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Aliphatic ketones/water/alcohol as a new photoinitiating system for the photografting of methacrylic acid onto high-density polyethylene

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Abstract

The photografting of methacrylic acid (MAA) onto high-density polyethylene (HDPE) initiated by aliphatic ketones, butanone, pentanone, heptanone, etc. has been reported. When these ketones were used alone or just with ethanol, grafting did not occur. However, grafting took place when a proper butanone/water/ethanol mixed solvent was used. When the volume ratio of butanone was fixed, the grafting of MAA onto HDPE became easier with an increase in the volume ratio of water. The grafting of MAA onto HDPE became easier and faster with a decrease in the volume ratio of butanone. The grafting rate increased with the increase of monomer concentration. The nature of the alcohol also affected the self-initiation by aliphatic ketone; ethanol was found to be better than methanol. Possibly, hydrogen bond formed between aliphatic ketone and water increases the energy and lifetime of the excited state of the ketone, permitting it to act as a grafting and polymerisation initiator. FTIR characterization of the grafted samples proves the successful grafting of MAA onto HDPE. The water absorbency of the grafted samples increased almost linearly with the extent of grafting both in air and in water. The PE films grafted in the butanone/water/ethanol solvent adsorbed approximately 30–40 mass% water per *p*-MAA.

Keywords: Graft copolymer; Aliphatic ketone; Initiation

1. Introduction

Photo-induced grafting has become a very popular technique for the modification and functionalization of the surfaces of polymeric materials due to its significant advantages over other methods, such as easy and controllable introduction of graft chains without affecting the bulk polymer, and due to the long-term stability of the grafted chains [1–5]. Much work has been done on the improvement of wettability of polyethylene surfaces (mostly low-density polyethylene, LDPE) by the photografting of hydrophilic monomers onto them. Methacrylic acid (MAA) and acrylic acid (AA) are the most commonly used monomers [6–8].

Normally, a grafting system consists of a polymer substrate, a monomer(s), a solvent, a photoinitiator and sometimes an additive(s). For a given polymer substrate and monomer, the solvent and the photoinitiator play an important role in the grafting. In most of the work done on photografting, benzophenone (BP) and its derivatives have been used as photoinitiators [6–8]. BP and most of its derivatives are not water-soluble, so they can only be used in organic solvents. The industrial applications of photografting technology are strongly impeded by the use of organic solvents which induce environmental problems. The development of water-soluble photoinitiators for UV curing of coatings and inks by the introduction of a positive or negative ionic group or a hydrophilic non-ionic group into the chemical structure of BP and anthraquinone has achieved some success in the past two decades [9]. However, the

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development of water-soluble photoinitiators for photografting seems to be difficult and slow as few reports can be found. Only in recent years some water-soluble photoinitiators such as (4-benzoyl benzyl) tri-methylammonium chloride (BTC), a water-soluble derivative of benzophenone, and anthraquinone-2-sulfonate sodium salt have been developed and used to initiate the photografting of acrylamide onto the surface of thin films of various hydrocarbon polymers or copolymers [10,11].

Aliphatic ketones have not been used as photoinitiators because of their low photoinitiation efficiencies [7]. The photoinitiation effect of aliphatic ketones was not known until the vapor photografting of acrylic acid onto polyethylene film without the use of a photoinitiator was reported [12]. In this case acetone acts as both solvent and photoinitiator. More importantly, acetone is miscible in water, therefore, it can be used as a water-soluble photoinitiator. In recent years, the acetone-initiated photografting of MAA onto LDPE film mainly in a water solvent was reported [13]. We [14,15] reported the acetone-initiated photografting of MAA and AA onto high-density polyethylene (HDPE) and the significant difference in the wettabilities between HDPE samples grafted in organic solvents (where BP is used as photoinitiator) and in acetone/water mixed solvents (where acetone acts as solvent and photoinitiator).

Other aliphatic ketones, such as butanone, pentanone, heptanone, etc., have very similar chemical structures to that of acetone. However, they become less soluble in water with increasing length of the alkyl chain and hence cannot be used to initiate photografting carried out in water. In addition when these ketones are used alone or with organic solvents, such as methanol or ethanol, they cannot initiate photografting. It has been found that the aliphatic ketones are soluble in mixed solvents of water and ethanol, and more importantly, they initiate photografting [16]. Aliphatic ketone/water/alcohol mixed solvents can be used as a new photoinitiating system for water-soluble photografting.

The grafting of MAA onto HDPE initiated by several aliphatic ketone/water/alcohol mixed solvents is described herein.

2. Experimental

2.1. Materials

High-density polyethylene (HDPE) was supplied by Nova Chemicals Ltd., Ontario, Canada; its melt flow index (MFI) is 0.39 g/10 min, with a density of 0.949 g/cm^3. The HDPE film (ca. 200 μm in thickness) was cut into 2 cm × 3 cm rectangular samples, and then subjected to Soxhlet extraction with acetone for 24 h to remove impurities and additives before use.

Aliphatic ketones, acetone, butanone, pentan-2-one, pentan-3-one and heptan-3-one, and solvents, methanol and ethanol (all are AR grade), were used without purification. Monomer, methacrylic acid (MAA, AR grade), was used without purification. 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 film samples and 5.0 mL of solution. The Petri dish was covered with polyethylene foil 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 is 0.024 W cm^{-2}. The reaction temperature was not controlled.

Because MAA is a water-soluble monomer, polymerized films were washed with water in an ultrasonic bath for 1 h and extracted with 90 °C water for at least 14 h to remove homopolymer and unreacted monomer, and then dried at 50 °C for 24 h. The extraction is known to be sufficient for removing most of the homopolymer in the film.

The extent of grafting (G), in μg/cm^2, was expressed as the weight increase per surface area of the sample, and was calculated from the following equation:

$$G = \frac{W_g - W_0}{S}$$

where W_g and W_0 are the weights of the PE sample after and before grafting; S is the surface area of PE sample. The mass was determined using an electronic balance (0.1 mg). Typical relative errors in G of three samples were ±5%.

2.4. FTIR characterization

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

2.5. Measurement of water absorbency of grafted PE films

Before the measurement of water absorbency, the grafted samples were dried in vacuum oven for 24 h and then weighed. To measure the water absorbed from air by the grafted samples, they were kept in air at room temperature for one month and weighed. To measure the water absorbed in water, a grafted film, weight (W_g, g), was immersed into deionized water at 50 °C for 48 h. After the treatment, excess water on the film surface was wiped off with tissue, and then the weight (W_s, g)