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Reactive Extrusion Grafting of Glycidyl Methacrylate onto Low-Density and Recycled Polyethylene Using Supercritical Carbon Dioxide

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Featured Application: Authors are encouraged to provide a concise description of the specific application or a potential application of the work. This section is not mandatory.

Abstract: Glycidyl methacrylate (GMA) was grafted onto (recycled) polyethylene (PE) to design a new adhesive with better mechanical properties compared to non-grafted PE. The effects of the amount of GMA, the amount of dicumyl peroxide (DCP) and the use of supercritical carbon dioxide (scCO$_2$) in a reactive extrusion (REX) were evaluated based on the grafting degree and efficiency of the grafted samples. Generally speaking, higher amounts of GMA led to higher functionalization degrees (FD), whereas higher amounts of DCP resulted in a lower FD due to the occurrence of more unfavorable side reactions. The influence of scCO$_2$ showed different outcomes for the two substrates used. Higher FDs were obtained for the low-density polyethylene (LDPE) samples while, by contrast, lower FDs were obtained for the recycled polyethylene (RPE) samples when using scCO$_2$. Additionally, adjusting the screw speed and the temperature profile of the extruder to the half-life time of the radical initiator appeared to have the highest positive impact on the FD. According to the tensile tests, all the grafted samples can withstand higher stress levels, especially the grafted RPE, compared to the non-grafted samples.

Keywords: recycled polyethylene; reactive extrusion; grafting

1. Introduction

Polyolefins, especially LDPE, high-density polyethylene (HDPE), and polypropylene (PP), are thermoplastics that are widely used for multiple industrial and technological applications due to their mechanical properties, ease of processing, versatility, and low price [1]. This automatically results in an enormous amount of plastic waste streams, in addition to the fact that most plastics are still produced from fossil fuels. Therefore, efficient processes are being developed to limit the disposal of plastic waste. One of these options is material recycling. During this process, plastic waste is converted into a recycled type of raw material for the production of new materials with possible changes in their chemical structures [2].

Indeed, the compatibility of polyolefins with other polymers and fillers is often very limited due to the lack of polar groups [3]. The grafting of polyolefins with monomers containing reactive groups is one of the methods used to improve their compatibility and interfacial adhesion with other materials. A grafting process is usually performed by adding a free-radical initiator to the monomer to be grafted and the polyolefin mixture. Historically, maleic anhydride (MAH) [4] has been one the monomers used for grafting to improve the properties of polyolefins. However, several authors have reported similar processes with GMA in the recent years. The epoxide functional group enhances the possibility of further

reactions (at the interface) with other functional groups, such as hydroxyl groups. This results in effective compatibilizers that are usable for blends of polyolefins with immiscible nonpolar and polar polymers [5–11]. The advantages of using GMA are their faster grafting reactions, the non-formation of water or other side products, and a reduction in crosslinking due to the bulky molecular structure of GMA compared to MAH or acrylic acid (AA) [8].

The grafting of GMA onto the polymer backbone would enable the design of a new product out of (recycled) PE with better mechanical properties and compatibility compared to non-grafted PE. The main chain ($-CH_2-CH_2-$)$_2$ is non-polar, while the grafted GMA is polar, and it can help to form multilayer composite films or act as a hot melt adhesive between metal plates.

Wang et al. (2019) [12] successfully performed melt grafting experiments in a torque rheometer with GMA, AA, and RPE. The tensile strength improved by 70% and the elongation at break increased by five times. Furthermore, the melt index decreased, indicating that longer polymer chains were formed. Furthermore, the crossover frequency decreased as well, due to the increased degree of chain entanglements in the grafted polymer. The mechanical properties of grafted RPE significantly improved compared to the un-grafted RPE. A study performed by Fang et al. (2013) [13], focused on the reuse of plastic waste, used PE-g-MAH as one of the compatibilizers for blending waste polypropylene and polyethylene in a twin-screw extruder. The usage of PE-g-MAH led to an improvement in impact strength but a decline in tensile strength. Nevertheless, the use of compatibilizers improved the blending of waste PE and waste PP due to the improved crystallization of the blend. This resulted in a temperature decrease in the PP melting peak and an increase in the PE melting peak, leading to a smaller temperature difference between the two melting peaks for the mixed PP/PE samples. This in turn suggests that the compatibilization of blending was improved.

On the other hand, the grafting reactions of GMA and MAH often result in relatively low grafting degrees and efficiencies [7,14]. One of the upcoming techniques that has been used for several grafting processes is the use of supercritical CO_2 [15–21] because of its attractive properties. ScCO$_2$ is non-flammable, nontoxic, and relatively cheap, and it has moderate critical parameters (T_c = 31.3 °C, P_c = 7.38 MPa) [22]. Furthermore, scCO$_2$ has the advantage of lowering the viscosity of the melt phase due to its swelling effect, which leads to an increase in the specific volume of the polymer and the mobility of the chains. This results in a lower processing temperature, which ensures less chain degradation or side reactions in general [21]. Moreover, scCO$_2$ has a plasticizer effect, which results in a lower glass transition temperate (T_g) and a more flexible and softer polymer. The plasticizer effect combined with the swelling effect of scCO$_2$ enables interactions not only on the polymer surface, but also into the polymer matrix [23–27]. Several researchers found a higher grafting degree, less crosslinking, and lower processing temperatures when grafting under scCO$_2$ conditions [3,15–21,28–32].

Overall, it can be said that there is already a significant amount of research information available about polymer grafting and blending, even with the use of scCO$_2$. Nevertheless, a systematic comparative (with and without scCO$_2$) study on GMA grafting is still lacking and constitutes the objective of the present work. The effect of using scCO$_2$ in a reactive extrusion process (REX) was evaluated based on the grafting degree and efficiency of the grafted samples. The grafting results were compared to those of virgin LDPE. Furthermore, the adhesive properties of the grafted samples were tested.

2. Materials and Methods

2.1. Materials

LDPE (1922NO, Sabic, Geleen, The Netherlands) and RPE (Attero, Wijster, The Netherlands) were used for the preparation of PE-g-GMA without further purification. Glycidyl methacrylate (purity of 97%, Aldrich, Darmstadt, Germany) as grafting monomer was also used without further purification. DCP (98% purity, Darmstadt, Germany) was used as radical initiator without further purification. Carbon dioxide (CO$_2$, SOL Nederland BV, Tilburg,

The Netherlands) was fed during the grafting reaction under $scCO_2$. Tetrahydrofuran (THF, >99% purity from Acros, Geel, Belgium) was used during the purification process.

2.2. Synthesis and Purification of PE-g-GMA

2.2.1. Melt Grafting

PE grafting was conducted in Three-Tec ZE12 twin-screw extruder (see Figure 1) with a screw length-to-diameter ration (L/D) of 30. The screw speed was set on 20 rpm to yield a residence time set at six times the half-life time of DCP. Indeed, the temperature profile of the extruder was set to 175–180–185–180–175 °C because the half-life time of DCP is 30 s at 180 °C. The reactant composition, extruder temperature profile and screw rotational speed were adjusted throughout the study.
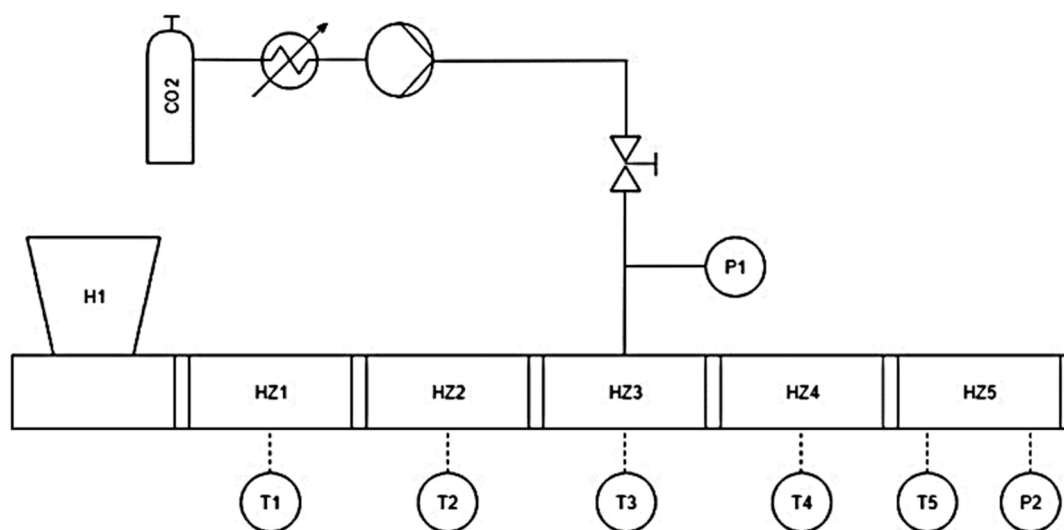

Figure 1. Schematic picture of the twin extruder.

The samples were prepared by premixing GMA and PE pellets together. Once the GMA was soaked into the PE pellets, and after approximately 10 min, the DCP was added into the beaker. The materials were briefly mixed before being fed into the extruder. The samples were shredded by Brabender CHG Duisberg before purification.

2.2.2. Grafting of $scCO_2$

The $scCO_2$ enters the extruder halfway. The $scCO_2$ flow was set at 4 g/min at 130 bar for almost all the experiments. In some of the experiments, a different flow (8 g/min) and a different pressure (90–170 bar) were used to determine whether these changes would influence the process. An overview of all grafting experiments is given in Table 1 (p = 130 bar, flow = 4 g/min and 20 rpm). For all the experimental data, see Appendix B, Tables A1–A5.

Table 1. One way ANOVA.

Variable	p-Value	Verdict
Variation in (GMA)	0.0004	Rejected
Variation in (DCP)	0.7900	Accepted
Variation in (GMA) + $scCO_2$	0.0002	Rejected
Variation in (DCP) + $scCO_2$	0.8630	Accepted

2.3. Purification

Soxhlet extraction (ST 243 Soxtec^{TM}, Foss) was used to remove the remaining reactants and side products from the PE-g-GMA. The extraction time was set to 4 h of boiling and

2 h of rinsing with THF. Next, the solid phase was collected and dried under vacuum for 24 h (200 mbar and 80 °C).

The use of Soxtec extraction contrasted the approach in other studies [9,21]. However, Soxtec appeared to be the most reliable method for the determination of the FD according to the different purification methods (Appendix C).

2.4. Characterization of Samples

2.4.1. Fourier-Transform Infrared Spectroscopy (FTIR)

In order to characterize the PE-g-GMA samples, FTIR measurements were performed. There were two distinguishable peaks belonging to PE-g-GMA at wavenumber 1735 cm^{-1}, which corresponded to the carbonyl group of GMA and the methylene group of PE at wavenumber 722 cm^{-1}. To determine the amount of GMA grafted onto the polymer matrix, the ratios of these FTIR peak heights were considered. Each sample was measured from 600–4000 cm^{-1}, using a resolution of 4 cm^{-1}, 2–4 times.

A calibration curve was obtained from a commercial PE-g-GMA (Sigma Aldrich, Darmstadt, Germany) sample with 8 wt.% GMA, which was diluted with LDPE pellets and blended in the Brabender plasticorder at 155 °C for 8 min at 60 rpm (see Appendix A, Figure A1). The ratio between the peak heights was plotted as function of the GMA content in the samples to the calibration curve to obtain the functionalization degree (FD).

Furthermore, the efficiency of the grafting process, E, was defined by dividing the value of [GMA]$_g$ (grafted) by [GMA]$_i$ (initial concentration) according to:

$$E\ (\%) = \frac{[\text{GMA}]_g}{[\text{GMA}]_i} \times 100 \tag{1}$$

2.4.2. Differential Scanning Calorimetry (DSC)

DSC measurements in Discovery DSC 25 by TA Instruments were conducted for the analysis of both the melting points of the two substrates. Small flat pieces (5–10 mg) were placed into a reference pan covered by an aluminum lid by TA Instruments. A heat–cool–heat cycle starting at 50 °C to 200 °C was used (heating rate and cooling rate at 10 °C/min).

2.4.3. Rheometer

Rheology measurements were performed to determine the flowing properties of the two polymers. The pellets were molded into an 8 mm disc and placed inside the Discovery HR30 by TA instruments for analysis. A constant oscillation strain was required when conducting the temperature ramp analysis. Therefore, the oscillation amplitude at the highest and lowest temperature of the temperature range needed to be evaluated first. Moreover, the gap between the plates needed to be adjusted so that the sample was in contact with the plates without excessive force.

2.5. Gel Content Measurement

In total, 0.1 g of RPE, 2 g of solvent and a magnetic stirring bar were added in a vial. Nine different solvents (acetone, benzene, diethyl ether, dimethyl sulfoxide, ethanol, ethyl acetate, n-hexane, toluene and xylene) were used. The nine samples were left at room temperature for 24 h. Subsequently, the samples were heated on a hot plate and removed from the plate once they had boiled for 10 min. Toluene was chosen as solvent to check the gel content in the samples by means of visual inspection.

The gel content of the samples was determined through Soxhlet extraction (ST 243 Soxtec^{TM}, Foss). The samples were initially weighed (0.5 g) and were extracted for 6 h (4 h boiling and 2 h of drying). The insoluble samples were vacuum-dried for 24 h at 200 mbar and 80 °C. The gel content was calculated as follows:

$$\text{Gel content}\ (\%) = \frac{\text{mass}_{\text{after drying}}}{\text{mass}_{\text{initial}}} \times 100\% \tag{2}$$

2.6. Statistical Analysis

To quantify the significance of the difference in results, one-way and two-way ANOVA were conducted with IBM SPSS Statistics 25 software with the following hypotheses:

- Null hypothesis: The data are drawn from populations with equal means;
- Alternative hypothesis: There is at least one mean that differs from the other means.

The alpha was set to 0.05 and the decision of whether to either accept or reject the null hypothesis was determined by the *p*-value. If $p > 0.05$, the null hypothesis of equal means was accepted; thus, the difference in the compared variables was insignificant.

2.7. Tensile Strength Grafted Samples

The recycled samples were pressed at 180 °C and 100 kN, whereas a temperature of 130 °C and 100 kN were used for the LDPE sample. A total press time of 10 min was used in the LabManual 300 press from Fontijne presses to form a film with a thickness of 0.09–0.1 mm. The formed films were cooled down and settled for at least 20 h.

A single-lap joint shear test was performed using the Tinius Olsen H25KT machine to obtain the adhesive strength of the produced samples. The study was conducted with 1.3 mm/min velocity. The surface area of the film was 2.5 × 2.5 cm^2, with a thickness of 0.09–0.1 mm. Aluminum plates measuring 10 × 2.5 × 2.5 with a thickness of 1 mm were used. Five samples were tested for each adhesive formulation.

The adhesive shear strength (MPa) is defined by:

$$\text{Adhesive shear strength} = \frac{\text{Max. total force}}{\text{Adhesive surface area}} \tag{3}$$

3. Results and Discussion

PE-g-GMA is synthesized via radical polymerization [3,5–7,9–11,14,33]. Radicals are formed after the thermal decomposition of the peroxide and these formed radicals can react via several pathways (Figure 2).
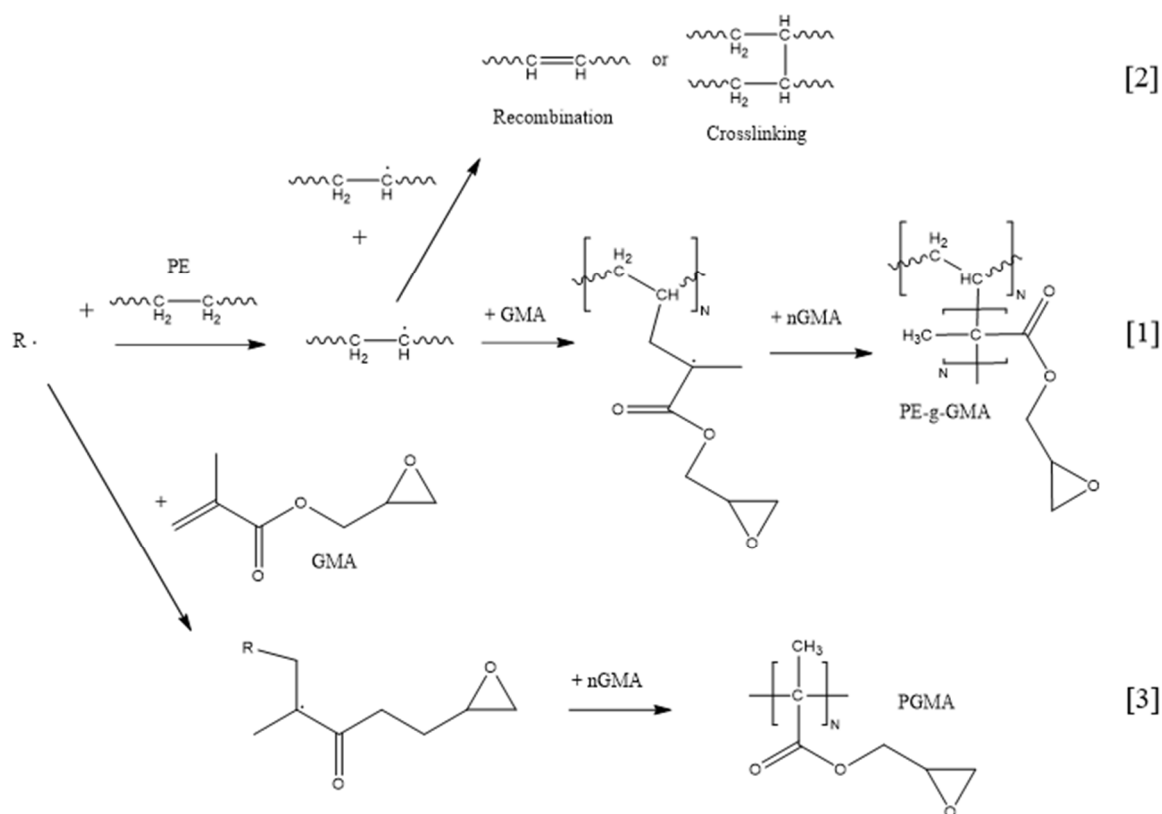

Figure 2. Reaction mechanism based on the literature [3,5–7,9–11,14,33,34].

As depicted in Figure 2, the primary radical can abstract a hydrogen from PE to form a macro-radical (reaction 1). The formed macro radicals attack the GMA's sigma bond and, via termination, the growing chain forms a grafted polymer chain, PE-g-GMA. However, macro-radicals have limited accessibility to the GMA monomers due to steric hindrance. Therefore, PE crosslinking and recombination might occur (reaction 2). Furthermore, the primary radical might directly initiate GMA homo-polymerization (reaction 3) [7,9,14,33].

Multiple side reactions are possible. They should be minimized to yield the highest FD. Several conditions, such as DCP and GMA concentration, temperature, pressure, and the use of $scCO_2$ can minimize these side reactions.

In this study, we started by studying the influence of the feed composition (GMA and DCP) on the FD values for both virgin LDPE and RPE.

Overall, the amount of GMA being grafted increased with the initiator intake until it reached a plateau, as shown in Figure 3. Similar results were found in the literature [6,7,9–11,33]. The main reason for this was the increase in the number active sites, which enhanced unfavorable side reactions, such as crosslinking and the homo-polymerization of GMA [6,7,9–11,35,36]. Overall, the RPE yielded lower FD values compared to the LDPE.
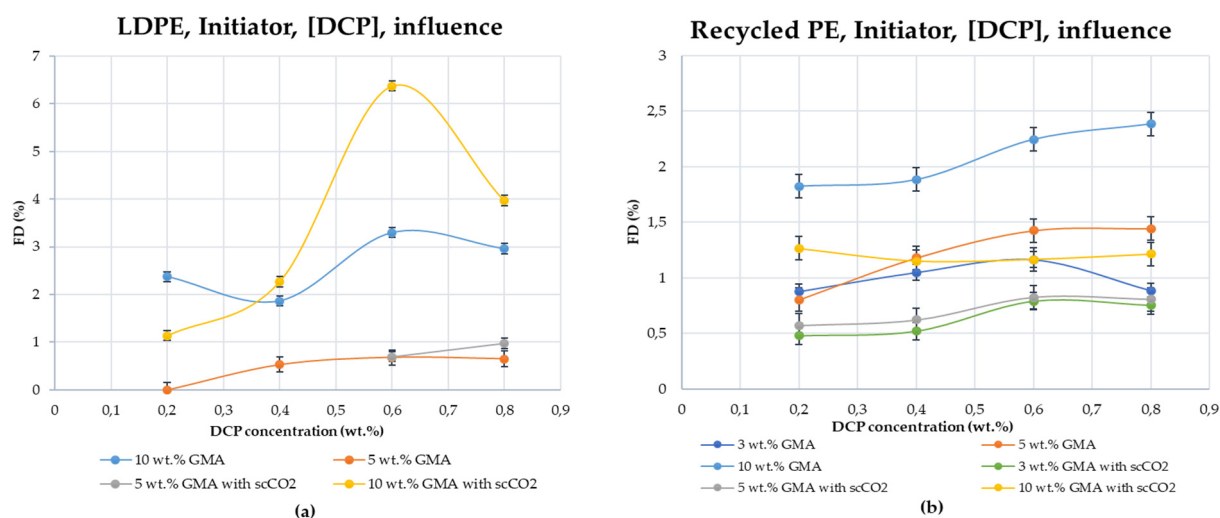

Figure 3. Effect of initiator concentration on the FD for LDPE (**a**) and RPE (**b**).

As shown in Figure 4, an increase in the amount of GMA at constant DCP concentration resulted in a higher FD. The highest FD was found when using 10 wt.% GMA for all the samples.
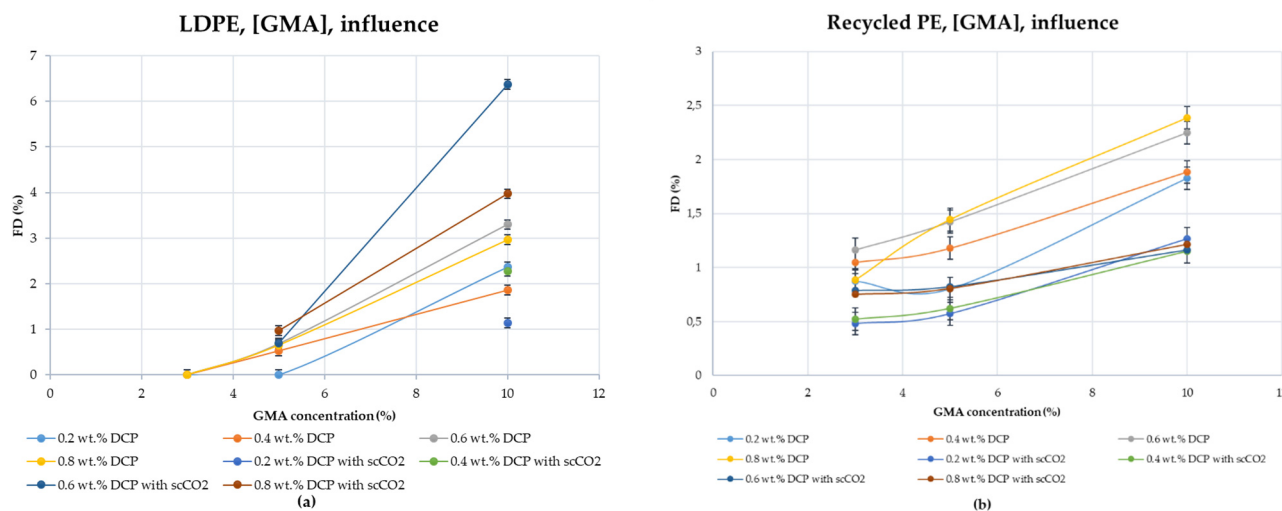

Figure 4. Effect of GMA concentration on the FD for LDPE (**a**) and RPE (**b**).

This was in agreement with literature-based expectations because a larger amount of GMA monomers allows more molecules to be grafted onto the matrix and less active sites are available for the crosslinking of PE [11]. The grafting efficiency increased with the DCP intake for the LDPE, according to Figure 5a. However, the GMA grafting efficiency declined significantly for RPE, according to Figure 5b. It was assumed that GMA homo-polymerization may exceed GMA grafting in reaction rate with the increase in the monomer concentration. As a result, the efficiency decreased in the grafted GMA based on initial GMA concentration. These observations were also made in other grafting studies [6,7,9–11,33].
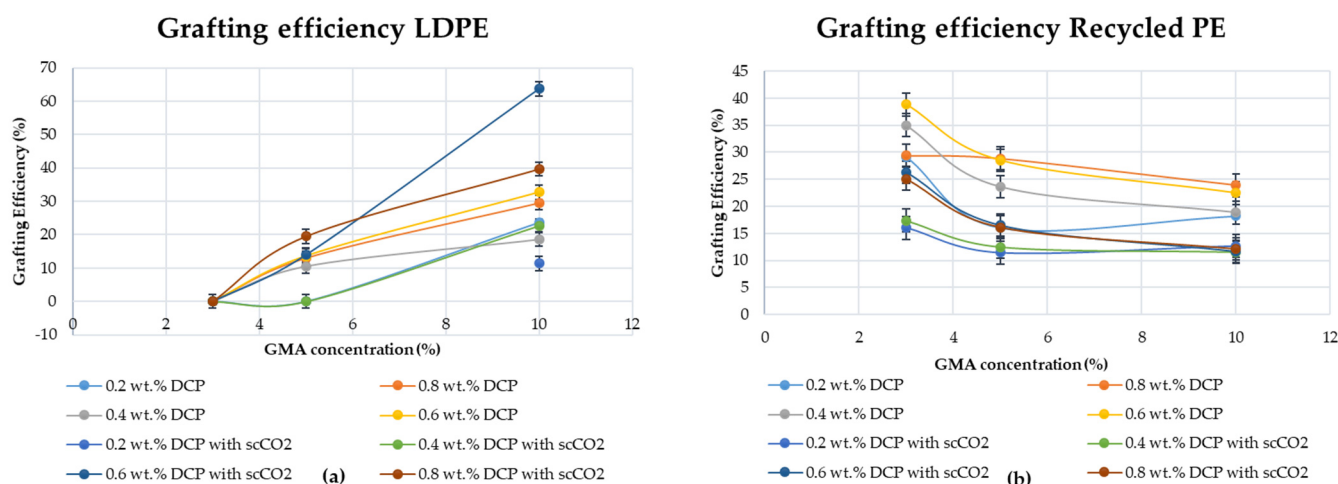

Figure 5. Grafting efficiencies for LDPE (**a**) and RPE (**b**).

To assess which parameters were more influential in changing the FD of the RPE-g-GMA, a statistical test using one-way ANOVA was conducted. The results are shown in Table 1.

As shown in Table 1, $p < 0.05$ for the variation of the (GMA) was conducted on the RPE regardless of the presence of scCO$_2$. This indicated that the null hypothesis of equal means was rejected. Therefore, tuning the (GMA) had a higher influence on altering the FD compared to tuning the (DCP). This was also reported by M. Saeb et al. (2017) [36], through a mathematical modeling approach of grafting GMA onto HDPE.

Overall, using pure, i.e., fresh and non-recycled, LDPE resulted in higher FD for all the samples, as expected. There are several possibilities that could account for this observation. First of all, it is very likely that there were radical quenchers present in the RPE, such as carbon black, which may have influenced the reaction rate and the grafting reaction. The presence of carbon black could also explain the color difference, with the RPE being light gray, as opposed to white, for the fresh LDPE.

Moreover, there were traces of PP present in the RPE pellets, according to the DSC results. Therefore, extra grafting experiments were performed with the PE and PP mixtures (Table 2) to check whether the presence of PP had an influence on the grafting degree.

Table 2. FD of several substrates without the use of scCO$_2$.

		FD		
Inlet	LDPE	RPE	10 wt.% PP and 90 wt.% LDPE	20 wt.% PP and 80 wt.% LDPE
0.6 wt.% DCP 10 wt.% GMA	3.30	2.25	0.65	1.115
0.8 wt.% DCP 10 wt.% GMA	2.96	2.39	0.79	1.08

It can be concluded that the samples containing PP yielded significantly lower FD values. The different results might have been caused by the involvement of the polymer macro-radical via the chain scission (β-scission) of the unstable PP macro-radicals. This is highly undesirable if a high graft yield is desired for use in a secondary process.

On the other hand, the difference in the composition led to the different viscosity of the melt. The rheology measurements pointed out that the viscosity of the RPE was six times higher than that of the LDPE at 130 °C. This high viscosity led to insufficient mixing in the extruder and favored the cage effect, which may explain the lower FD [14]. The exact reason for this difference is that viscosity was yet to be found. However, it probably stemmed from the post-consumer nature of RPE and the presence (vide supra) of different contaminants.

In order to obtain a higher FD value, the use of $scCO_2$ during the reactive extrusion might help, due to its advantages. According to Dorscht et al. (2002) [37], who investigated the influence of $scCO_2$ on the levels of MAH grafted onto polypropylene through reactive extrusion, $scCO_2$ had a positive impact on the grafting level when working with higher inlet concentrations of MAH (4 wt.%). Moreover, using certain levels of $scCO_2$ (2, 3 wt.%) led to less chain degradation compared to working with lower inlet concentrations of MAH (2 wt.%). On the other hand, Cao et al. (2010) [29] discovered that both the grafting degree and efficiency drastically improved, with an efficiency up to 85%, when lower concentrations of MAH and DCP were used.

The use of $scCO_2$ gave different results for the two types of PE used, as shown in Figures 2 and 3. $ScCO_2$ had a positive impact on the FD for the PE-g-GMA (0.6 wt.% DCP and 10 wt.% GMA) prepared with LDPE, reaching an FD of 6.3% compared to 3.2% without the use of $scCO_2$. Nevertheless, the influence of $scCO_2$ was more significant at higher concentrations of GMA compared to the results of Dorscht et al. (2002) [37] and Cao et al. (2010) [29].

On the other hand, $scCO_2$ had a negative impact on the FD for all the RPE-grafted samples, as can be seen in Figures 2 and 3. According to the gel content measurements with toluene, using higher concentrations of DCP favored a crosslinking instead of a grafting reaction. This observation was also reported by Zhou et al. (2017) [38], where an increase in the DCP concentration increased the gel content in HDPE. Furthermore, Hwang et al. (2012) [39] studied the use of $scCO_2$ during a reactive extrusion of PP/polystyrene blends and noticed that chain scission reaction by peroxides became more prominent at high DCP levels. This might also have occurred during our process, in which the use of $scCO_2$ during the reactive extrusion probably further enhanced the crosslinking effect and, therefore, resulted in lower FD values.

Despite the negative initial results of using $scCO_2$ for the grafting of RPE, $scCO_2$ has the advantage of lowering the viscosity of the melt phase due to its swelling and plasticizing effects, which can result in a lower process temperature [23–27,29]. In Figure 6, the results are shown of the temperature effect for different inlet concentrations. The residence time was set to 5 min, with a screw speed of 20 rpm.

Again, the highest FDs obtained at 190 °C and 200 °C were achieved for the samples not treated with $scCO_2$. The reason why higher temperatures resulted in a decrease in FD might be that the processing temperature exceeded the ceiling temperature of the GMA (150–220 °C). At higher temperatures, the polymerization of GMA becomes reversible. Moreover, the residence time was set to 20 rpm, which is not the most suitable time for all the different temperatures due to the different half-life times of DCP at different temperatures.
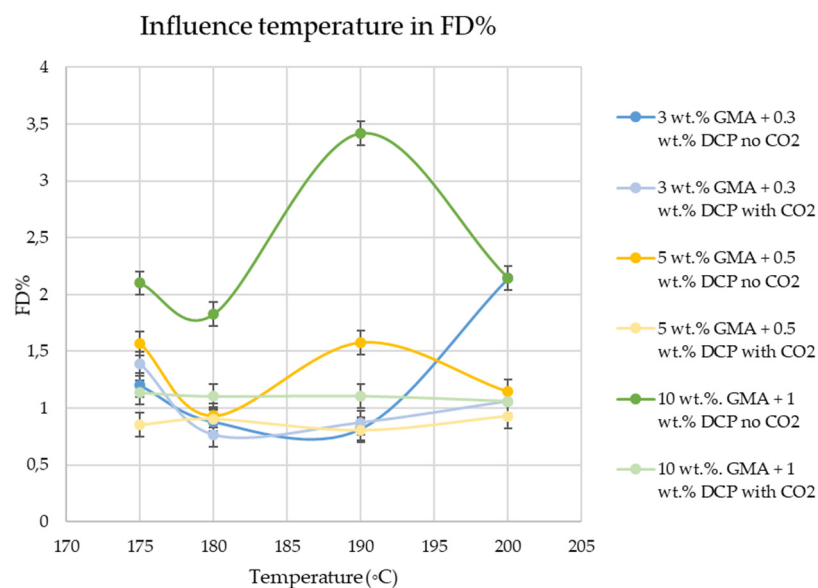
Figure 6. Temperature influence of FD on RPE samples.

The influences of $scCO_2$ and a different process temperature on the FD of the RPE was not significant at all for the samples with higher inlet concentrations. However, a small increase was seen for the 3 wt.% GMA + 0.3 wt.% DCP at 175 °C compared to the results in Figure 3. This difference in FD values as functions of temperature with and without $scCO_2$ is relevant and yet difficult to explain. Generally speaking, the influence of temperature on FD values for melt processes is related to the occurrence of side reactions [5,6]. This can be also be the case in $scCO_2$ conditions, with one additional remark. The monomer used in this work (GMA) is soluble in $scCO_2$; this causes a dilution effect, according to which, side reactions as GMA homo-polymerization become less probable. At the same time, with GMA present in the supercritical phase, a mass transfer barrier has to be overcome in order to obtain grafting.

The optimal residence time in the extruder is linked to the temperature profile and, therefore, the screw speed. An excessively long residence time is unfavorable and can result in a decline in GMA grafting due to the depolymerization of the GMA [7,9]. Therefore, the screw speed was adjusted to the ideal residence time and temperature, as shown in Table 3.

Table 3. Half-life-time DCP at different temperatures.

Temperature (°C)	Half-Life-Time DCP (min)	Residence Time (min)	Screw Speed (rpm)
175	0.79	8	4
180	0.50	5	20
190	0.21	2	42
200	0.09	1	66

The results are given in Figure 7.

Adjusting the screw speed resulted in a significant improvement of the FD for the samples prepared without $scCO_2$ while working at 200 °C. The mixing was probably improved due to the increase in the rotational screw speed to 66 rpm, resulting in the exertion of a large amount of shear by the screws.

The samples grafted under $scCO_2$ did not show any serious improvement. Presumably, the $scCO_2$ could have swollen the polymer more due to a lower viscosity at higher temperatures. Therefore, the initiator could diffuse better into the matrix, which would have led to the crosslinking of the PE instead of GMA grafting.
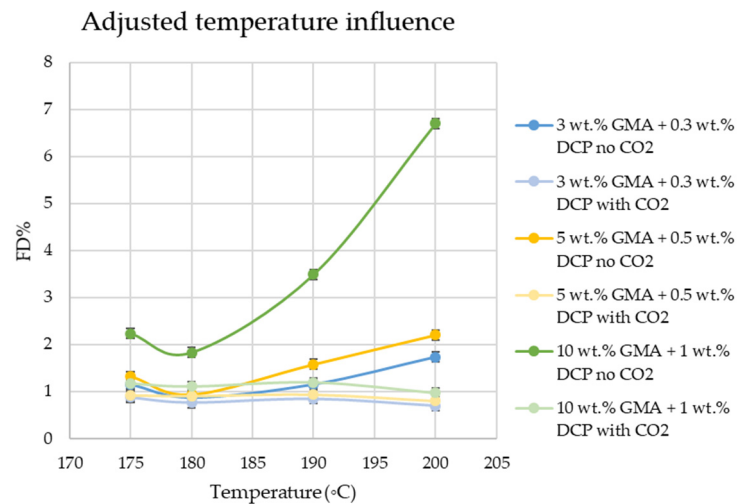
Figure 7. Influence of temperature while using the ideal screw speed for RPE samples.

Having considered the screw speed, as well as the temperature profile of the extruder, it was also reasonable to observe the different properties of the $scCO_2$ itself. The solubility, solvation power, and transport properties of the $scCO_2$ were all related to the temperature and pressure [24]. Some experiments were carried out with different pressures (90–170 bar) at a constant temperature (180 °C). The results are shown in Figure 8.
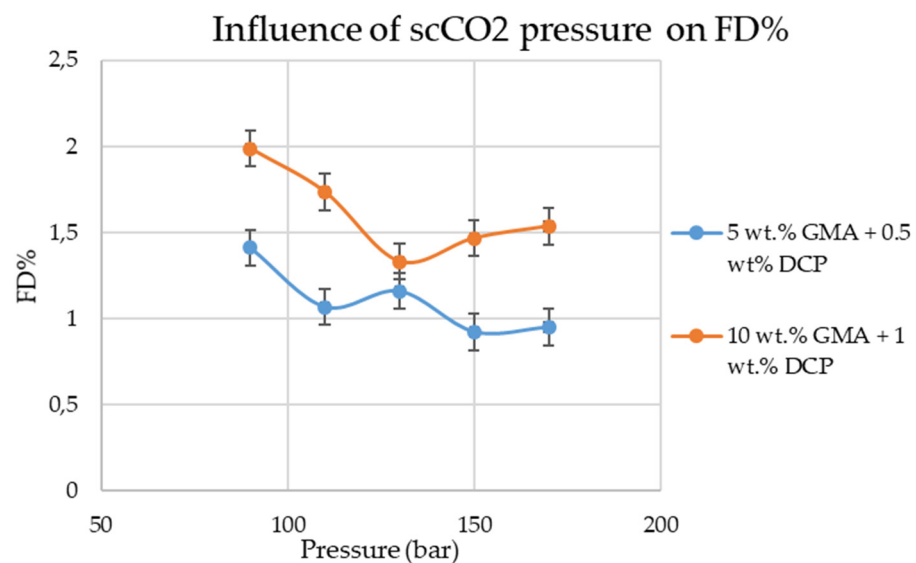

Figure 8. Influence of CO_2 inlet pressure on FD.

Higher pressures did not favor the GMA grafting process. This was also reported by Galia et al. (2004) [40] during the grafting of MAH onto isotactic PP. According to their findings, there was more polymer swelling due to the higher density (increasing solubility parameter) of the $scCO_2$. This automatically led to more diffusion of the MAH, but also to that of the free radicals formed by the decomposition of the peroxide inside the polymer. Therefore, this enhanced the occurrence of more unwanted side reactions. Furthermore, the stabilizing effect of the $scCO_2$ at higher pressure increased, leading to more side reactions due to the longer radical lifetime.

Areerat et al. (2002) [41] reported a decrease in LDPE viscosity as the $scCO_2$ concentration in the system increased. Lowering the viscosity of the melt enhances the $scCO_2$ infiltration in the matrix and lowers the cage effect. However, in the present study, an increasing flow of $scCO_2$ resulted in the opposite observation, as shown in Figure 9. Just

as in the case of using higher pressure, the higher swelling of the matrix resulted in more unwanted side reactions.
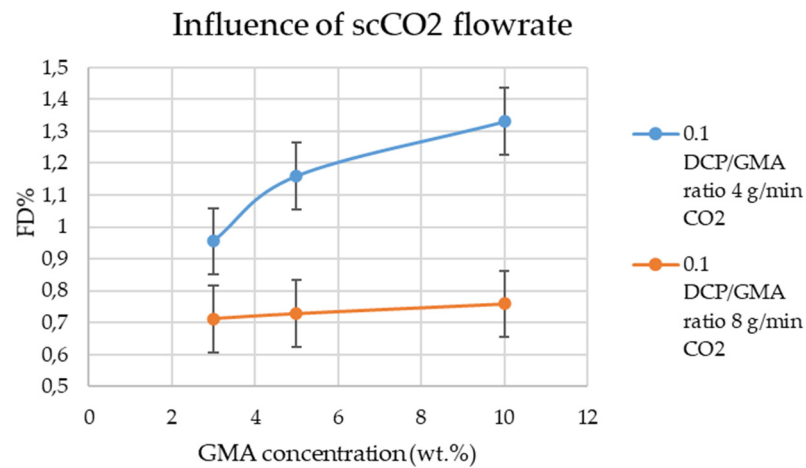
Figure 9. Influence in the $scCO_2$ flow.

Mechanical Properties of PE-g-GMA

A series of laboratory shear tests were carried out to evaluate the bonding strength between the aluminum plates and the grafted samples in order to preliminarily evaluate the applicability of the prepared samples as hot melt adhesives. The mechanical properties of the grafted LDPEs with different FDs are plotted in Figure 10.

Figure 10. Strain (**a**) and stress (**b**) at break for grafted LFPE samples with different FD.

The samples with a FD of 3.3 did not break at all. The LDPE-g-GMA glue was stronger than the aluminum plates, which were torn apart in all five samples. This was also confirmed by observing the strain, which was significantly higher compared to the other FDs.

The tensile test results of the grafted RPE samples are shown in Figure 11.

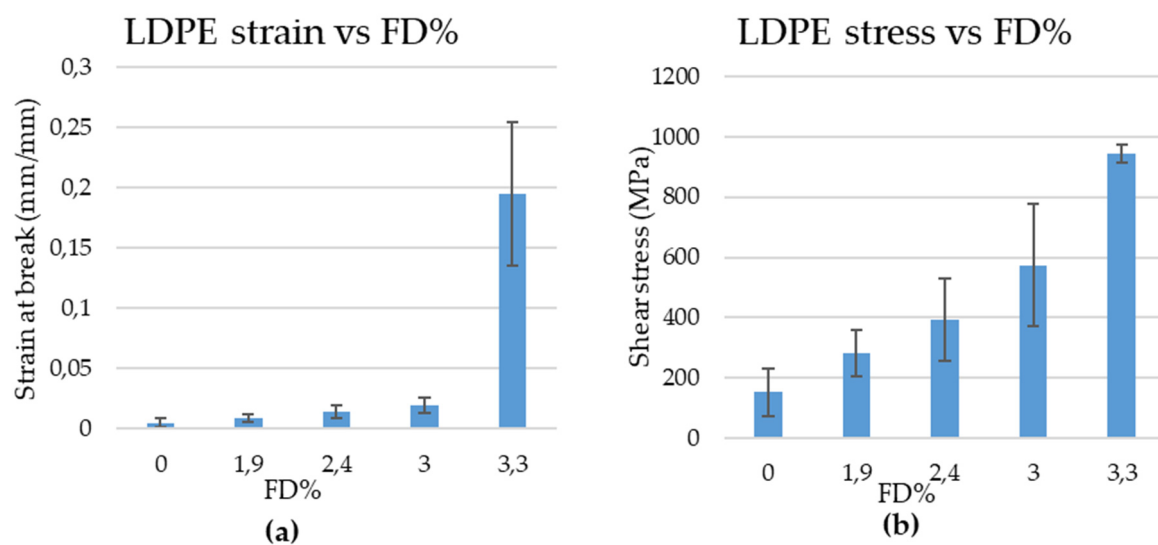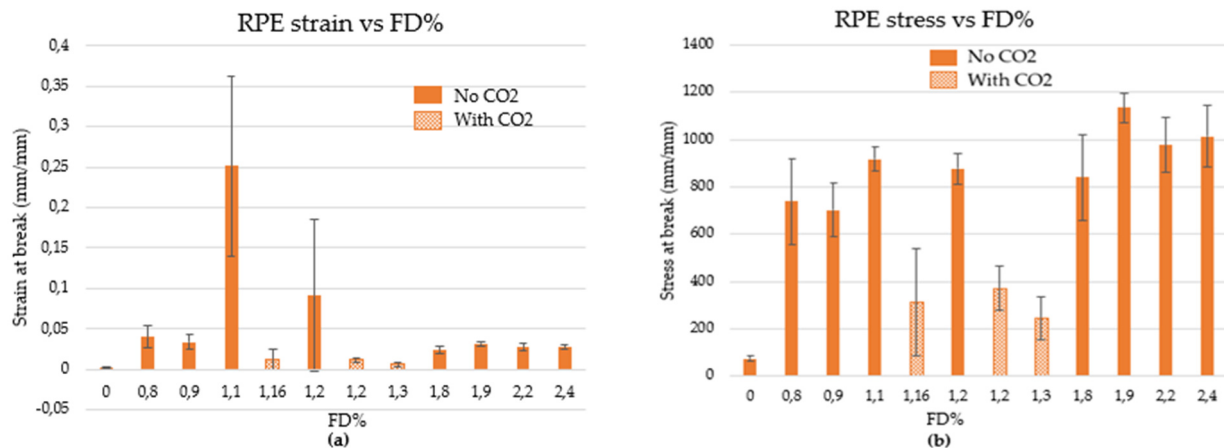**Figure 11.** Strain (**a**) and stress (**b**) at break for grafted RPE samples with different FD.

The glue was stronger than the aluminum plates for all the glued samples with the 1.1 FD, as well as 3 out of 5 for the 1.2 FD. Overall, it can be concluded that all the grafted samples withstood higher stress rates compared to the non-grafted samples. On the other hand, a higher FD does not automatically entail the breaking of the substrate. In the case of the grafted LDPE, only the highest FD resulted in the aluminum breaking, but for the grafted RPE, lower levels of FD were sufficient. Apparently, the use of $scCO_2$ during the grafting process not only had a negative impact on the FD, as stated previously, but it also negatively impacted the adhesive properties. The RPE samples prepared with $scCO_2$ with a similar FD to those made without $scCO_2$ had a significantly lower stress allowance.

Figure 12 shows sheets of LDPE and RPE on aluminum foil at a $100\times$ magnification. The RPE sheets contained waste particles and had a yellow color, whereas the LDPE was free of particles and colorless.
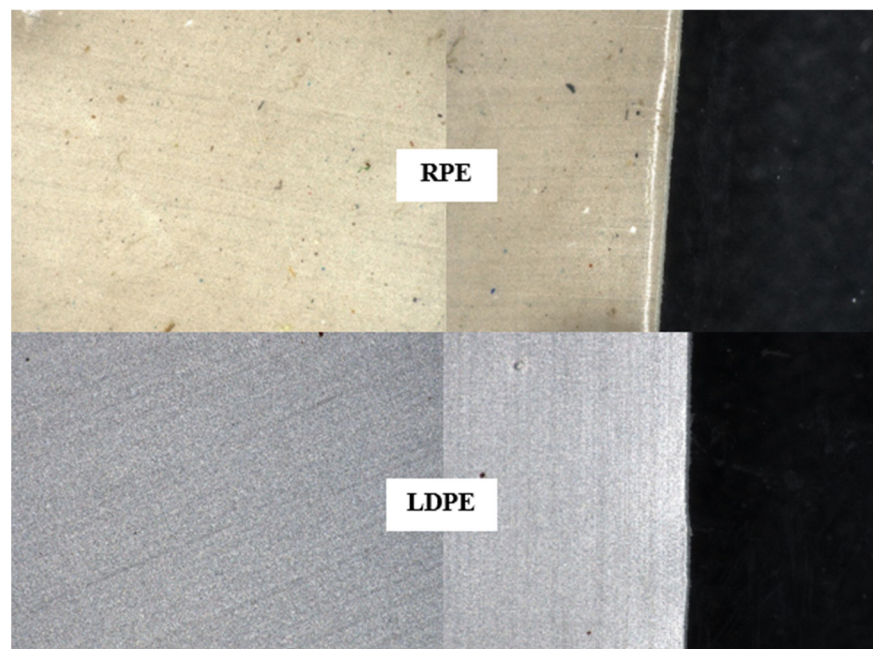

Figure 12. RPE and LDPE sheets on aluminum foil at $100\times$ magnification, pressed at 130 °C (LDPE) and 200 °C (RPE) at 100 kN for 15 min (2.5 min warmup at 0 kN, 12.5 min at 100 kN). The edges of the films are shown on the left and in the center of the films on the right.

4. Conclusions

In this work, the grafting of GMA onto LDPE and RPE was investigated. Several process conditions, such as concentrations of DCP and GMA, the use of $scCO_2$, and process temperature and reaction time, were adjusted in order to provide a better insight into which of the settings influenced the grafting process and adhesion properties the most. Increasing the DCP and, especially, GMA concentrations initially resulted in a higher FD in both substrates but, at higher concentrations, a decrease was shown due to the occurrence of more unfavorable side reactions. The influence of $scCO_2$ clearly showed different outcomes for the two substrates used. For all the grafted samples, the LDPE samples showed the highest FD and using $scCO_2$ had a positive impact. However, the $scCO_2$ had a negative impact on the FD of all the grafted samples made out of RPE, enhancing more unfavorable side reactions. Adjusting the temperature and rotational screw speed in accordance with the half-life time of the DCP resulted in higher FD, with the highest FD recorded as 6.7%. This value was obtained under the following conditions: 10 wt.% GMA, 1 wt.% DCP, a temperature of 200 °C, and a screw speed of 66 rpm. The tensile test showed that all the grafted samples appeared to have better adhesive properties. However, the tensile property increase for the recycled LDPE was less pronounced. An increase in FD for the grafted LDPE resulted in higher maximum stress. Even better were the results for the grafted RPE. These samples did not even need extremely high FDs to make the aluminum plates break.

On a more general level, the purpose of this work was twofold: on the one hand, to investigate the possibility of using a post-consumer RPE for grafting purposes, and, on the other, to use $scCO_2$ as a processing aid. Both questions were shown to have a positive answer as far as the mere possibility is concerned. However, the $scCO_2$ seemed to have a slightly negative effect on the FD values, although the validity of this statement needs to be checked by analyzing other polymers before it can be stated generally. The use of a post-consumer RPE was shown to have little influence, if any, on the quality of the end-product, envisioned here as an adhesive. However, form a purely scientific point of view, the presence of contaminants does require extra effort in terms of characterization and dedicated extra experiments in order to fully elucidate the influence of different processing parameters on the final product structure. The strategy used in this work, including, for example, the use of pure LDPE/PP blends to clarify the obtained FD values, might be seen, in this context, as a general approach to the presence of polymeric contaminants.

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Appendix A

PE-co-GMA (Sigma Aldrich) with a known GMA amount of 8 wt.% was diluted with LDPE pellets and blended in a Brabender plasticorder at 155 °C for 8 min at 60 rpm. Each sample was measured in an FTIR (Shimatzu Ir tracer-100), and the characteristic peak height was determined for the carbonyl group of GMA at 1732 cm^{-1} and the group of PE at 715 cm^{-1}. The ratio between these peak heights was plotted against the GMA content in the samples to obtain the calibration curve. The calibration curve of the LDPE and PE-g-GMA is given in Figure A1.
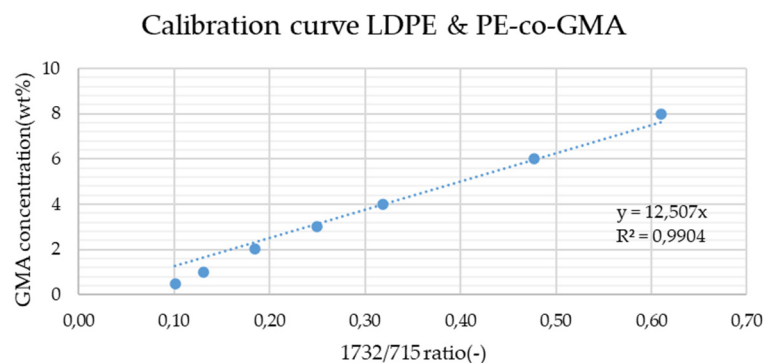
Figure A1. Calibration curve of LDPE and PE-g-GMA.

Appendix B

All the experimental data and conditions are listed in Tables A1–A5.

Table A1. Extruder temperature: 175–180–185–180–175 °C. Screw speed: 20 rpm. PscCO$_2$: 130 bar. Flowrate: 4 g/min.

GMA (wt.%)	DCP (wt.%)	Average FD	E (%)	GMA (wt.%)	DCP (wt.%)	Average FD	E (%)
	Pure LDPE without CO$_2$				Pure LDPE with CO$_2$		
5	0.6	0.682	13.631	5	0.6	0.699	13.990
	0.8	0.652	13.037		0.8	0.975	19.502
	0.2	2.374	23.741	10	0.2	1.137	11.368
10	0.4	1.866	18.67		0.4	2.269	22.686
	0.6	3.297	32.969		0.6	6.374	63.741
	0.8	2.962	29.619		0.8	3.973	39.730
	RPE without CO$_2$				RPE with CO$_2$		
	0.2	0.875	29.157	3	0.2	0.480	15.997
3	0.4	1.049	34.962		0.4	0.521	17.365
	0.6	1.165	38.842		0.6	0.789	26.316
	0.8	0.883	29.422		0.8	0.752	25.066
	0.2	0.804	16.090	5	0.2	0.572	11.441
5	0.4	1.180	23.608		0.4	0.622	12.433
	0.6	1.425	28.493		0.6	0.825	16.497
	0.8	1.443	28.858		0.8	0.807	8.070
	0.2	1.825	18.254	10	0.2	1.266	12.659
10	0.4	1.885	18.850		0.4	1.149	11.488
	0.6	2.247	22.470		0.6	1.165	11.651
	0.8	2.386	23.864		0.8	1.214	12.144

Ratio	GMA (wt.%)	RPE without CO$_2$ Average FD (%)	E (%)	Ratio	GMA (wt.%)	RPE with CO$_2$ Average FD (%)	E (%)
0.1	3	1.003	33.425	0.1	3	0.955	31.829
	5	1.199	23.977		5	1.160	23.197
	10	2.016	20.157		10	1.331	13.314
0.1 duplo	3	0.879	29.303	0.1 duplo	3	0.763	25.435
	5	0.933	18.651		5	0.902	18.049
	10	1.827	18.266		10	1.103	11.033
0.2	3	0.893	29.775	0.2	3	1.013	33.772
	5	1.313	26.254		5	1.043	20.850
	10	1.992	19.918		10	1.144	11.440
0.4	3	1.079	35.974	0.4	3	1.067	35.581
	5	1.522	30.445		5	1.108	33.214
	10	2.302	23.021		10	1.514	15.314
0.6	3	1.106	36.855	0.6	3	0.804	26.816
	5	1.555	31.110		5	0.985	19.706
	10	N.A.	N.A.		10	1.072	10.723

Table A2. Effect of temperature and rotational screw speed on recycled PE-g-GMA. $PscCO_2$: 130 bar. Flowrate: 4 g/min.

Temperature (°C)	Run	GMA (wt.%)	RPM	Average FD	E (%)	Average FD	E (%)
				Without CO_2		With CO_2	
175	1	3	20	1.200	40.004	1.392	46.408
	2	5	20	1.566	31.323	0.851	17.027
	3	10	20	2.100	20.995	1.135	11.348
175	1	3	4	1.151	38.362	0.877	29.238
	2	5	4	1.322	26.432	0.916	18.322
	3	10	4	2.228	22.281	1.162	11.625
190	1	3	20	0.818	27.258	0.871	28.300
	2	5	20	1.578	31.555	0.802	18.584
	3	10	20	3.421	34.205	1.106	11.060
190	1	3	42	1.155	38.499	0.849	28.300
	2	5	42	1.578	31.565	0.929	18.584
	3	10	42	3.489	34.888	1.186	11.863
200	1	3	20	0.978	32.599	0.840	28.007
	2	5	20	1.114	22.877	0.929	18.575
	3	10	20	2.144	21.443	1.060	10.599
200	1	3	66	1.729	57.636	0.698	23.280
	2	5	66	2.204	44.079	0.799	15.982
	3	10	66	6.701	67.006	0.969	9.688

Table A3. Cyclic GMA grafting onto PE. Extruder temperature: 175–180–185–180–175 °C. Screw speed: 20 rpm. $PscCO_2$: 130 bar. Flowrate: 4 g/min. Ratio: 0.1. GMA 10 wt.%.

Cycle	Substrate	Average FD	E (%)
1	LDPE	2.005	20.048
	RPE	1.754	17.542
2	LDPE	2.170	10.851
	RPE	2.823	14.117
3	LDPE	2.980	9.932
	RPE	3.219	10.728

Table A4. Effect of variation in $scCO_2$ pressure on recycled PE-g-GMA results. Extruder temperature: 175–180–185–180–175 °C. Screw speed: 20 rpm. $PscCO_2$: 130 bar. Flowrate: 4 g/min. Ratio: 0.1.

Pressure (bar)	GMA (wt.%)	Average FD	E (%)
90	5	1.412	28.243
	10	1.986	19.864
110	5	1.068	21.367
	10	1.734	17.337
130	5	1.160	23.197
	10	1.331	13.314
150	5	0.923	18.467
	10	1.467	14.670
170	5	0.950	19.005
	10	1.536	15.363

Table A5. Effect of variation in scCO$_2$ flow on recycled PE-g-GMA results. Extruder temperature: 175–180–185–180–175 °C. Screw speed: 20 rpm. PscCO$_2$: 130 bar. Flowrate: 4 g/min. Ratio: 0.1.

Pressure (bar)	GMA (wt.%)	Average FD	E (%)
	3	0.955	31.829
4 g/min	5	1.160	23.197
	10	1.331	13.314
	3	0.712	23.745
8 g/min	5	0.728	14.563
	10	0.759	7.593

Appendix C

Different purification methods were used to determine the amount of GMA grafted onto the polymer matrix. Some researchers dissolved a small amount of the polymer in refluxing xylene, and used acetone for the precipitation [9,21]. Therefore, several purification methods were performed to determine the most reliable method for the determination of the FD.

The PE-g-GMA was produced in the Brabender using a GMA concentration of 3 wt.% and a TRI concentration of 0.4 wt.%. Note that this is a different peroxide from that used in previous studies. However, these experiments were performed to investigate the differences between the purification methods. The unwashed product had an FD of 0.98. The product was purified using different methods after it was characterized using FTIR to obtain the FD. The results are presented in Table A6, which shows that the different cleaning methods yielded quite significantly different FDs. The purification method involving an extraction with THF yielded the lowest FD, suggesting that this purification method had the highest extraction efficiency. When using the purification method using xylene as the solvent and acetone or methanol as the anti-solvent, the FD was much higher. This indicated that the grafting degrees of the grafting experiments performed in the literature are rather high. Too much p-GMA is still present in the product, leading to a higher IR peak, which in turn leads to a higher FD.

Table A6. Purification methods.

Purification Method	FD
None	0.98
Precipitation with acetone	0.83
Precipitation with methanol	0.87
Soxtec with acetone	0.98
Soxtec with THF	0.59

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