamide (AAm) [7], *N*-isopropylacrylamide (NIPAAm) [7–9], 2-hydroxyethyl methacrylate (HEMA) [10], glycidyl methacrylate (GMA) [11,12], etc. have been photografted onto several polymeric materials surfaces to improve their wettability, adhesion, biocompatibility, and glycidyl methacrylate (GMA) is one of the commonly used monomers. The melt grafting or reactive extrusion grafting of GMA onto polymeric materials has been extensively studied to improve the compatibility of polymer blends [13,14]. The grafting of GMA onto polymeric materials can also be initiated by several other ways, such as chemical (peroxide) [15], high-energy irradiation [16] and photo or UV-induced initiation [17]. Because of the presence of epoxy group in GMA molecule, once GMA is grafted onto the surface of polymeric material, the epoxy group on GMA molecule can further react with other chemicals to endow the surface with properties as required [18–21].

Atomic force microscopy (AFM) is extremely useful for the studies of polymer surfaces, because it provides real-space polymer morphology and nanostructure [22]. The investigations have been performed on a large number of polymer samples [23–25] and polymer blends and related nanocomposites [26]. AFM has also been widely used to study the morphology of the grafted polymer surfaces [27,28] and the dynamic behavior and lateral structure of polymer brushes in water [29]. It was found that the surface roughness increases substantially with the graft concentrations, and is governed by UV-irradiation time and monomer concentration.

We have reported the gamma radiation-induced grafting of GMA onto HDPE [16] and the SEM study of the morphologies of the grafted surface [30]. It was found that monomer concentration had a significant effect on the grafting rate and the final adhesion property of grafted HDPE. The monomer concentration may affect the microstructure of the grafted chains and the morphology of the grafted surface, both are critical for adhesion property. However, since the surface must be coated with gold, the SEM investigations could not give the true information of where the grafting occurs and how the grafted chain grows. We have studied the microstructures of the grafted chains of the photografting of GMA onto HDPE surface carried out in different solvents [31] and the initiation rate of the surface photografting reaction [32] with AFM. These studies were carried out in the initial stage ($\leqslant 1$ min) of grafting reaction and the monomer concentration was usually low (1 mol/L). But there are not a detailed study on how the morphology of grafted

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surface changes from the beginning of grafting reaction and why monomer concentration has such a significant effect on the morphology of grafted surface.

In this article, we report the UV-induced grafting of GMA onto HDPE carried out in solutions with different monomer concentrations and the AFM studies of the morphologic change of the grafted surfaces, the growth models of the grafted granules or clusters are also proposed.

2. Materials and methods

2.1. Materials

High-density polyethylene (HDPE, Type 4000s) was supplied by Yanshan Petrochemical Co., Ltd., Beijing, China. HDPE films for grafting and AFM study were prepared by heating at 160 °C for 7 min and molded under a pressure of 20 MPa for 3 min and quenched immediately in tap water. Silicon wafer with roughness less than 1 nm was used. It was put on the bottom stainless steel plate with the smooth side facing up, and then the mold and granular HDPE were applied. The silicon wafer was carefully removed after quenching. The HDPE film (≈0.5 mm in thickness) was cut into 1 cm × 1 cm square samples, and then subjected to Soxhlet extraction with acetone for 24 h to remove impurities and additives before use.

Monomer glycidyl methacrylate (GMA, 97%) was from Mitsubishi Gas (Tokyo, Japan). Photoinitiator benzophenone (BP) (chemically pure grade) was from Yuanhang Chemicals Co. Ltd. (Tianjin, China). The solvent acetone (AR grade) was from Beijing Beihua Fine Chemicals Co. Ltd. (Beijing, China). All the chemicals were used without further purification.

2.2. UV equipment

The UV system with shutter assembly was supplied by Run-Wing Co. Ltd., Shenzhen, China. The input power of the high pressure mercury UV lamp was 2 kW. No filter was used to isolate UV light.

2.3. Grafting procedure

Photografting was carried out in an 8-cm-diameter Petri dish containing three HDPE samples with the smooth side facing up, 5.0 mL solution was added, and then the Petri dish was put into water bath and covered with quartz plate to prevent the evaporation of solution. The Petri dish was put at a fixed position 10 cm below the UV lamp, where the UV intensity was about 20 mW/cm^2 (250 ± 10 nm). The grafting reactions were carried out at room temperature, and the temperature increase during the grafting process was less than 5 °C.

The polymerized samples were Soxhlet extracted with acetone for 24 h to remove homopolymer and unreacted monomer, and then dried at 50 °C for 24 h.

The extent of grafting (G) was expressed as the weight increase per surface area of the sample, and was calculated from the following equation:

$$G = \frac{W_g - W_0}{S} \quad (\mu\text{g/cm}^2)$$

where W_g and W_0 are the weights of PE sample after and before grafting; S is the surface area of PE sample.

2.4. FTIR characterization

Transmission FTIR spectra were obtained from pristine HDPE film and HDPE films grafted with GMA on an Avatar-360 spectrometer (Nicolet Analytical Instruments, Madison, WI). The number of scans was 32 at a resolution of 4 cm^{-1}.

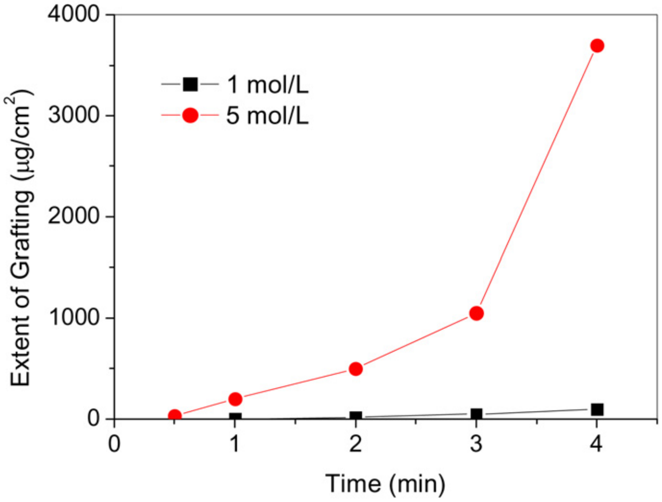

Fig. 1. The extent of grafting as a function of UV irradiation time. Grafting carried out in 1 mol/L and 5 mol/L GMA acetone solutions.

2.5. AFM measurement

AFM experiments were performed using a Digital Instruments multimode AFM equipped with a Nanoscope IIIa controller (Digital Instruments, Santa Barbara, CA). The results were obtained in tapping mode AFM. A vertical engage 4842 JV-scanner and Si probes were applied in all experiments. The driving frequency in tapping mode was chosen at the resonant frequency of the free-oscillating cantilever in the immediate vicinity of the sample surface. Height and phase images were recorded simultaneously.

The average roughness (R_a) of the PE surface was calculated directly from the AFM image.

3. Results and discussion

3.1. Grafting

The grafting of glycidyl methacrylate (GMA) onto HDPE has been carried out in 1 mol/L and 5 mol/L GMA acetone solution, 1% BP (mol/mol of monomer) was added as the photoinitiator.

As shown in Fig. 1, when the UV irradiation time was less than 0.5 min, there was no grafting possibly due to the retardation effect of inhibitor and/or the oxygen dissolved in the solution, but after then the extent of grafting increased with irradiation time. The monomer concentration had a significant effect on the photografting of GMA onto HDPE. When the monomer concentration was 1 mol/L, the extent of grafting was very low, only about 100 μg/cm^2, even after 4 min UV irradiation. However, when the monomer concentration was 5 mol/L, the extent of grafting increased almost linearly with UV irradiation time in 1–3 min, after then there was a rapid increase in extent of grafting from 3 to 4 min. The extent of grafting reached 3700 μg/cm^2 at 4 min.

3.2. FTIR characterization

FTIR spectroscopy is a convenient way to characterize the grafting of monomers with functional group(s) different to those of the polymeric substrate to be grafted. Fig. 2 shows the transmission FTIR spectra of pristine HDPE film and the grafted HDPE films. The FTIR spectrum of pristine PE has a very weak absorption band near 1743 cm^{-1} which is the characteristic absorption band of the carbonyl group (C=O) formed in HDPE due to the oxidation of HDPE in thermal processing and storage. In the FTIR spectra of the