

Atomic force microscopy study of the photografting of glycidyl methacrylate onto HDPE and the microstructure of the grafted chains

Huiliang Wang^{a,b}, Hugh R. Brown^{a,*}

^a *Engineering Faculty, University of Wollongong, Northfields Avenue, Wollongong, NSW 2522, Australia*

^b *College of Chemistry, Beijing Normal University, Beijing 100875, China*

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Abstract

This article presents an atomic force microscopy (AFM) study of the initial stage of the photografting of glycidyl methacrylate (GMA) onto high-density polyethylene (HDPE) surface and the microstructure of the grafted chains. The grafting was carried out in acetone, dichloromethane and tetrahydrofuran (THF), as well as without solvent. Granular structures were found on the surface of the samples grafted in the solvents. The height of the granules increased linearly with their diameter. Each granule was thought to be a single grafted chain with a highly branched (or superbranched) microstructure. The grafting density on HDPE was quite small when the grafting was carried out in the solvents. The grafted chains were more branched when grafting was carried out in THF than when the grafting was carried out in acetone and dichloromethane. The bulk (no solvent) grafting of GMA onto HDPE was much faster and more uniform than that carried out in the solvents. The thickness of the bulk grafted materials was a few nanometers after 30 s irradiation, and possibly, the grafting density was much higher and the grafted polymers were much less branched than those produced in solvent.

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1. Introduction

Photo-induced grafting has become a very popular technique for the modification and functionalization of polymeric materials due to its significant advantages, such as low cost of operation, mild reaction conditions, easy and controllable introduction of graft chains without affecting the bulk polymer, and the long-term stability of the grafted chains [1]. The technique involves initiation of the polymerization of vinyl or acrylic monomers at reactive sites generated usually through abstraction of hydrogen atoms from polymer surfaces by the excited triplet state of photoinitiator [2].

However, a major problem of conventional photografting is the difficulty in the control and characterization of both the grafting density (number of grafting sites per surface area) and the microstructure of graft polymer, including chain length

and branches, etc. In recent years, with the extensive research on controlled/living radical polymerization to precisely control the polymerization and the polymer structure [3], living radical graft polymerization onto polymeric materials has been developed and has drawn a lot of attention. Nitroxide stabilized free radical graft polymerization [4], typical and reverse atom transfer radical graft polymerization (ATRP) [5] and reversible addition-fragmentation chain-transfer (RAFT) graft polymerization [6] are the most widely used techniques. Yang and Rånby [7] and Ma et al. [8] developed two sequential ultraviolet (UV)-induced living graft polymerization methods to modify polymeric materials. Ma's method consists of two steps. In the first step, a surface initiator is formed on a substrate under UV irradiation in the presence of benzophenone (BP) solutions; in the second step, the monomers are grafted to the substrate by a living polymerization initiated by the surface photoinitiator. Therefore, grafting density and graft polymer chain length could be controlled independently since initiator formation and graft polymerization occur

* Corresponding author. Tel.: +61 2 42213820.

E-mail address: hbrown@uow.edu.au (H.R. Brown).

independently in the successive steps. Because of the unavoidable drawbacks of these controlled/living graft polymerization methods, such as the slow reaction speed and the strict reaction conditions, these methods are not commercialised yet although precisely controlled graft polymer can be obtained. Therefore, the study of the control and characterization of the microstructure of the conventionally grafted polymer is still of great importance.

To study the microstructure of the grafted polymer, first of all we need to know the location of the grafts, i.e., are they on the surface or in the bulk of polymer substrate? In this context we are concerned with the question of whether the majority of a grafted chain is within the bulk or on top of the substrate, not with the precise depth of the grafting point. The location can be simply observed by optical microscopy in some cases. Recently, Cardona et al. [9] used a micro-Raman spectroscopic technique to determine the penetration depth of the graft in the γ -radiation induced grafting of styrene onto polymer substrates in different solvents. They confirmed that the grafting takes place not only on the surface but also in the bulk of the substrates, and the increase in the overall degree of grafting was accompanied by a proportional increase in the amount of the grafts to be found within the bulk of the substrates.

Because the grafted polymer chains are chemically attached to the polymer substrate, there is no way to separate them non-destructively. Therefore, the microstructure of the grafted polymer cannot be measured by the convenient methods used for conventional homopolymers. Measurement of the water absorbency [10], adhesion [11] and some other final properties of the grafted layer can be used as indirect methods to elucidate the microstructure of the grafted polymer. For example, for the grafted samples with high adhesion in our previous work, the grafting density must be high and the grafted polymer chains must be long to permit inter-chain entanglement under hot-pressing [11]. However, there is not yet a direct method to characterize the microstructure of the grafted polymer. New methods need to be developed. Recently Yang and co-workers [12] used high-resolution solid state NMR and FTIR spectroscopy to characterize the microstructure of maleic anhydride grafted polyethylene.

Since its development in 1980s, atomic force microscopy (AFM) (otherwise and more correctly called scanning force microscopy) has become an advanced microscopic method for examining polymer materials. AFM is extremely useful for the study of polymer surfaces, because it provides real-space information on polymer morphology and nanostructure. Investigations have been performed on a large number of polymer samples [13]. Recent developments in the AFM characterization of polymers involve measurements at different temperatures [14], determination of local material properties and surface compositional mapping in heterogeneous samples. Furthermore, these techniques allow examination, not only of the top-most surface features, but also the underlying near-surface sample structure [13d].

AFM has also been widely used to study the morphology of the grafted polymer surfaces [15] and the dynamic behavior and lateral structure of polymer brushes in water [16]. For

example, Ikada et al. studied the topography of polymer chains, grafted on a polymer surface, in situations where water is a poor solvent [16a] and a good solvent for the polymer brushes [16b]. To our knowledge, no AFM studies specifically on the grafting process and the microstructure of the grafted polymer have been done. The purpose of this work is to investigate the grafted polymers formed in the initial stage of grafting, and shed some light on the microstructures of the grafted polymers.

2. Experimental section

2.1. Materials

High-density polyethylene (HDPE) supplied by Nova Chemicals Ltd., Ontario, Canada had a melt flow index (MFI) of 0.39 g/10 min, with a density of 0.949 g/cm³. HDPE films for grafting and AFM study were prepared by heating granules at 160 °C for 7 min before they were molded under a pressure of 20 MPa for 3 min against silicon wafers and quenched immediately in tap water. Silicon wafers with roughness less than 1 nm were used. A wafer was put on the bottom stainless steel molding plate with the smooth side facing up, and then the window-frame mold and granular HDPE were applied. The silicon wafer was carefully removed after quenching. The HDPE film (\approx 0.5 mm in thickness) was cut into 0.5 cm \times 0.5 cm square samples, and then subjected to Soxhlet extraction with acetone for 24 h to remove impurities and additives before use.

Solvents such as acetone, dichloromethane, tetrahydrofuran (THF) (all of AR grade), and monomer glycidyl methacrylate (GMA) (AR grade) were used without purification. Photoinitiator benzophenone (BP) (chemically pure grade) was used as received. All the chemicals were obtained from Sigma–Aldrich, Milwaukee, USA.

2.2. UV equipment

The UV system with shutter assembly was supplied by Amba Lamps Australasia Proprietary Limited, Sydney, Australia. The input power of the UV medium pressure mercury lamp was 2 kW. No filter was used to isolate UV light. The output UV intensity was measured by using UV Power Puck™ from Electronic Instrumentation and Technology, Inc., VA, USA. It measures the intensities of UVA (320–390 nm), UVB (280–320 nm), UVC (250–260 nm) and UVV (395–445 nm) simultaneously.

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 covered with polyethylene film to prevent the evaporation of solution. The Petri dish was put at a fixed position 4 cm below the focal point of the UV lamp, where the UVC intensity was 0.024 W/cm². The reaction temperature was not controlled or

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