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Free-radical grafting of co-monomer systems onto an ester-containing polymer

V.M. Hoo, R.A. Whitney*, W.E. Baker[1]

Department of Chemistry, Queen's University, Kingston, ON, Canada K7L 3N6

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Abstract

Maleic anhydride was melt-grafted onto poly(ethylene-*co*-methyl acrylate) using a free-radical initiator, Lupersol 231, in an internal batch mixer at 140°C. The grafting was conducted in the presence of a second monomer (synergistic co-monomer): vinyl 4-*t*-butylbenzoate, styrene or 1-dodecene. The effects of varying monomer:co-monomer ratio and the initiator concentration on the weight percent of anhydride grafted were examined; melt flow indices were determined as an indicator of crosslinking. It was observed that styrene and vinyl 4-*tert*-butylbenzoate could be used to significantly increase the amount of anhydride grafted.

Keywords: Poly(ethylene-*co*-methyl acrylate); Maleic anhydride; Free-radical grafting

1. Introduction

Free-radical grafting is a commonly employed method of introducing reactive functional groups onto polymeric materials [1]. The chemistry associated with specific functional groups may change the properties of the graft-modified polymer and potentially improve its usability in applications requiring reactivity, paint-ability, adhesion, stability or impact strength.

One graft-modified polymer of great interest is the maleic anhydride (MAn) grafted polyolefin system [2–4]. MAn is an excellent candidate for free-radical grafting for several reasons: it contains a double bond that is susceptible to radical reactivity, the grafted MAn provides a highly reactive functional group for subsequent chemical modification, and MAn does not readily homopolymerise under grafting conditions [5]. Grafting of MAn is easily implemented in both batch mixer [6] and screw extruder [7] systems. Unfortunately, melt grafting is limited by obstacles such as poor monomer conversion, changes in polymer structure (crosslinking, e.g. ethylene–propylene co-polymer rubber [8] and low-density polyethylene (LDPE) [9], and β-scission, e.g. polypropylene (PP) [10]) and phase separation of the monomer from the polymer melt.

Recently, research has been conducted on the effects of simultaneously grafting two monomers onto polymer substrates by various grafting methodologies. For example, systems of methacrylic acid and *N*,*N*′-methylene-bisacrylamide, methacrylic acid and trimethylol propane triacrylate [11], and acrylic acid and *N*-isopropylacrylamide [12] have been photo-grafted onto LDPE film. These systems were examined for their effect on water absorbency. Acrylamide and MAn have been grafted onto poly(ethylene terephthalate) fibres [13] with azobisisobutyronitrile to improve dye-ability. Also, γ-radiation has been used as an initiator for the graft polymerisation of acrylonitrile and 4-vinylpyridine onto isotactic polypropylene (i-PP) [14] as well as methyl acrylate and 4-vinylpyridine onto polyethylene (PE) [15] via the pre-irradiation method in an aqueous medium.

Recently an examination of the grafting of MAn/co-monomer systems onto high-density polyethylene (HDPE) has been conducted [16] in an attempt to develop polyolefin/polyamide compatibilisation agents. The study focused on comparing the utility of several types of co-monomers such as: (i) vinyl monomers (styrene, acrylic acid); (ii) esters of unsaturated dicarboxylic acids; and (iii) ethylenically unsaturated cyclic dicarboxylic anhydrides. It was concluded that styrene was the most effective in increasing the amount of anhydride grafted onto HDPE.

Other research groups have investigated the free-radical grafting of glycidyl methacrylate (GMA) and styrene onto PP in a batch mixer in order to determine the effect of

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* Corresponding author. Tel.: +1-613-533-2616. Ext.: 2641; fax: +1-613-533-6669.

E-mail address: whitney@chem.queensu.ca (R.A. Whitney).

[1] Current address: AT Plastics, Brampton, Ontario, Canada.

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Table 1
Melt flow indices (data obtained on unpurified samples; TC-130 has an MFI of 20 dg/min)

MAn: co-monomer ratio	Initiator concentration (%)	No co-monomer	Vinyl 4-*tert*-butylbenzoate	Styrene	1-dodecene
1.00:0.25	0.250	11	12	1	10
1.00:0.50	0.250	13	16	1	11
1.00:0.75	0.250	13	1	1	13
1.00:1.00	0.250	15	[a]	2	17
1.00:1.25	0.250	12	[a]	4	14
1.00:1.50	0.250	13	[a]	4	19
0	0.000	–	31	22	30
1:00:1.00	0.125	10	17	10	22
1.00:1.00	0.250	9	0	1	17
1.00:1.00	0.500	5	[a]	0	8
1.00:1.00	0.750	1	[a]	[a]	4
1.00:1.00	1.000	1	[a]	[a]	3

[a] Material was highly crosslinked (determined from torque values), MFI not evaluated.

styrene on the degree of grafting of GMA onto PP in a polymer melt [17–19]. Research efforts have also been focused on the reactive extrusion of PP/co-monomer systems. In one study [20], electron-donating co-monomers such as styrene, or co-monomers that could form Diels–Alder adducts with MAn, were used to increase MAn grafting.

In this communication, the effect of grafting both MAn and a synergistic co-monomer onto poly(ethylene-*co*-methyl acrylate) (EMA) by free-radical grafting using Lupersol 231 (L-231) in an internal batch mixer was investigated. The co-monomers studied were vinyl 4-*tert*-butylbenzoate (VBB), styrene and 1-dodecene (DD), all electron-donating co-monomers intended to complement the reactivity of MAn. Both the effects of varying co-monomer:MAn ratio and initiator concentrations on anhydride weight percent incorporation were examined. Melt flow indices (MFI) were determined to estimate the extent of crosslinking in the modified polymers.

2. Experimental

2.1. Materials

MAn (Aldrich Chemical Co., 99%) was re-crystallised from chloroform. VBB (Aldrich Chemical Co., 99%) and DD (Aldrich Chemical Co., 99%) were used as received. Styrene (Aldrich Chemical Co., 99%) was stored under refrigeration and filtered through alumina prior to use. L-231 (Atochem, 90%), 1,1-di(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane, was stored refrigerated and used as received. EMA (Exxon TC-130, 21 wt% methyl acrylate, MFI = 20 dg/min) was used as received.

2.2. Free-radical melt grafting

All grafting reactions were carried out in a Haake Buchler Rheomix 600 internal batch mixer (50 cm^3) driven by a Haake Rheocord System 40 microprocessor (140°C, 100 rpm). The EMA pellets (38.4 g) were first added to the melting chamber and allowed to melt while mixing for 2 min, after which the MAn (1.6 g, 4 wt%) was added. After 1 min of further mixing, the co-monomer was added. After an additional minute of mixing, the L-231 was added. The reaction was allowed to proceed for 25 min (approximately $6t_{(1/2)}$ of the initiator), then the polymer melt was removed from the batch mixer, cooled to room temperature and stored in a sealed container.

2.3. Purification

The modified polymer (5 g) was dissolved in boiling toluene (150 ml) and then precipitated by drop-wise addition to acetone (400 ml) at room temperature. The grafted polymer was filtered from the solution and was then vacuum dried at 80°C for 24 h to remove any remaining solvent from the polymer.

2.4. Calibration curve

The calibration curve for weight percent anhydride was produced using blends of EMA and 2-dodecen-1-ylsuccinic anhydride (DoSAn, vacuum distillation at 0.5 mm Hg, 130°C; 37 wt% anhydride). Pre-determined weight percents of DoSAn were calibrated against IR spectra peak-area-ratios of 1788–718 cm^{-1}. The weight percents of anhydride were confirmed by titration [7]: blends of EMA (1.5 g) and distilled DoSAn were dissolved in boiling solutions of toluene (150 ml) and methanol (1 ml) for 10 min. Indicator was added (1% thymol blue in methanol, 5 drops) then the solutions were titrated with tetra-*n*-butylammonium hydroxide (0.1 N in toluene/methanol).

2.5. Characterisation—infrared spectroscopy

The infrared (IR) spectra for the crude and purified polymer were recorded on a Bomem-MB 1200 FTIR spectrophotometer. Polymer films were pressed at 120°C

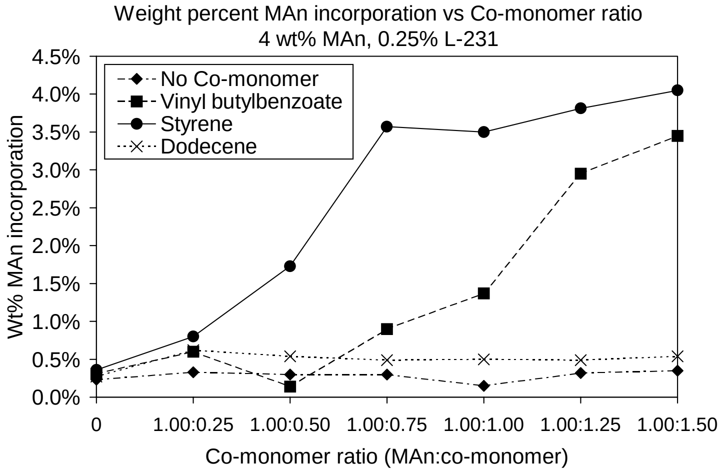

Fig. 1. Effect of increasing co-monomer:MAn ratio on anhydride grafting: ◆ no co-monomer; ■ vinyl 4-*tert*-butylbenzoate; ● styrene; × 1-dodecene (data obtained from purified samples).

and 40 000 psi. Weight percent anhydride in the crude and purified polymers was determined by determining the peak-area-ratio of the peaks at 1788 and 718 cm^{-1} and interpolation from the calibration curve values.

2.6. Melt flow indices

The Tinius Olson Extrusion Plastometer (melt indexer) was charged with the crude polymer (8 g); MFI values were collected as per ASTM D1238 [21] (190°C under 2.16 kg). The MFI for highly crosslinked samples could not be collected since samples could not be extruded from the melting chamber under the given temperature and weight conditions.

3. Results

The styrene and VBB systems were characterised by low MFI values while high MFI values were observed for systems where either no co-monomer or DD was used, regardless of manipulated variable (Table 1). It should be noted that in all systems, the MFI dropped with increasing initiator concentration. However, it can be observed that with increasing co-monomer:MAn ratio and constant initiator concentration, the MFI increased for the DD and styrene systems, but decreased for the VBB system.

The effect of increasing co-monomer:MAn ratio was examined for the reaction conditions of 4 wt% MAn, 0.25% L-231 (v/w), and with the MAn:co-monomer ratio ranging from 1:0.25 to 1:1.50 (Fig. 1). With increasing co-monomer:MAn ratio, the weight percent of incorporated anhydride increases for both the styrene and VBB system, with the styrene system resulting in the highest and VBB system the second-highest incorporation. It should be noted that the DD system shows slightly higher anhydride incorporation than in the absence of a co-monomer, but

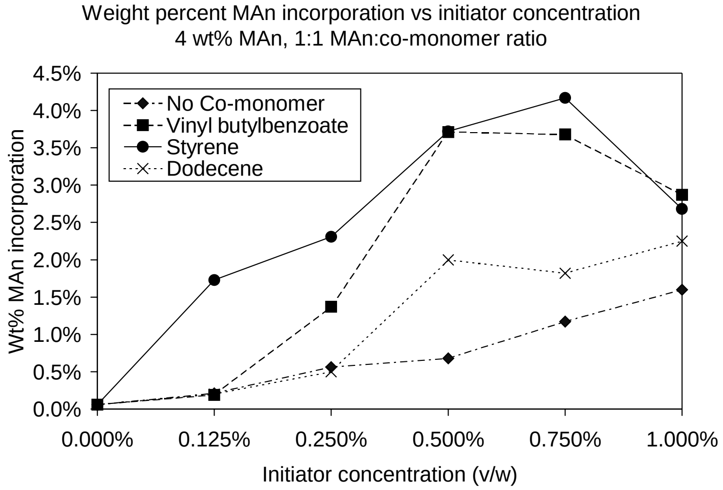

Fig. 2. Effect of increasing initiator concentration on anhydride grafting: ◆ no co-monomer; ■ vinyl 4-*tert*-butylbenzoate; ● styrene; × 1-dodecene (data obtained from purified samples).

the incorporation does not increase with increasing co-monomer:MAn ratio.

The effect of increasing initiator concentration was studied for the reaction conditions of 4 wt% MAn, 1:1 MAn:co-monomer ratio and initiator concentration ranging from 0.125 to 1.00% L-231 (v/w) (Fig. 2). In the absence of a co-monomer, the amount of incorporated anhydride increases with increasing initiator concentration. This is also observed for the DD system, with values being greater than those obtained when no co-monomer is present. The styrene system resulted in the greatest while the VBB system resulted in the second-greatest anhydride incorporation; both systems achieved a maximum incorporation value when initiator concentration was at 0.750% L-231 (v/w).

4. Discussion

Regardless of the manipulated variable, the styrene co-monomer system resulted in the greatest anhydride incorporation. Not only did weight percent anhydride increase with increasing styrene:MAn ratio, it also increased with increasing initiator concentration (although it reaches a maximum). It is conceivable that when both styrene and MAn are grafted onto EMA, the styrene reacts with the EMA macro-radicals at a greater rate than the MAn monomer thereby producing a styryl macro-radical. The MAn monomers then react readily with the styryl macro-radicals, resulting in an overall synergistic effect. As a result, the EMA polymer would likely be grafted with styrene:MAn oligomeric grafts.

This ‘co-monomer effect’ was proposed by Sun et al. for the grafting of GMA and styrene onto PP [20]. In this system, it was suggested that styrene monomers reacted more quickly than GMA monomers with the PP macro-radicals. This styrene grafting was then followed by the preferential reaction of the GMA to the newly formed styryl radical sites than to the PP macro-radicals. For this ‘co-monomer effect’ to be synergistic, the overall PP–styrene–GMA reaction proceeds more rapidly than GMA reacting with PP macro-radicals alone.

The ‘co-monomer effect’ also explains the increased grafting of MAn in the VBB system. In this system, the VBB monomer would first graft onto EMA radicals, followed by MAn grafting onto the new macro-radical sites on the VBB. However, in this case, the grafting is accompanied with greater crosslinking than that of the styrene system (lower MFI values). Due to processing difficulties (increased viscosity), there may have been less mixing in the VBB system resulting in poorer migration of both VBB and MAn to radical sites, leading to an overall decreased anhydride incorporation when compared to the styrene system.

With increasing initiator concentration in both the styrene and VBB systems, maximum anhydride incorporation was observed. Further, with increasing initiator concentration, the MFI values decreased (indicating poorer melt mixing). Should poorer mixing with increasing initiator concentration have occurred, a maximum anhydride incorporation in both the VBB and styrene systems could have been the result of the competition between increasing monomer migration restraints and the increasing availability of radical sites. It can be hypothesised that this would result in a decrease in anhydride incorporation above a specific initiator concentration due to insufficient mixing in a crosslinked polymer melt.

One of the major differences in the DD system was the dramatic increase in MFI values. The DD monomer may have been acting as a plasticiser in the melt and was likely not involved in the MAn grafting. This may explain why the anhydride incorporation did not increase with increasing DD:MAn ratio. Although the anhydride incorporation was greater than that in the absence of a co-monomer, it did not increase with increasing DD concentration because the DD monomer did not play a role in MAn grafting. Instead, the DD may have acted as a plasticiser and may have allowed greater migration of MAn units to EMA macro-radical sites during the grafting reaction and would have resulted in increased anhydride incorporation than in the absence of a co-monomer.

In addition, there was no maximum anhydride incorporation value for the DD system when initiator concentration was increased. In this situation, the presence of DD resulted in greater MFI values, indicating greater processability of the polymer, and potentially suggesting increased mixing of the reactants. Unlike the styrene and VBB systems where increased initiator concentrations resulted in crosslinking (and potentially restrained monomer migration to the macro-radical sites), the DD may have sufficiently plasticised the polymer melt. As a result, the MAn monomers were free to migrate to the macro-radical sites regardless of the increased initiator concentration; anhydride incorporation increased with increased initiator concentration and number of macro-radical sites.

5. Conclusion

Co-monomer systems can be used to improve the grafting of MAn onto an EMA co-polymer. The choice of co-monomer, co-monomer:MAn ratio, and initiator concentration, and the processability of the polymer all have an effect on melt grafting. Styrene and vinyl 4-*tert*-butylbenzoate can be used to increase the amount of anhydride incorporated during EMA graft modification through a synergistic co-monomer effect while 1-dodecene appears to exhibit primarily a plasticiser effect.

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