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Bulk graft modification of polyolefin membranes by combining pre-irradiation-induced graft and supercritical CO_2-swelling polymerization

Yi-Ming Wang [a], Yu Pan [a], Yi-Long Wang [a], Guang-Peng Wu [a], Yan-Juan Wang [a], Lev N. Nikitin [b], Xiao-Bing Lu [a,*]

[a] *State Key Laboratory of Fine Chemicals, Dalian University of Technology, 116012 Dalian, PR China*
[b] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Science, 119991 Moscow, Russia*

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Abstract

Uniform bulk graft modification of vinyl monomers to polypropylene or polyethylene membranes was achieved by combining gamma (γ)-ray pre-irradiation-induced graft copolymerization and supercritical carbon dioxide ($scCO_2$)-swelling polymerization techniques. In the first step, the polymer membranes were irradiated with γ-rays originated from cobalt-60 resource under oxygen or air atmosphere at ambient temperature, and thus potential active sites, hydroperoxides and diperoxides, were uniformly formed on the polymer backbone. Then, graft copolymerization of vinyl monomers such as styrene, *N*-vinylpyrrolidone (*N*-VP), methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) impregnated into polymer substrates with the aid of $scCO_2$ was initiated thermally within the host polymer by the polymer radicals ($PO^{\bullet}$) resulting from the decomposition of peroxides uniformly distributed in the irradiated polymer samples. The process parameters were controlled by the properties of the fluid phase (CO_2/monomer mixture) and experimental conditions, such as monomer concentration, temperature and time. The bulk graft modification of polyolefin membranes was confirmed by element analysis, spectroscopy and microscopy.

Keywords: Supercritical carbon dioxide ($scCO_2$); Pre-irradiation-induced graft copolymerization; $scCO_2$-swelling polymerization; Peroxide; Vinyl monomers; Polyolefin

1. Introduction

Polypropylene (PP) and polyethylene (PE) are by far the most widely used commercial polymers in the form of fabrics, fibers, films and plastics, due to their excellent chemical and physical properties along with low cost. However, the lack of reactive groups on saturated organic backbone and their inadequate compatibility with many other polymers have limited their end uses. To resolve this problem, most researchers have developed methods of chemical modification for the polymer backbone by introducing functional monomers via a graft-polymerization process in which functional monomers are covalently bonded to the polymer substrate, and then polymerization is used to generate side graft-chains that provide the desired properties. Among these methods, gamma-rays radiation-induced graft copolymerization is extensively used for chemical surface modification of preformed polymeric materials, due to its relative simple operation as well as lack of need for an initiator [1]. This method is well known for its merits in modifying the surface properties of pre-existing polymeric materials usually without changing their inherent properties. It is worth noting that radiation in high dose rate or high dose can cause degradation or crosslinking of some polymers. However, pre-irradiation-induced graft copolymerization can provide a method to combine two highly incompatible polymers [2,3]. Uniformly bulk graft modification of preformed polymer materials, especially with high viscosity or limited solubility, presents formidable challenges not normally encountered in their surface modification [3].

The use of supercritical carbon dioxide ($scCO_2$) as an alternative to traditional organic solvents has attracted interest in polymer syntheses and processing with regard to green chemistry [4–6]. Apart from its tunable physical properties and

* Corresponding author. Tel.: +86 411 88993864; fax: +86 411 88993848.
E-mail address: lxb-1999@163.com (X.-B. Lu).

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environmental advantages, the low viscosity of $scCO_2$ and its ability to plasticize glassy polymers have implications in polymer processing [7]. The use of a low viscosity supercritical fluid as medium is beneficial in decreasing solvent cage effects in free-radical initiator decompositions [8]. The swelling and plasticizing effects enable vinyl monomers, which are dissolved in the $scCO_2$, to diffuse into the internal layers of polymer substrates [7,9–11]. The unique properties associated with $scCO_2$ stimulated McCarthy and colleagues to develop an elegant method denoted as $scCO_2$-swelling polymerization for preparing polymer blends with $scCO_2$ as both a solvent and a swelling agent [12–15]. Various polymer blends have been successfully prepared by this method [16–22]. The general procedure has been to use $scCO_2$ as a swelling agent to impregnate a CO_2-insoluble polymeric host with a mixture of monomers and an initiator. Polymerization is then initiated thermally (up to 120 °C) within the host polymer to form a blend, either in the presence of $scCO_2$ or after venting the CO_2 replacement with N_2. Unfortunately, no evidence of grafting has been observed [13], and transmission electron microscopy (TEM) reveals that the formed polystyrene (PS) homopolymer exists as discrete phase-segregated regions throughout the thickness of the polymer substrates. An attempt of gamma radiation induced maleation of polypropylene was carried out by the charging of maleic anhydride and dicumyl peroxide into polypropylene matrices using $scCO_2$ and then through gamma radiation at CO_2 atmosphere of 0.1 MPa and 25 °C, but the grafting yield is very low because of a limited amount of monomer available in the polymer substrate [23]. Filardo et al. have designed an apparatus for gamma radiation carboxylation of LDPE and high-pressure gamma-rays initiated dispersion polymerization of MMA in dense CO_2 [24,25].

Herein, we describe a versatile route to uniformly bulk graft modification of polyolefin membranes by the combination of pre-irradiation-induced graft copolymerization and $scCO_2$-swelling polymerization techniques (Fig. 1). Thus, the polymer samples were first irradiated with gamma (γ) rays originated from cobalt-60 resource under oxygen atmosphere at ambient temperature, and then potential active sites, hydroperoxides and diperoxides, were uniformly formed on polymer backbone [26]. In the following step, graft copolymerization of vinyl monomers impregnated into polymer substrates with the aid of $scCO_2$ is initiated thermally within the host polymer by the polymer radicals ($PO^{\bullet}$) resulted from the decomposition of peroxides uniformly distributed in the irradiated polymer samples. Our strategy takes advantage of the fact that γ-ray has high penetration depth to various polymers and will lead to a uniform distribution of radical initiating sites on polymer backbone throughout the thickness of the irradiated samples. On the other hand, a key advantage of the use of $scCO_2$ is that the presence of CO_2 does not interfere with the chain-growth process during polymerization [27].

2. Experimental

2.1. Materials

Polypropylene (PP) (~65% crystallinity) and low-density polyethylene (LDPE) without any additive were kindly provided by Liaoyang Petrochemical Corporation Ltd. PP and LDPE membranes with a thickness of 2–5 mm were prepared by

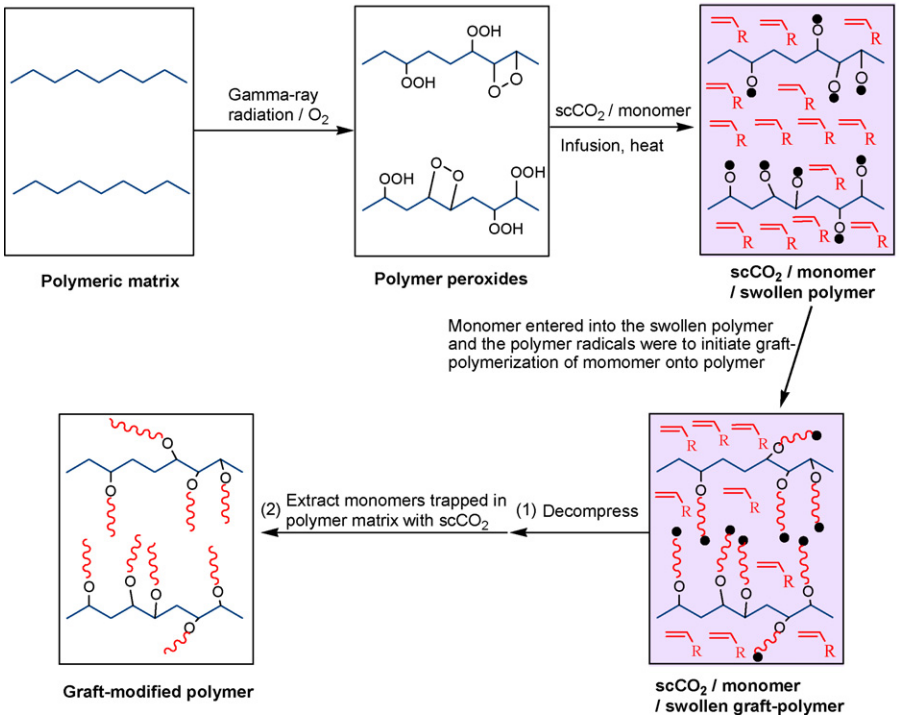

Fig. 1. Schematic representation of bulk graft modification of vinyl monomers onto polyolefin membranes by combining pre-irradiation-induced graft copolymerization and $scCO_2$-swelling polymerization techniques.