

Glycidyl Methacrylate–Grafted Linear Low-Density Polyethylene Fabrication and Application for Polyester/Polyethylene Bonding

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ABSTRACT: The grafting of glycidyl methacrylate (GMA) onto linear low-density polyethylene (LLDPE) was investigated. The grafting was performed by free-radical grafting in the melt state in a twin-screw extruder using an organic peroxide as initiator. The effect of initial GMA and peroxide concentration, styrene comonomer addition, as well as initial resin viscosity, on the final content in grafted moieties, unbound homopolymer, and unreacted monomer was assessed. The effect of process parameters such as flow rate, screw rotation speed, and barrel temperature was also investigated. Chemical composition was shown to be the main parameter for controlling grafting level and grafting efficiency. Grafting levels up to 1.8% and efficiency of 90% were reported even though in most conditions, the graft efficiency

was severely decreased by the homopolymerization of GMA into polyGMA chains not bound to LLDPE. Finally, the effect of grafting level and the presence of unbound GMA-based species on the efficiency GMA-grafted LLDPE as adhesive between polyethylene and polyester were discussed. Good adhesion to poly(ethylene terephthalate) copolymer was found for low viscosity grafted polyethylene resins. A significant improvement in adhesive strength on polyester was observed when the molecular weight of the grafted LLDPE was increased. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3180–3191, 2004

Key words: functionalization of polymers; reactive extrusion; free-radical grafting; adhesion; chain

INTRODUCTION

Free-radical grafting of polyolefin has been widely studied.¹ Use of modified resins bearing reactive groups is an easy way to promote interaction between polyolefins and other polar materials. Efficient coupling is usually required in mineral-reinforced systems, polymer blends, and coextruded products, where adhesion between the different phases determines to a great extent the properties of the final product. Acrylic acid (AA) and maleic anhydride (MAH) grafted polyolefins are commercially available products. For example, they efficiently react with amine end groups and promote adhesion in polyamide/polyolefin systems. However, their nonreactivity with the carbonyl end groups and their low reactivity with the hydroxyl end groups of polyesters have prompted research on the grafting of other vinyl monomers.

Glycidyl methacrylate (GMA) has shown good potential as a reactive monomer for polyolefin modification. Unfortunately, only low grafting efficiency has been obtained so far. The low reactivity of GMA toward polyolefin macroradicals and its natural ten-

dency toward homopolymerization explain this observation. Grafting is usually done by adding a free-radical initiator to a mixture of GMA and polyolefin, although polyolefins are very sensitive to free radicals. Depending on the nature of the polyolefin used, free-radical-induced side reactions will widely differ. In the case of polyethylene, the major side reaction is branching and crosslinking of the polymer.¹ In the case of polypropylene, free radicals generate tertiary radicals that evolve into β -chain scission. The molecular weight then decreases, leading to a decrease of the viscosity. For ethylene/propylene copolymers, both crosslinking and chain-scission phenomena can occur. For example, Machado et al.² showed that the crosslinking is favored in copolymers containing up to 70% propylene. For higher propylene content copolymers, chain scission outweighs crosslinking reactions leading to molecular weight decrease.

It was generally found that an increase in the initiator content, usually an organic peroxide, increases the amount of GMA being grafted during reactive extrusion. The grafted GMA content increases with the initiator content,^{3–18} often to a plateau value as reported in some studies.^{5,9–13,15} Unfortunately, this is accompanied by an increase of the side-reaction rate resulting in molecular weight changes.^{5,7,8,10–16,19}

The GMA grafting level can also be enhanced by increasing the initial GMA concentration.^{3,4,6–11,13,16,17,20} Some authors also report a plateau value in the depen-

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dency of the grafting level to the initial GMA content.^{9–11,13} A higher initial GMA concentration increases the number of GMA molecules available per free radical. This favors both the grafting and the homopolymerization reactions, that latter of which is an undesirable side reaction. Because part of the radicals are used by the polymerization reaction, less chain scission or crosslinking is observed in the presence of higher initial GMA concentrations. Overall, the efficiency of the grafting reaction (the ratio between the grafted and the initial GMA) decreases, leading to higher unbound GMA concentrations and greater demand on the devolatilization process.¹³

Studies have shown that the addition of a comonomer selected for its affinity for the macroradicals and its capacity to copolymerize with GMA can increase the grafted GMA content.^{10,15} Styrene-assisted GMA grafting onto polypropylene (PP), for example, was reported to increase the grafted GMA content and, at the same time, to decrease chain scission.^{5,8,10} In polyethylene (PE) and ethylene propylene rubber (EPR), styrene was also effective for improving the grafting level but it was less useful for preventing the crosslinking reaction.^{11,13,14,16}

Few attempts have been made to understand the effect of processing parameters on the free-radical grafting of polyolefins and most of these studies were carried out with maleic anhydride (MAH). Callais and Kazmierczak^{21,22} studied the free-radical grafting of MAH on low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and PP in a single-screw extruder. They found that LDPE was easier to functionalize than LLDPE. The grafted level increased by lowering the screw speed. The grafting level increased with temperature for LDPE, whereas it remained unchanged for LLDPE. These same parameters had little influence on the grafted level onto PP. Ganzeveld and Janssen,²³ studying the grafting of MAH on HDPE, found that the conversion went through a minimum as the screw speed was increased. This was interpreted as the result of competing effects: the improvement of mixing and the decrease of the residence time as a function of screw speed. They also found that the grafting level increased with temperature but was limited by the effective temperature range of the initiator. Oostenbrink and Gaymans²⁴ found that the MAH grafting level onto EPDM decreased with the throughput and the barrel temperature of the twin-screw extruder.

While investigating the free-radical grafting of GMA onto PP and PE in a twin-screw extruder, Sun et al.¹⁷ and Cartier and Hu¹⁸ found that the grafting level decreased with the screw rotation rate and the throughput, especially with PP. During their extrusion trials, all the materials were introduced in the hopper. They found then that the free-radical grafting reaction was nearly completed at the end of the plastification

zone. The best grafting levels were obtained with low screw rate and low throughput in PP, whereas for PE, the final grafting level was essentially determined by the initial chemical composition.

In addition to the grafting level, the structure of the grafts is also an important parameter for the end use of the modified polyolefins. Characterization of the microstructure of grafts in modified polyolefins is complicated by their low concentration on the polymer chains. Most of the work on this subject has been done with maleic anhydride and some controversy remains. In this case, the unfavorable MAH homopolymerization naturally limits the length of the grafts.²⁵ De Roover et al.^{26,27} showed by detailed FTIR analysis of PP-g-MAH and polyMAH that short oligomers are grafted. They concluded that β -scission occurred before grafting and led to the grafting of MAH at the end of PP chains. Size-exclusion chromatography performed on unbound species also showed the presence of some MAH oligomers. Heinen et al.²⁸ used ¹³C-enriched MAH to enable detailed ¹³C-NMR analysis. In these conditions, they showed that single units and small oligomers were grafted onto LDPE and HDPE, whereas only single-unit grafts were found on PP and high propylene content ethylene-propylene copolymers.

Contrarily to MAH, homopolymerization of GMA is a favorable reaction. Gallucci and Going³ presented indirect evidences of long GMA chains grafted onto LDPE by measuring the level of crosslinking after reacting LDPE-g-GMA (10% GMA_g) with a diamine compound. They observed very limited crosslinking that pointed out to a structure with a low number of sparsely located long GMA chains rather than a structure made of a high number of uniformly distributed single GMA units.

The effect of the grafting level and graft microstructure on the efficiency of GMA-modified polyolefins used as adhesion promoters has not been widely covered in the literature. Indirect evidences are often presented through compatibilization studies. Chen et al.,⁷ studying the compatibilization of PP/NBR blends with PP-g-GMA, showed that better compatibilization was obtained with a large concentration of lightly grafted polymer than with a small addition of highly grafted material. The emulsification efficiency also decreased when the molecular weight of the grafted PP decreased. Styrene, added to improve the grafting efficiency, also appeared to decrease the compatibilization efficiency. Champagne et al.²⁹ found similar results while studying the compatibilization of PP/PET blends with PP-g-GMA.

In this study, free-radical grafting of GMA onto LLDPE was carried out in an extrusion process to study the effect of the chemical composition, resin viscosity, and processing parameters on the grafting of GMA and on the efficiency of the resulting LLDPE-g-

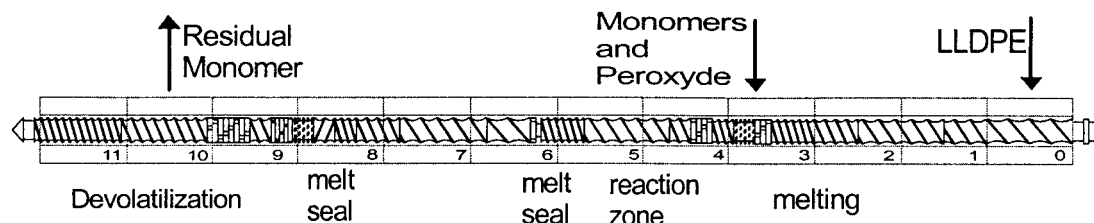


Figure 1 Twin-screw configuration used for the reactive extrusion experiments.

GMA to promote adhesion within LLDPE/PETG polyester copolymer.

EXPERIMENTAL

Materials

Three resins supplied by ExxonMobil Chemical (Baytown, TX) were used: LL-6201, LL-5202, and LL-1108 with melt indices of 50, 12, and 0.8 respectively. They will be referred as PE1, PE2, and PE3 in this article. According to the supplier's data sheets, these three grades have the same comonomer content (butene) and a similar density, in the 0.925–0.926 g cm⁻³ range. The resin mostly used in this study was PE2. The other grades were used to specifically investigate the effect of the initial molecular weight on the grafting results.

The organic peroxide used as initiator was 1,1-di(terbutylperoxy)-3,3,5-trimethyl cyclohexane, supplied by Atofina under trade name Lupersol 231. Glycidyl methacrylate and styrene were supplied by Aldrich (Milwaukee, WI) and used as received. Adhesion tests were made on PETG sheets extruded from Eastman's Eastar 6763 (Eastman Chemical, Kingsport, TN).

Processing conditions

Extrusion trials were carried out on a Leistritz 34-mm corotating twin-screw extruder. The screw profile is depicted in Figure 1. The barrel is modular and consists of twelve 120-mm-long barrel sections, numbered 0 to 11. The LLDPE was introduced in the hopper in section 0. Mixing elements were used in sections 3 and 4 to melt the polymer. A blend of GMA, peroxide, and eventually styrene was pumped at the second third of section 3 using a HPLC pump. A shear disk in section 6 was used to build some pressure and prevent monomer vapor from exiting the reaction zone. A reverse conveying element was used in section 8 to generate some pressure to seal the devolatilization section. Volatiles were removed under vacuum through a devolatilization port in section 10. In this step, unreacted GMA was removed from the material, which increases the efficiency of the product as a compatibilizer or adhesion promoter³⁰ and decrease its toxicity,

given that free GMA is a highly toxic compound and could further exude from the material. The extrudates were cooled in a water bath, palletized, and then dried.

Grafted PE characterization

PE-g-GMA produced in the extruder must be purified to discriminate concentration of GMA chemically bound to polyethylene chains from the free (unbound) GMA-based species. Purification was achieved by dissolving the material in hot xylene and followed by precipitation in cold acetone. This treatment enables removal of the unbound GMA-based materials from the grafted polymer. The latter was analyzed by infrared spectroscopy, FTIR, to determine the grafted GMA concentration. The acetone and *p*-xylene liquid fractions were analyzed by size-exclusion chromatography (SEC). A second purification procedure was conducted on the grafted polymer with the highest initial GMA content. FTIR measurements showed no evolution of the grafted GMA content while comparing material after the first and the second purification stages. It was then concluded that a single purification would be sufficient to remove any residual monomers and homopolymers.

The FTIR procedure was as follows. PE-g-GMA was compression molded at 190°C under 4 T for 3 min, quenched in cold water, and then dried. The IR spectrum was obtained on a Nicolet Magna IR 860 spectrometer (Nicolet Analytical Instruments, Madison, WI). The GMA content was obtained from the area of GMA-specific absorption bands and a calibration curve. The calibration curve was obtained from blends of LLDPE with polyGMA according to the method developed by Cole et al.³¹ The polyGMA was prepared by solution polymerization in benzene at 60°C using benzoyl peroxide as the initiator.³² The GMA concentration measurements were carried out on both the as-extruded and the purified materials. The unbound GMA concentration ($GMA_{u,i}$) is defined as the concentration difference between the as-extruded and purified samples. The initial GMA (GMA_i) and peroxide concentrations were calculated from the ratio of reactant mass flow rate over the total flow rate. The

difference between GMA_i and the GMA concentration in the as-extruded samples yields the volatile concentration (GMA_v), which is removed under vacuum in the devolatilization step of the extrusion process. For some PE-g-GMA, a second sample was purified and analyzed by FTIR to verify the reproducibility of the method. An error of 2% was found.

SEC analyses were performed on solvent-extracted unbound GMA species using a Waters 150C chromatograph (Waters Chromatography Division/Millipore, Milford, MA) equipped with two Polymer Laboratories columns (Amherst, MA; 5 and 10 nm pore size, respectively). Measurements were made at 23°C using THF as permeation solvent.

Rheological characterization was performed on a parallel plate rheometer (ARES, Rheometrics). Data were recorded in oscillatory mode at 190°C under a nitrogen blanket to minimize thermal degradation during measurements.

PE-g-GMA graft microstructure characterization

Reaction of the grafted material with a diamine was used to assess the structure of the graft according to the indirect method developed by Gallucci and Goring.³ An amine-terminated polypropylene glycol containing two amine end groups per molecule (Jeffamine D230, supplied by Huntsman) was added to the grafted PE. The reactions of purified PE-g-GMA with the diamine were run in a 60-cm³ internal mixing chamber at 190°C. The polymer was first introduced and mixed for 5 min at 50 rpm leading to complete melting and stabilization of the applied torque. The diamine was then added and mixed with the polymer for 5 min at the concentration required by the reaction stoichiometry. The insoluble fraction in the mixture was determined by solvent extraction in *p*-xylene.

Measurements of PE-g-GMA adhesion to polyester

The adhesion of PE-g-GMA onto PETG was measured by the double-cantilever beam (DCB) method.³³ First, 80- μ m-thick PE-g-GMA films were compression molded at 190°C for 3 min. Then, 2-mm-thick PETG sheets were joined by a PE-g-GMA film in a mold heated at 240°C for 10 min under low pressure. These three-layer samples were then cut into 10-mm-wide strips. A razor blade was inserted between the PETG sheets and a crack was allowed to propagate slowly at room temperature for 24 h. The crack length was measured with an optical microscope. The interface fracture toughness G_a is a direct measure of adhesive bond strength and is given by the following equation³⁴:

$$G_a = \frac{3u^2Eh^3}{16a^4 \left[1 + 0.64 \left(\frac{h}{a} \right)^4 \right]} \quad (1)$$

where u is the razor blade thickness, h is the PETG sheet thickness, E is the Young modulus of the PETG, and a is the crack length. Four tests were conducted on each sample; the average and standard deviation were determined and reported. Insufficient adhesion prevented the use of this test with neat PE resins; the three-layer samples spontaneously delaminated when they were removed from the mold.

RESULTS AND DISCUSSION

Free-radical grafting of GMA onto PE

The GMA present in the extruded samples was either chemically bound to polyethylene chains or unbound and free in the system. The unbound fraction was composed of polyGMA and GMA oligomers that could not be removed by the devolatilization step during the extrusion process. The grafted polyethylene can improve emulsification and solid-state adhesion by reacting with polyester directly at the PE/polyester interface to form a graft LLDPE-polyester copolymer. On the other hand, the unbound GMA polymer will at best form its own phase and leave the PE/PET unmodified or, in the worst case, will compete with the grafted PE for reaction with the polyester end groups. In the latter case, the unbound GMA would decrease the efficiency of the unpurified material. It is therefore important to evaluate the effect of initial chemical composition and processing parameters on the grafted and unbound GMA concentrations. Chemical composition effects were first investigated using resin PE2 and keeping the operating conditions constant with throughput being set at 10 kg/h, screw rotation speed at 250 rpm, and barrel temperature at 190°C. Figure 2 presents the evolution of grafted (filled symbols) and unbound (open symbols) GMA as a function of the peroxide to initial GMA ratio for three values of GMA_i (1, 2, and 3 wt %). Both the grafted and unbound levels increase with the peroxide/ GMA_i ratio and with the initial GMA concentration. The highest grafting level, 1.2 wt %, was obtained at the highest initial concentration in GMA and peroxide, 3 and 1.2%, respectively. The unbound GMA concentrations are always higher than the grafted GMA levels.

GMA_g , however, increased more quickly with the peroxide/ GMA_i ratio, especially at higher initial GMA concentrations. Increasing the peroxide ratio from 0.2 to 0.4 almost doubled the grafted GMA content in the system extruded with GMA_i sets at 3 wt %. Therefore, the increase in initiator content favors the grafting reaction over the GMA homopolymerization. This latter observation would suggest that materials with more grafted than unbound GMA could be made by further increasing the initial peroxide level.

The grafting efficiency can be defined as the GMA_g/GMA_i ratio. Figure 3 presents the efficiency as a func-

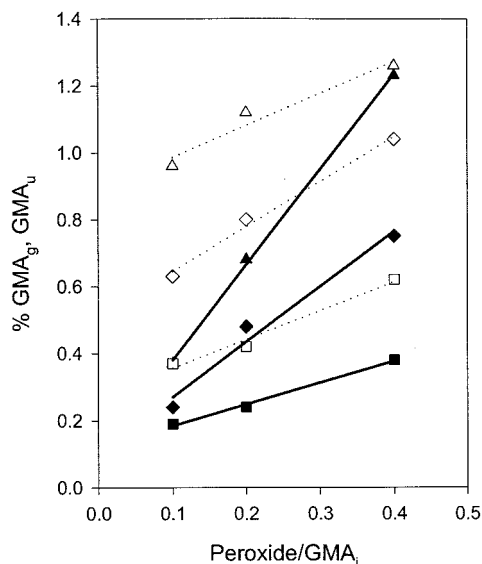


Figure 2 Concentration of grafted GMA (GMA_g , filled symbols) and unbound GMA (GMA_u , open symbols) as a function of peroxide/ GMA_i ratio for GMA_i equal to: 1 wt % (■ and □), 2 wt % (◆ and ◇), and 3 wt % (▲ and △).

tion of the peroxide/ GMA_i ratio. The efficiency increases linearly with the peroxide/ GMA_i ratio. Data for the 1, 2, and 3 wt % GMA_i all fall on a single curve, indicating that at lower GMA concentration, less peroxide is needed to achieve the same efficiency. Overall, the highest reaction efficiency, about 40%, was obtained with peroxide/ GMA_i ratio sets at 0.4.

The volatile content (GMA_v) is the concentration of unreacted monomer removed by devolatilization in the final portion of the twin-screw extrusion setup.

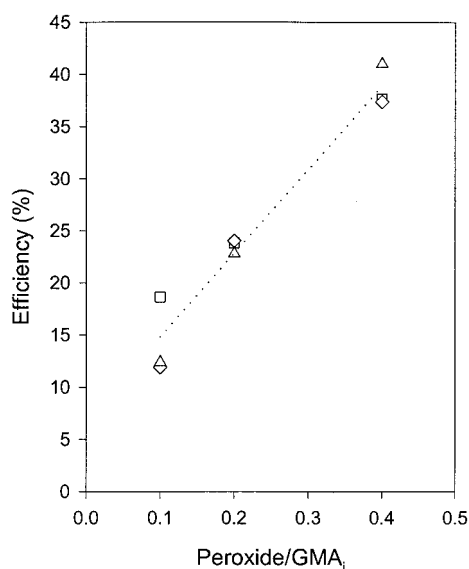


Figure 3 Grafting efficiency as a function of the peroxide/ GMA_i ratio for GMA_i equal to: 1 wt % (□), 2 wt % (◇), and 3 wt % (△).

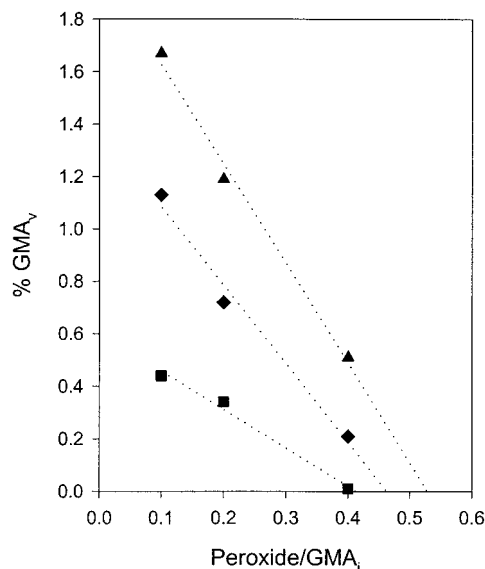


Figure 4 Volatile GMA-based compounds concentration (GMA_v) as a function of the peroxide/ GMA_i ratio for GMA_i equal to: 1 wt % (■), 2 wt % (◆), and 3 wt % (▲).

Figure 4 presents GMA_v as a function of the peroxide/ GMA_i ratio. For a given GMA_i , GMA_v decreases with the peroxide/ GMA_i ratio as expected because the increase in initiator content favors the grafting and polymerization reactions. For GMA_i of 1 wt %, the monomer can be completely consumed using the higher peroxide levels resulting in GMA_v value close to zero. This can be a very advantageous feature in a commercial production where devolatilization can become a major issue limiting the production rate. The volatile content curves are shifted to higher values when using higher initial GMA concentrations. The peroxide/ GMA_i that would be required to eliminate the volatile content were out of the investigated range but could be extrapolated to about 0.5. This translates to initial peroxide concentrations of 1 and 1.5 wt % for the 2 and 3 wt % GMA_i , respectively. The possible drawback at such high peroxide concentration is the polyethylene crosslinking side reaction. This aspect was investigated using viscosity measurements as an indirect measure of molecular weight changes. Figure 5 presents the complex viscosity as a function of shear oscillation frequency for the unmodified PE2 and three grafted materials at 190°C. The grafted materials were obtained with GMA_i content of 3 wt %. The viscosity curves were shifted upward with the increase in peroxide/ GMA_i ratio. However, the Newtonian plateau at low shear rate was always present, indicating that the materials did not significantly crosslink, even at the highest peroxide content (1.2 wt %) used in this study.

Figure 6 presents the zero-shear viscosity (η_0) as a function of the peroxide/ GMA_i ratio for the different

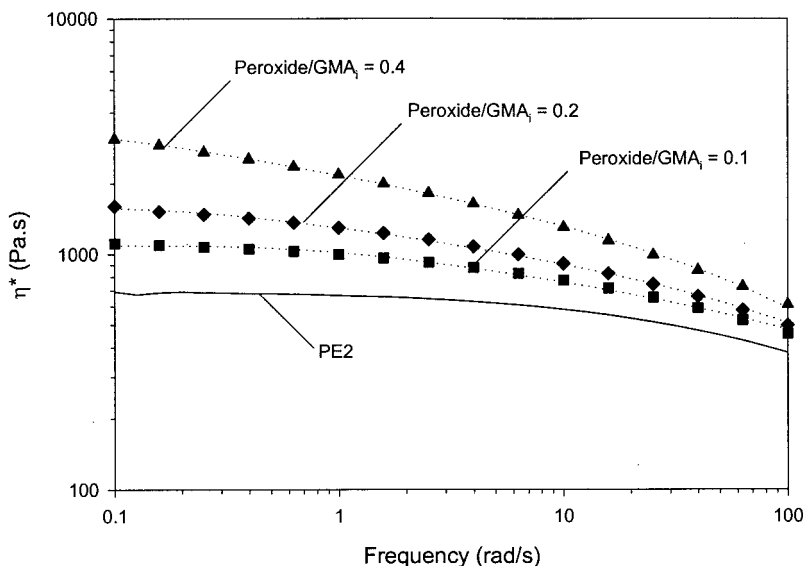


Figure 5 Complex viscosity as a function of shear frequency for pure PE2 at 190°C (—) and for PE-g-GMA made with GMA_i equal to 3 wt % and peroxide/GMA_i ratio sets at: 0.1 (■), 0.2 (◆), and 0.4 (▲).

PE-g-GMAs. The zero-shear viscosity was determined by curve fitting using the Carreau model.³⁵

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{[1 + (\tau\dot{\gamma})^2]^{(1-n)/2}} \quad (2)$$

where η_0 and η are the upper and lower Newtonian viscosities, respectively; τ is the relaxation time; and $\dot{\gamma}$ is the strain rate.

For a given GMA_i content, the zero-shear viscosity increases with the peroxide content, as expected from the increased number of generated free radicals. As

seen for the highest GMA_i system, the zero-shear viscosity is increased in the worst case by a factor 6 compared to that of the unmodified PE. The zero-shear viscosity of polyolefins was reported to increase with the average molecular weight to a power around 3.4, which indicates that in the worst case investigated here, molecular weight was increased by about 70% through branching/crosslinking reactions during extrusion grafting. From a processing point of view, the viscosity increase should be examined in the higher shear rate range. At 100 s⁻¹, the viscosity was increased by less than 60%. Grafted LLDPE processabil-

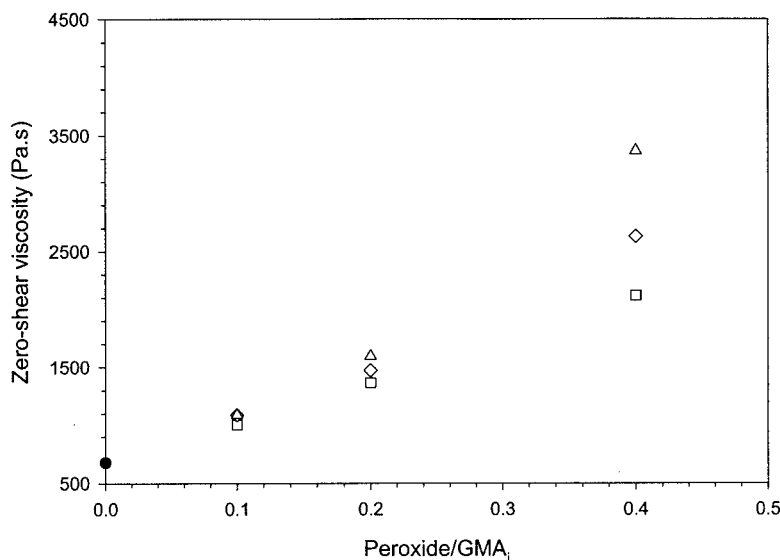


Figure 6 Zero-shear viscosity (η_0) as a function of peroxide/GMA_i ratio for pure PE2 at 190°C (●) and PE-g-GMA made using GMA_i equal to: 1 wt % (□), 2 wt % (◇), and 3 wt % (△).

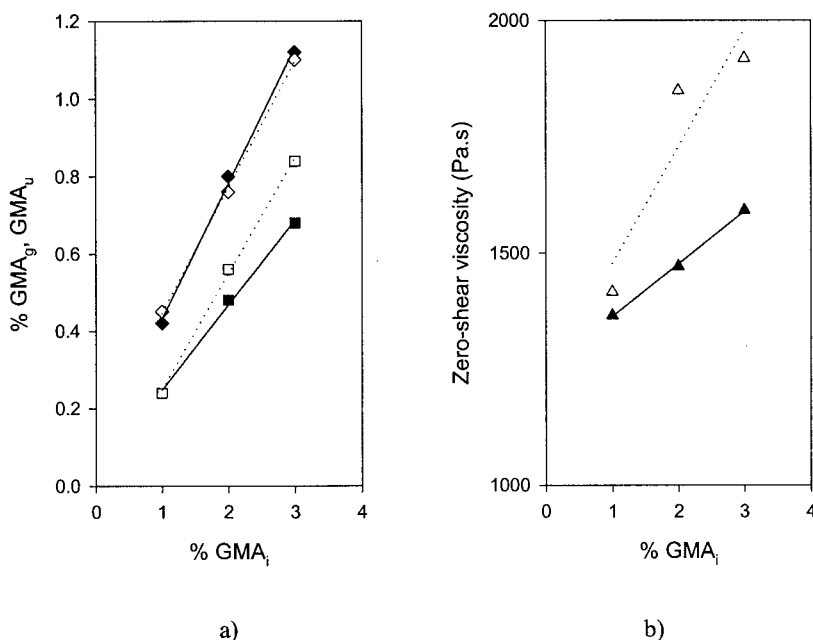


Figure 7 (a) Concentrations of grafted GMA (GMA_g , ■ and □) and unbound GMA (GMA_u , ◆ and ◇); (b) Newtonian viscosities as a function of GMA_i . The filled symbols represent materials extruded without styrene and the open symbols represent systems with styrene/ GMA_i ratio of 0.2. All results obtained with a peroxide/ GMA_i ratio of 0.2.

ity is then not significantly reduced compared to the neat resin.

The obtained data also show that at a constant peroxide content an increase of initial GMA limits the crosslinking. The two other reactions of grafting and homopolymerization compete with the crosslinking reaction.

It was noted earlier that the addition of styrene was reported to favor the grafting reaction over crosslinking but may have an adverse effect on the end uses of the modified polyolefin. Therefore, in this study, only a low concentration of styrene was used. All styrene-assisted extrusion runs were carried out using a styrene/ GMA_i ratio and a peroxide/ GMA_i ratio of 0.2. The effect of styrene on the grafted and unbound fractions, GMA_g and GMA_u , respectively, is summarized in Figure 7. No specific styrene infrared absorption bands were measured during FTIR analysis. This is probably attributable to the low styrene concentrations used. Figure 7(a) shows that the presence of styrene slightly favors the grafting reaction while GMA_u does not evolve, indicating that homopolymerization is unaffected. The addition of styrene increases the efficiency of the grafting reaction: for example, in these conditions and in the presence of 3 wt % of GMA_i , the efficiency increased from 20 to 30%. However, as shown in Figure 7(b), the styrene also promoted polyethylene branching reaction. In the case of the previous example, it resulted in zero-shear viscosity close to 2 kPa s⁻¹ instead of 1.5 kPa s⁻¹ observed when the grafting was done without styrene.

The effect of the initial polyethylene viscosity on the grafting levels was assessed using three different resins. The grafting was performed using GMA_i equal to 2 wt % and a peroxide/ GMA_i ratio of 0.2. The viscosity curves of the resins and of their grafted versions are presented in Figure 8, whereas Table I presents the grafting levels, grafting efficiency, and zero-shear viscosity increase. Surprisingly, the initial polyethylene viscosity has a remarkable effect on the final grafting levels. The PE-g-GMA made from the higher-viscosity PE3 (lowest MFI) presents a grafting level GMA_g of 1.8 wt %. In addition, grafted GMA concentration in the material is 9 times higher than the unbound species content. The grafting efficiency reached 90%, a very high value for this type of reaction. The higher viscosity therefore seems to favor the grafting reaction over GMA polymerization. For the high-viscosity PE, however, the polyethylene branching reaction is also more important. Although modest changes in viscosity are observed on Figure 8 for the lower-viscosity PE1 and PE2 resins, the high-viscosity PE3 resin did not exhibit any Newtonian plateau in the shear frequency range investigated. The high screw rotation speed and the intense mixing found in kneading blocks and mixing elements of the twin-screw extruder enable thorough mixing but also generate a large amount of shear. The higher-viscosity polymer may affect the grafting process by creating shear-induced free radicals and by generating local overheating in mixing sections of the twin-screw process. In fact, overheating was observed for PE3 in barrel zones 8 and 9 and the final product

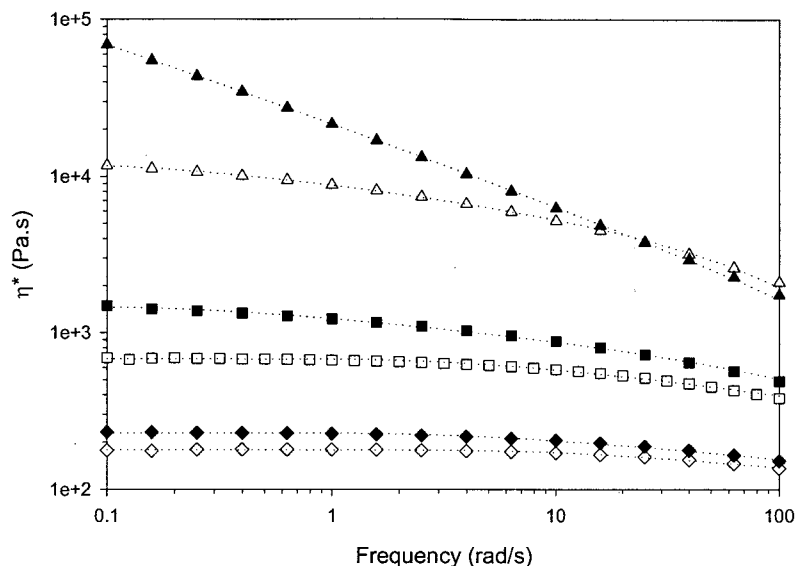


Figure 8 Complex viscosity as a function of shear frequency for pure PE1 (\diamond), PE2 (\square), and PE3 (\triangle), at 190°C and for their grafted versions PE-g-GMA, respectively, \blacksquare , \blacklozenge , and \blacktriangle , made with 2 wt % GMA_i and peroxide/GMA_i = 0.2.

was slightly colored. Shear-induced generation of additional free radicals would have a similar effect to an increase of peroxide content and thus promote grafting as well as polyethylene branching/crosslinking. The increased temperature arising from shear heating could also modify the half-life of the peroxide and change the reaction dynamics. However, this would unlikely result in increased grafting level because changes in process temperature (discussed below) did not result in appreciable changes in grafting or unbound GMA concentration.

The effect of extruder throughput, screw rotation speed, and extruder barrel temperature was investigated. Grafting and viscosity results are reported in Table II. The chemical composition was kept constant with a GMA_i of 2 wt % and a peroxide/GMA_i ratio of 0.2. The grafting efficiency varied only between 20 and 30% even though processing parameters were varied over a wide range. Therefore, processing parameters appear to be less influential on grafting level and grafting efficiency than the initial chemical composition.

The efficiency did not increase when throughput was doubled. It was increased more significantly, by 5%, when the screw rotation speed was increased from 250 to 380 rpm. An increase in rotation rate can have detrimental effects in reactive extrusion by decreasing the residence time. Typically, the residence time in such an extruder ranges from 1 to 3 min. In our case however, residence time was not a controlling factor because it is long compared to the half-life of the peroxide, around 2 s at 190°C, and to the free-radical grafting process. Therefore, the enhanced mixing at the higher rotation speed outweighs the adverse residence time effect, resulting in higher grafting efficiency. The grafting efficiency decreased with processing temperature from 25 to 20 in the investigated temperature range. The half-life of the peroxide at processing temperatures of 170, 190, and 240°C were, respectively, 6, 2, and 0.6 s. This would indicate that a gradual peroxide decomposition is more favorable to grafting. Similar effects of screw speed and through-

TABLE I
Grafting and Viscosity Data for PE-g-GMA Made from Resins of Increasing Viscosity Using 2 wt % Initial GMA and a Peroxide/GMA_i Ratio Sets at 0.2

Resin	GMA _g (wt %)	GMA _u (wt %)	Efficiency (%)	$\Delta\eta_0/\eta_0$
PE1	0.3	1.4	16	0.28
PE2	0.5	0.8	24	1.17
PE3	1.8	0.2	89	4.85 ^a

^a Ratio arbitrarily taken at oscillation rate of 0.1 rad/s because no Newtonian plateau was observed in the investigated frequency range.

TABLE II
Grafting and Viscosity Data for PE-g-GMA Processed in Different Extrusion Conditions^a

T (°C)	Q (kg/h)	N (rpm)	GMA _g	GMA _u	Efficiency	$\Delta\eta_0/\eta_0$
190	10	250	0.48	0.80	24	1.17
190	20	250	0.50	0.85	25	1.18
190	10	380	0.57	0.67	29	1.51
190	20	380	0.63	0.77	31	1.60
170	10	250	0.53	0.83	27	1.39
240	10	250	0.42	0.74	21	0.8

^a All specimens were made from 2 wt % initial GMA and peroxide/GMA_i ratio sets at 0.2.

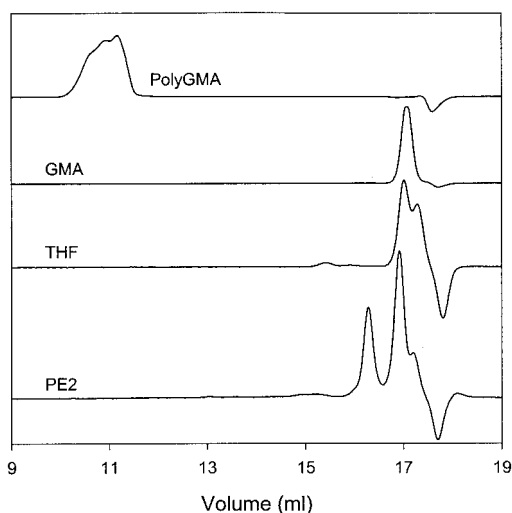


Figure 9 Size-exclusion chromatograms of polyGMA, GMA, THF, and the extractable fraction of the pure PE2 resin.

put on the free-radical grafting of GMA onto HDPE¹⁸ were reported.

Structure of GMA-grafted PE

The ¹H spectra confirm the grafting of GMA onto PE, given that four different resonances were found between 3 and 5 ppm. These resonances were associated with different protons of GMA.³⁶ However, because of the low GMA content in grafted materials, NMR analysis cannot be used to determine the microstructure of the GMA grafts.

Size-exclusion chromatography was conducted on the soluble fractions that were obtained from the purification of the extruded PE-g-GMA. Similar analyses were conducted on GMA, polyGMA, and the PE2 resin as well as on the different solvents used (acetone, *p*-xylene, THF). Control chromatograms obtained for polyGMA, GMA, THF, and the extractable fraction from neat ungrafted PE2 are reported in Figure 9. The polyGMA, synthesized for this study, presents a rather broad peak and has a number-average molecular weight of 5.6 kg mol⁻¹. Unfortunately, elution volumes for GMA and THF are similar in the conditions used for these experiments. Consequently, peaks from THF and GMA could not be resolved with the column combinations used in this work. Interestingly, the chromatogram from the extractable fraction of neat PE2 evidenced a low molecular weight compound soluble in the solvent used for PE-g-GMA purification.

Figure 10 presents the chromatogram from the extractable fraction of PE-g-GMA made with 3 wt % of GMA and 1.2 wt % of peroxide. From the comparison with the previous chromatograms, peak I can be as-

signed to the solvent, whereas peak II obviously corresponds to the extractable compound present in the PE2 resin. More interestingly, broad and low intensity peaks are also observed for lower elution volume. These peaks cannot be related to any solvent used during the purification. Obviously some polymerization of GMA occurred during reactive extrusion leading to low molecular weight polymers (lower than 5 kg mol⁻¹). Similar results were obtained on the extractable fraction of all other grafted materials. This supports the finding of Chen et al.⁷ obtained on GMA-grafted PP, reporting the synthesis of low molecular weight oligomers (<0.5 kg mol⁻¹) and low molecular weight polymers (4–6 kg mol⁻¹) during grafting.

Therefore, polymerization of GMA is possible during reactive extrusion despite a ceiling temperature reported at about 165°C.^{7,11} However, inference on the structure of the grafted GMA from unbound GMA must be done with care, given that the two reactions are not believed to proceed by the same mechanism.

Four purified LLDPE-g-GMAs were selected and reacted with a diamine to evaluate the structure of the grafts in a manner similar to that reported by Gallucci and Going.³ Three of these LLDPE-g-GMAs were synthesized from resin PE2 and did not show any gel fraction, whereas the fourth material was generated from resin PE3 and had a gel fraction < 0.05.

The reaction of the diamine with a grafted PE containing sufficient concentration of single graft units should generate a significant gel fraction through interchain bridging. On the other hand, the same dia-

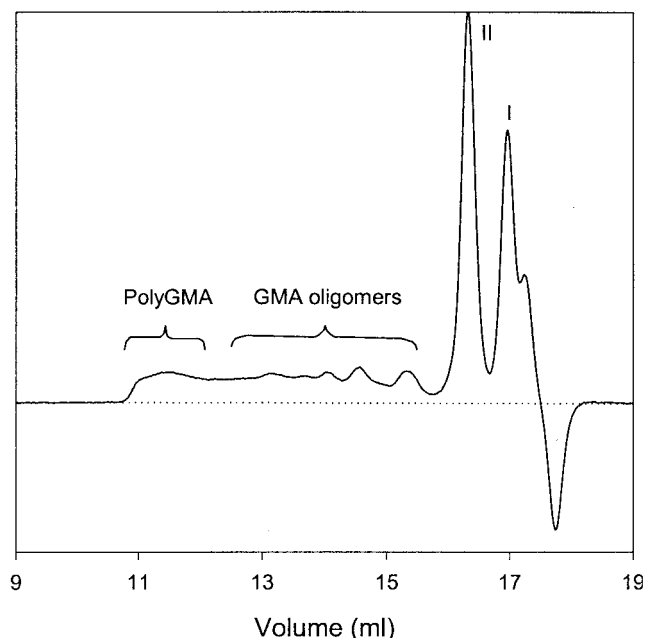


Figure 10 Size-exclusion chromatogram of the extractable fraction of the grafted PE2 resin (GMA_i equal to 3 wt % and peroxide/GMA_i ratio sets at 0.4). Peaks I and II are the THF and neat PE2 extractable peaks, respectively.

TABLE III
Gel Fraction and Swelling Data of Purified PE-g-GMA
After Reaction with a Low Molecular Weight Diamine

Resin	GMA _g (wt %)	GMA _g (mol %)	Gel fraction (%)	Swelling (%)
PE2	0.37	0.0026	0	—
PE2	0.48	0.0034	0	—
PE2	1.2	0.0087	77	1041
PE3	1.8	0.013	87	853
PE-MAH ^a	1 ^b	0.010 ^c	86	885

^a Uniroyal PolyBond 1009.

^b wt % of MAH.

^c mol % of MAH.

mine added in a grafted PE containing mostly polyGMA grafts should not produce a noticeable gel fraction. Intrachain bridging should be dominant in the latter case.

The gel fraction and swelling ratio obtained for the four different PE-g-GMAs and for a commercially available maleic anhydride grafted polyethylene are reported in Table III. The swelling is defined as the weight ratio of the swollen gel fraction before and after drying. The GMA grafting levels were low (from 0.37 to 1.78 wt %) compared to the 10 wt % reached by Gallucci and Going.³ No gel fraction was obtained after the reaction for the materials with 0.37 and 0.48 wt % of grafted GMA, probably because of an insufficient number of GMA units per chain (three GMA units per chain is a minimum that leads to some gel fraction). However, the highly grafted materials show gel fractions as high as 77 and 87% for the grafting levels of 1.2 and 1.8 wt % obtained in PE2 and PE3, respectively. Large gel fractions indicate a structure

primarily made of single GMA units or short GMA oligomers grafts well distributed along the PE chains. These results are especially relevant compared with those reported by Gallucci and Going,³ who observed only 54 wt % of crosslinked phase for a material with 10 wt % of grafted GMA. The swelling observed for our gel fractions was also large, over 1000% for the grafted PE2; slightly smaller swelling was noted for grafted PE3. Swelling of polymer networks is known to increase with decreasing crosslinking density and increasing molecular weight between entanglements.^{37,38} The swelling data indicate that a rather loose network is created after reaction with the diamine. This is not surprising considering the relatively low level of grafted GMA in these specimens. Finally, it is interesting to note that gel fraction and swelling data of the GMA-grafted materials are comparable to the results obtained with PE-MAH, a material known to have predominantly single MAH grafts.

In summary, homopolymerization of GMA occurs during the extrusion process to form unbound polyGMA, although the GMA grafts on LLDPE are formed by single units or short GMA-based oligomers.

Interface modification in LLDPE/polyester systems

Polyesters and polyethylene have one of the highest interfacial tension coefficients among all thermoplastic polymer pairs, at about 12 mJ m⁻². The main benefits expected from addition of modified polyethylene are the reduction in interfacial tension in the melt state and the improvement of solid-state adhesion. The DCB test was then performed to determine the adhesive strength between PET and grafted materials.

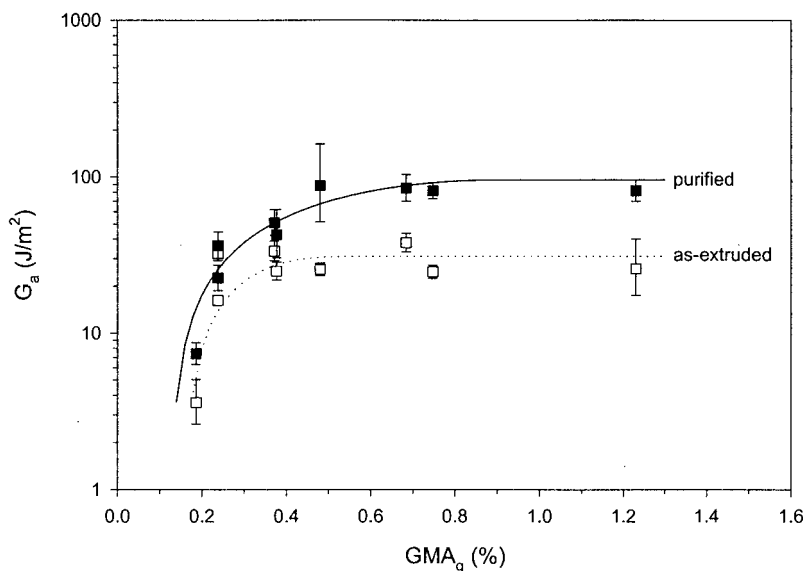


Figure 11 Interface fracture toughness G_a as a function of the grafted GMA concentration for as-extruded (□) and purified (■) materials.

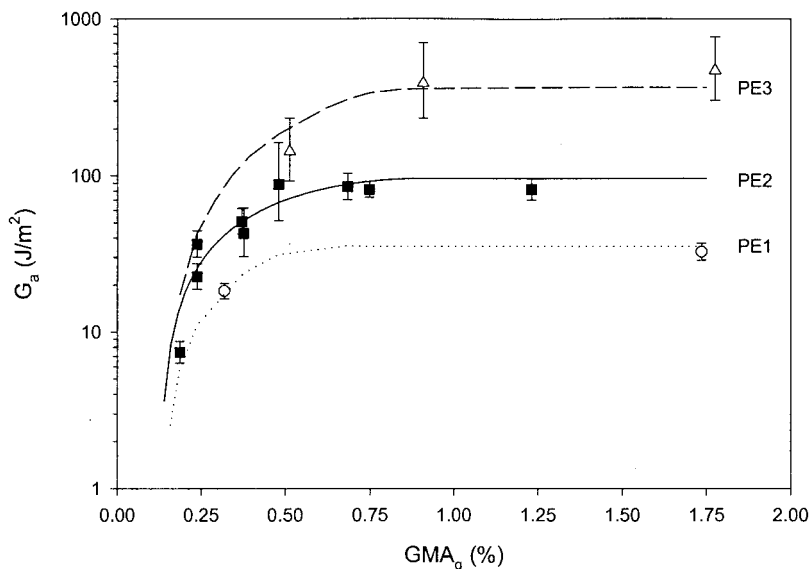


Figure 12 Interface fracture toughness G_a as a function of grafted GMA concentration for purified PE-g-GMA made from PE1 (○), PE2 (■), and PE3 (△).

Figure 11 presents the DCB results for as-extruded (with remaining unbound polyGMA species) and purified PE-g-GMA with different grafting levels. Unmodified PE spontaneously delaminates from PETG right after molding simply because of thermal stresses. We can therefore assume that the adhesion strength of the unmodified system is close to zero. The interface fracture toughness increases with GMA_g to grafting levels around 0.5 wt % and then reaches a plateau. A high content of grafted GMA is therefore not necessary for a good adhesion and a content as low as 0.5 wt % seems adequate. The best fracture toughness values are in excess of 80 J m^{-2} and were obtained with the purified material. The occurrence of this plateau, also observed by Zhang et al.,³⁹ can be explained by a saturation of the interfacial area with PE-PETG graft copolymer formed through reaction of the GMA moieties with the PETG end groups.

The toughness obtained using the as-extruded materials is systematically lower at $30\text{--}40 \text{ J m}^{-2}$ than the G_a values measured using the purified materials. This is a serious drawback and indicates that the concentration of unbound GMA, even in polymerized form, should be minimized to benefit from the full potential of GMA-grafted PE. No correlation has been observed between interface toughness reduction and unbound GMA concentration or GMA_g/GMA_u ratio. By reacting more readily than grafted species with the PETG end groups available in the interfacial area, small amounts of unbound polyGMA are then sufficient to severely decrease adhesion.

Figure 12 presents the interface fracture toughness for the PE-g-GMA made from PE1, PE2, and PE3 resins. For sake of clarity, only the results with puri-

fied materials are reported here but, as previously, the unpurified materials also presented lower interface fracture toughness. Similar behavior was observed for each of the three resins with an initial increase in fracture toughness followed by a leveling off. The higher-viscosity PE3 presents higher plateau values reaching over 600 J m^{-2} .

Interfacial adhesion between polymers benefits from the use of block or graft copolymers where each block of the copolymer can entangle at a molecular level and cocrystallize with the bulk of the material. In the present case, the molecular weight of all polyethylene resins is well above the critical molecular weight for entanglement. The improved adhesion observed with the increase in initial resin molecular weight can be related to improved entanglement yielding improved cohesive strength within the polyethylene phase.

CONCLUSIONS

The free-radical grafting of GMA onto linear low-density PE was investigated. The grafting level was found to increase with initial GMA and peroxide concentrations. Grafting level up to 1.8 wt % was achieved but in general the grafting efficiency remained low. The main factor preventing full conversion was the homopolymerization of the GMA to form unbound polyGMA. The use of a high-viscosity resin provided the highest grafting level and the lowest unbound GMA-based species content. Graft microstructure analysis indicated that the grafts were not formed by long polyGMA chains but rather by single GMA units or short oligomers. The grafted resins

proved to adhere well to polyester substrate for a grafting level over 0.5 wt %. The best results in terms of the fracture toughness at the interface were obtained with the higher-viscosity grafted resin, probably attributable to increased cohesive strength within the polyethylene phase. The presence of unbound polyGMA in the grafted materials was found to severely hinder the adhesion performance and purified versions are clearly advantageous with respect to adhesion applications.

NOMENCLATURE

a	crack length
E	Young modulus of PETG
G_a	interface fracture toughness in J m^{-2} as measured through the DCB experiment
GMA	glycidyl methacrylate
GMA_i	GMA concentration fed in the extruder
GMA_g	grafted GMA concentration onto PE resin as measured by FTIR
GMA_u	unbound GMA-based oligomers and polymer concentration generated in the PE resin as measured by FTIR
GMA_v	volatile GMA monomer concentration removed during the devolatilization (value calculated by subtracting GMA_g and GMA_u from GMA_i)
h	PETG sheet thickness
u	razor thickness
η_0	zero-shear viscosity (upper Newtonian viscosity)
η	lower Newtonian viscosity
$\dot{\gamma}$	strain rate
τ	relaxation time

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