Available online at www.sciencedirect.com

SCIENCE DIRECT®

Reactive & Functional Polymers 66 (2006) 984–992

REACTIVE & FUNCTIONAL POLYMERS

www.elsevier.com/locate/react

Neodymium oxide co-catalyzed melt free radical grafting of maleic anhydride onto co-polypropylene by reactive extrusion

Lianchao Zhu [a,b], Gongben Tang [a], Qiang Shi [a,b], Chuanlun Cai [a,b], Jinghua Yin [a,*]

[a] *State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625, Renmin Street, Changchun 130022, People's Republic of China*

[b] *Graduate School of the Chinese Academy of Science, Beijing 100039, People's Republic of China*

Received 19 June 2005; received in revised form 22 December 2005; accepted 21 January 2006
Available online 7 March 2006

Abstract

Rare earth oxide, neodymium oxide (Nd_2O_3), co-catalyzed melt grafting of maleic anhydride (MAH) onto co-polypropylene (co-PP) in the presence of dicumyl peroxide (DCP) was carried out by reactive extrusion. The experimental results reveal that the addition of Nd_2O_3 as a coagent leads to an enhancement in both MFR and the grafting degree of MAH, along with a simultaneous decrease in the gel content. When the Nd_2O_3 concentration is 6.0 mmol%, the increment of the grafting degree of MAH maximally is up to about 20% compared with the related system without adding Nd_2O_3, and the gel content decreases simultaneously to a very low level of about 3%. Attenuated total reflection FTIR (ATR-FTIR) indicates that the gel in the graft copolymers mainly arise from the cross-linking reaction between ethylene units of co-PP. A reasonable reaction mechanism has been put forward on the basis of our experimental results and other mechanisms reported in the literature. We also tentatively explain above results by means of synergistic effect between DCP and Nd_2O_3, which causes a higher concentration of the macroradical, in particular the tertiary macroradical.

Keywords: Graft copolymers; Co-polypropylene; Rare earth oxide; Reactive extrusion; Synergistic effect

---

1. Introduction

Organic peroxides are generally used as initiators for melt free radical grafting of unsaturated monomer onto polyolefin. A variety of factors need to be considered while selecting an initiator for the grafting experiment: the initiator decomposition rate (or half-life time); the reactivity and specificity of initiator-derived radicals towards the polyolefin substrate, the monomer, the initiator, and other components present in the melt; the initiator concentration to be used; the initiator solubility and its partition coefficient between the various phases; and the extent of cage reaction [1]. Melt grafting of MAH onto polyolefins was generally initiated by DCP for its low cost and easy operation. The half-life time of DCP depends mainly on its molecule structure and the processing temperature, says, 60 s at 175 °C. One can imagine that it would be difficult to disperse small fractions of low-viscosity

---

[*] Corresponding author. Tel.: +86 4315262109; fax: +86 4315262126.

E-mail address: yinjh@ciac.jl.cn (J. Yin).

1381-5148/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.reactfunctpolym.2006.01.007

MAH and DCP into highly viscous polyolefins melt in the limited residence time due to the difference between solubility parameters. A consequence is that the grafting reaction was accompanied by undesirable side reactions in the presence of peroxide initiator, chain scission in PP and cross-linking in polyethylene (PE) even the simultaneous existence of scission and cross-linking in ethylene-polypropylene copolymer [2–6]. More importantly, the grafting degree and the grafting efficiency of MAH were relatively low and homopolymerization of MAH was also hardly evitable.

Numerous works [7–10] attest that attempts to maximize grafting degree of monomer by simply increasing the initiator concentration are likely to be counterproductive because of the consequent increase in the extent of side reactions. In contrast, other strategies [1], for example, improving the mixing efficiency and thereby controlling the local monomer concentration, and adding appropriate coagents, can act to improve both the grafting degree and minimise the extent of side reactions. For instance, Gaylord [7] had reported some nitrogen-, phosphorus-, and sulfur-containing compounds that depressed both homopolymerization of MAH and degradation or cross-linking of the substrate polymer during melt grafting of MAH to a variety of polymers. Recently, Li et al. [11] also reported that the addition of styrene as a second monomer in the melt grafting system reduces the PP chain scission and increases the grafting degree of MAH.

The rare earth metals are, by definition, the Group IIIB elements Sc, Y, La and the 14 lanthanides, Ce–Lu. The principle interest in these elements is those properties that depend on the occupancy of the 4f electron shell, from 0 (La) to 14 (Lu) [12]. Since the middle of twenty centuries, many studies had been carried out on the graft copolymerization initiated by ceric ion redox systems in solution [13–16]. In our previous work [17,18], we tentatively introduced many kinds of rare earth compounds into the reactive system of melt free radical grafting of MAH onto polyolefins with the aim of increasing the grafting degree of MAH and inhibiting cross-linking and/or scission side reactions of the polyolefin matrix. The experimental results showed that some rare earth oxides, such as neodymium oxide (Nd_2O_3) and ceria (CeO_2) can serve as the co-catalyst and promote the grafting reaction somewhat. Here, we introduce Nd_2O_3 into the system of melt free radical grafting of MAH onto co-PP to investigate the influence of Nd_2O_3 on the grafting reaction. By summarizing the main reactions reported in the literature for grafting MAH onto PP or PE in the presence of organic peroxide, we put forward the reasonable reaction mechanism for this reactive system. We also explain the experimental results by tentatively proposing a synergistic effect between DCP and Nd_2O_3.

2. Experimental

2.1. Materials

The sample of co-PP, P340, was commercially obtained from Panjin Petrochemical Co., Panjin, China. It has ca. 5% ethylene content, a density of 0.91 g/cm^3 and MFR of 3.3 g/10 min (ASTM D-1238). Nd_2O_3 was prepared by ball milling in our laboratory, which purity was more than 99.9% and average particle size was less than 1 μm. DCP, reagent grade, was obtained from Shanghai Dongyi Chemical Agent Co., China, which was dried at room temperature under 0.02 MPa. MAH, reagent grade, was purchased from Beijing Yili Chemical Agent Co., China. Xylene, acetone, ethanol, potassium hydroxide, etc., were all reagent grades and used without further purification.

2.2. Preparation and purification of PP–g-MAH copolymers

PP–g-MAH samples were prepared by using a home-made co-rotating twin-screw extruder. The diameter of the screw is 30 mm and the ratio of length to diameter, L/D, is 44. The barrel of extruder is divided into 11 segments and each segment is heated independently, which the fluctuation of temperature is within ±5 °C. Temperatures of feeding zone, mixing zone, reacting zone and exit die were 175, 200, 200, and 190 °C, respectively. Rotating rates of the feeder screw and the main screw were 30 and 130 rpm, respectively, leading to a residence time of about 95 s. The mixture of co-PP (100 wt.), MAH (2 wt.), DCP (0.2 wt.) and Nd_2O_3 (0–9.0 mmol, abbreviates to 0–9.0 mmol%) was added through the main feeder and the obtained extrude was palletized after reactive extrusion. In order to verify the grafting reaction, a blank sample was prepared by the same procedures only without DCP and Nd_2O_3.

The PP–g-MAH is xylene-soluble and acetone-insoluble, while the oligomer of MAH if present