Chapter 9
Grafting Functional Groups onto Biodegradable Thermoplastic Polyesters

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Abstract A general awareness of the environmental impacts of plastics has caused behavioral changes in the public sector. This in turn has led to research related to biodegradable or sustainable alternatives to petrochemical plastics. Biodegradable polymers have been around for years (e.g. poly(ε-caprolactone) (PCL), poly(butylene succinate) (PBS) and poly(lactic acid) (PLA)). However, these have recently become an affordable alternative. PLA and poly(butylene adipate-*co*-terephthalate) (PBAT) are two polyesters that have gained significant research interest as biodegradable alternatives, especially for the preparation of natural or biobased polymer blends. Nonetheless, the lack of miscibility in some polymer blends limits their usefulness unless a compatibilizing agent is used. A very common strategy is to graft a functional monomer into the polymer backbone, of which maleic anhydride (MA) is the most common, but not the only one. This chapter explores the use of grafting functional groups onto polyesters in light of the well-established field of free radical grafting of polyolefins to achieve materials that are effective at compatibilizing biodegradable or compostable blends.

Keywords Blend · Compatibilizer · Polyester · Reactive extrusion

9.1 Introduction

The global polymer market typically grows approx. 7% annually and exceeded US $60 billion in 2016 (Smith and Verbeek 2018). The polymer industry is mature in many aspects, but research is being done to manipulate material properties for

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specific applications. The last few years have seen a rapid increase in the development of sustainable polymer materials, as well as those derived from natural resources. Globally, the market for biodegradable resins is expected to reach more than US $16 billion by 2022 (Smith and Verbeek 2018).

The widespread application of biodegradable polymers as commodity materials has been slow, mainly due to the higher cost of the resin compared to petroleum-based alternatives. For example, poly(lactic acid) (PLA) and poly(butylene adipate-*co*-terephthalate) (PBAT) generally sold for more than 3 USD/kg and poly(ε-caprolactone) (PCL) can be up to 20 USD/kg, compared to commodity polymers such as poly(ethylene) (PE) and poly(propylene) (PP) which are in the region of about 1 USD/kg (Smith and Verbeek 2018).

The processing and subsequent properties of biobased polymers can also be a challenge. They sometimes have narrow processing windows and mechanical properties that are often not suitable for the purpose with a lack of balance between stiffness, strength and toughness (or impact strength). This has significantly slowed their widespread adoption and it is generally concluded that commercialization would require inexpensive techniques to modify these materials (Raquez et al. 2008b).

As a result, research into polymer blends to achieve property and price advantages is continuously expanding. Achieving good mechanical properties in particular depends largely on the ability to manipulate and control interfacial properties and creating the correct morphology (Mani et al. 1999; Raquez et al. 2008b). However, this must be balanced against blend's biodegradability and careful consideration may offer a strategy to modify biodegradation rates for specific applications (Raquez et al. 2008b).

Biodegradable polyesters, such as PCL and PLA, are good examples of polymers that have been modified by melt blending with a focus on the dispersion of one in the another, using functional polymers as interfacial modifiers or incorporating block and random copolymers (Mani et al. 1999; Gutiérrez and Alvarez 2017a,b,c; Gutiérrez 2018).

Grafting is a convenient way to prepare these functional polymers and a variety of methods are available in melt, solid or solution states. The most convenient method is the melt or reactive extrusion (REx) for which free radical grafting of maleic anhydride (MA) onto polyolefins is probably the most widespread industrial application (Gutiérrez et al. 2017).

This chapter considers the free radical grafting of biodegradable polyesters for their application in polymer blends. More specifically, it reviews the common biodegradable polyesters used today, the functional groups used for grafting, and the mechanisms by which grafting occurs. It also considers the equipment used for producing these materials and how grafting affects the properties of the newly formed functional material. A significant amount of research has been done to examine MA grafting onto polyolefins, however, fewer studies focus on grafting functional groups onto polyesters (John et al. 1997a).

9.2 Reactive Extrusion

One of the main objectives of grafting polymers through REx is an improvement in the material properties by introducing chemical groups which alter the polymer's characteristics, such as adhesion and reactivity with other polymers (Herniou--Julien et al. 2019; Morais et al. 2019). Free-radical grafting functional groups onto polyolefins *via* REx has gained widespread industrial applications and several functional PP and PE grades are commercially sold. The general consensus is that the reaction pathway for grafting depends on the polymer's molecular structure, and therefore, some variations between grafting efficiencies can occur for different polymers. In addition, by using a peroxide as initiator, crosslinking and other side reactions occur at the same time (Fang et al. 2008).

One of the most used monomers for grafting is MA. However, there are many other functional groups available, such as carboxylic acids, epoxy groups, vinylsilanes and other anhydrides (Raquez et al. 2008b; Wenfei et al. 2010; Fink 2013; Xijun et al. 2013). The modified polyolefins are characterized by a change in polarity, adhesion and greater miscibility compared to polar polymers (Kučera et al. 2017). When carboxylic acids are used, the acid is sometimes neutralized using hydroxides or metal oxides, which further changes the properties and uses of the grafted polymer (Krivoguz et al. 2003).

On the other hand, the development of functional polyesters is a more challenging issue and has hardly been explored compared to polyolefins (Morais et al. 2019). Functional biodegradable polyesters can be prepared by ring opening polymerization or polycondensation starting from functional monomers, but it is a rather expensive proposition and depends largely on the scale. However, the technologies available to functionalize polyolefins could be adapted here and would minimize the economic impact of changing raw materials (Signori et al. 2011).

The general concept of grafting is not new, and dates back to the early nineteenth century after the development of oil-resistant butadiene-acrylonitrile synthetic rubbers and the modification of natural rubber in its latex state (White and Sasaki 2003). During the 1960s, an effort was made to develop continuous extrusion processes for free radical grafting using peroxides (White and Sasaki 2003). One of the first patents on the use of twin-screw extrusion for grafting was filed in 1972, for grafting anhydrides and carboxylic acids onto polyolefins. Since then, twin-screw extruders have been dominant (White and Sasaki 2003).

REx is thus also an attractive route for processing biodegradable plastics, since it improves the commercial viability and profitability of these materials (Fink 2013). Because of these characteristics, REx is often used for a variety of chemical reactions to:

- Produce high molecular weight (Mw) polymers.
- Controlled degradation and crosslinking of polymers.
- Functionalization of commodity polymers.
- Interchain copolymer formation.

Table 9.1 Benefits and challenges of REx

Benefits	Challenges
Solvent free	Intimate reagent mixing mandatory
Quick preparation	High reaction temperatures are required
Simple product isolation	Side reactions, e.g. degradation
Continuous process	Crosslinking or discoloration
Economic	

Compared to other methods, such as solution polymerization, the benefits and challenges of REx, can be summarized in Table 9.1. REx is considered one of the most practical and profitable methods, since it achieves a better degree of mixing, is solvent-free, has a shorter production time, and is suitable for mass production (Signori et al. 2011; Standau et al. 2019).

Part of the benefits of using REx is that it allows multiple feed, venting and provides a high intensity distributive and dispersive mixture. Grafting is thus achieved using one of the following methods:

- The free-radical initiator the polar monomer and the polymer are added simultaneously.
- The polymer can be melted in a mixer (low pressure system) before being injected into the extruder.
- The polymer is fed first, and then the free-radical initiator and the polar monomer are fed separately at different points along the barrel.

One of the major applications of graft copolymers is their use as compatibilizers in polymer blends, which is a widely used method to tailor the properties of materials. Several studies have been devoted to the issue and to the challenge for obtaining adequately dispersed blends using various combinations of polymers, including polyesters such as PCL and PLA. Achieving a good dispersion of one phase in another is essential, since the properties of the final material depends largely on the characteristics of the interface (Nocita et al. 2017). The properties of synthetic and natural polymer blends can also be improved with compatibilizers, e.g. using MA-grafted PBAT as a compatibilizer has resulted in fine domain sizes and good dispersion of the soy protein concentrate in PBAT (Chen and Zhang 2010).

The compatibility of modified polymer compositions with a polar material can be controlled by the selection of the monomer, the level of grafting and the blend processing conditions. Tailoring the compatibility of blends with modified polymer compositions leads to better processability and improved physical properties of the resulting blend.

It is recognized that the miscibility between polymers is determined by a balance of enthalpic (ΔH_m) and entropic (ΔS_m) contributions to the free energy of mixing (ΔG_m). While for small molecules the energy is high enough to ensure miscibility, for polymers the entropy is almost zero, which makes enthalpy decisive for determining miscibility (Zarrintaj et al. 2019).

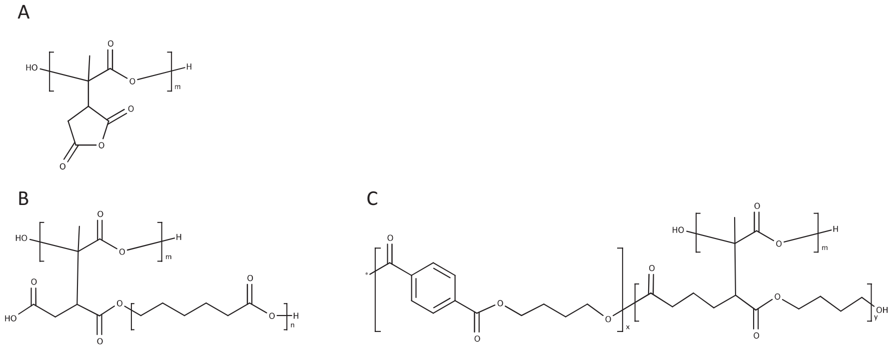


Fig. 9.1 (**A**) MA grafted onto PLA, (**B**) PLA crosslinked with PCL and (**C**) PBAT crosslinked with PLA. Reproduced with permission from Al-Itry et al. (2012)

For spontaneous mixing, ΔG_m must be negative, which means that the mixture is exothermic ($\Delta H_m < 0$, enthalpy of mixing) and will mix spontaneously, while for endothermic mixtures miscibility will only occur at high temperatures (Fink 2013). However, thermodynamic miscibility may not be required and compatibility, where the blend has useful properties, may be sufficient. This can be achieved by:

- Addition of a compatibilizer before or during processing.
- Adjustment of viscosity ratios to allow formation of a desired phase morphology.
- *In situ* formation of a compatibilizer.
- Introduction of crosslinks in one of the phases.

One approach to compatibilization is the addition of a block copolymer having segments with chemical structures or solubility parameters similar to those of the polymers that are blended. In general, this is extremely efficient, although it is rarely used for commercial applications. Another less costly approach is reactive composition, by which the compatibilizer is formed at the interface (Fink 2013). For example, PBAT and PLA or PCL and PLA can be reactively combined in the presence of a free radical initiator (dicumyl peroxide - DCP) and/or MA, which produce a compatible blend as is shown in Fig. 9.1 (Gardella et al. 2014; Ma et al. 2014).

9.3 Biodegradable Polyesters

Biodegradable and/or biobased polymers often struggle to compete in the market, currently dominated by low-cost petrochemical polymers. Despite this, the new biobased materials continue to receive academic and industrial interest. However, the redesign of products and materials requires the adaptation of processes currently tailored for polyolefin materials. Biodegradable aliphatic polyesters such as PLA, poly(butylene succinate) (PBS), poly(butylene succinate-*co*-adipate) are a

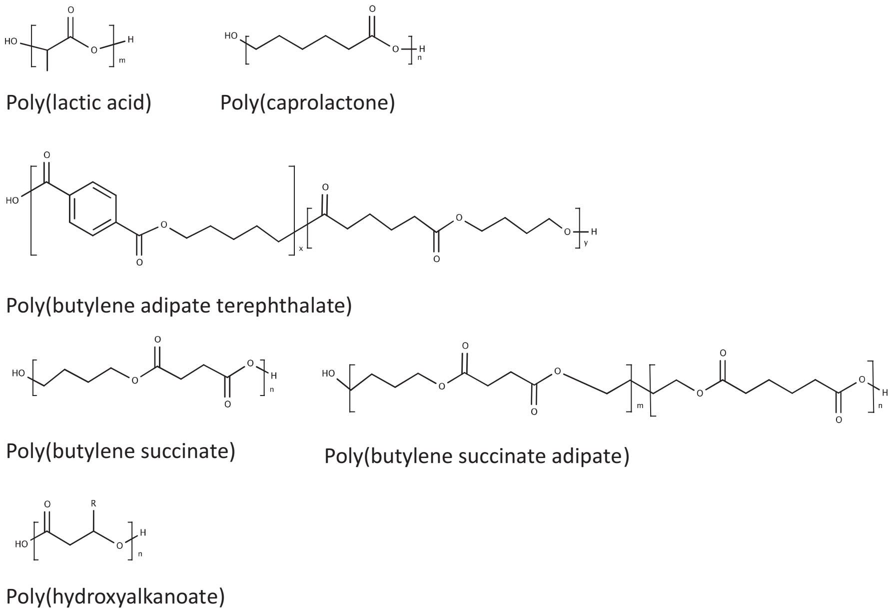


Fig. 9.2 Common biopolyesters

promising group of materials based on their performance, renewability and constant cost reduction (Fig. 9.2) (Signori et al. 2011; Morais et al. 2019).

The reason for grafting these polyesters is to modify properties such as impact resistance or melt strength, or to functionalize them to then be used as blend compatibilizers. An important limitation of PCL is the lack of functional groups, which limits its compatibility with other polymers (Riva et al. 2005). In addition, polyesters such as PBAT, PCL, PLA, poly(ester amide) (PEA), poly(hydroxybutyrate-*co*-valerate) (PHBV) and poly(hydroxy-ester ether) (PHEE) to be blended with starch, these polymers require some degree of functionality (Nabar et al. 2005). A similar behavior was observed by Wu (2015) for biopolyester/collagen blends, where better adhesion between collagen and polyhydroxyalkanoate (PHA) was observed after grafting PHA with MA.

9.3.1 Poly(Butylene Adipate-Co-Terephthalate) (PBAT)

Among the biodegradable polyesters mentioned, PBAT has attracted significant attention in the literature. PBAT is an aliphatic-aromatic polyester and has a high strain at break (ε_b) and is very suitable for packaging and agricultural films (Hayes et al. 2019; Merino et al. 2019). PBAT is a synthetic biodegradable polymer, based on adipic acid, butanediol and terephthalic acid. It is often used to improve the biodegradability of blends and composites or to improve the properties in other biobased materials. However, it requires the addition of a compatibilizer to ensure optimal properties. PBAT is most commonly grafted with MA using REx in the presence of a peroxide initiator (Nabar et al. 2005; Raquez et al. 2008a; Chen and Zhang 2009; Wu 2012a, b; Adrar et al. 2017; Kashani Rahimi et al. 2017; Liu et al. 2017; Muthuraj et al. 2017; Fourati et al. 2018).

9.3.2 Poly(Butylene Succinate) (PBS)

PBS is a very promising biodegradable polyester, synthesized *via* polycondensation of 1,4-butanediol with succinic acid (SA), and can be derived from fossil or renewable resources. PBS has mechanical properties similar to those of PE, as well as has very good processing behavior (Chikh et al. 2016). However, it has a low melt strength and a relatively low Young's modulus (YM) value (Calderon et al. 2019a).

PBS is often used in blends, but requires modification. For example, PBS has been blended with poly(L-lactic acid) (PLLA) and other polymers to improve mechanical properties and processing performance (Phua et al. 2013; Persenaire et al. 2014; Wu et al. 2014; Liu et al. 2015; Yin et al. 2015; Zhu et al. 2017; Picard et al. 2019). Generally, by adding grafted PBS (MAH-*g*-PBS) into blends or composites, a significant improvement in tensile and flexural strength can be expected over the corresponding uncompatibilized material (Signori et al. 2011; Muthuraj et al. 2015).

9.3.3 Poly(caprolactone) (PCL)

PCL is a synthetic aliphatic polyester which is generally considered biodegradable by enzymatic activity. It has good processability and high ε_b values, but low YM and tensile strength (σ_m) values. However, its high cost limits its applications. For this reason, PCL is often also mixed with other economical biodegradable polymers (Guaras et al. 2016). Several authors have described the grafting of PCL using MA, in the presence of peroxides and when used in blends having greatly improved the mechanical properties (Nitz et al. 2001; Wu 2003; Nabar et al., 2005; Morais et al. 2019). Some authors have also shown that the degree of grafting is higher than some conventional polymers and other biodegradable polyesters (Morais et al. 2019).

9.3.4 Poly(Lactic Acid) (PLA)

PLA is a thermoplastic aliphatic polyester derived from renewable biomass and is undoubtedly the most commercially successful biobased polymer. PLA is often used in compatibilized blends, either to improve the properties of the other polymer, or to try to overcome some of its own limitations, such as low melt strength and low impact strength (Gardella et al. 2014; Persenaire et al. 2014; Dawidziuk et al. 2018). PLA's reactivity for radical grafting is somewhat limited due to the low activity of MA towards the macro-radicals resulting from PLA's structural symmetry, but can be improved in the presence of electron-donating co-monomers (Ku Marsilla and Verbeek 2015b). As with other polyesters, there is an optimum concentration of radicals, which depends on the peroxide/monomer ratio and there are also other side reactions, such as chain scission and crosslinking, which can occur (Mani et al. 1999; Fink 2013).

9.3.5 Poly(hydroxyalkanoate)s (PHA)

This class of biodegradable thermoplastic polyesters are serious competitors for replacing petrochemical equivalents. PHAs are produced by bacterial fermentation as intracellular compounds. However, PHA-based materials are very expensive and this still limits their widespread industrial applications. PHA is often blended with other polymers to reduce cost. For example, poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBHH) can be blended with PBAT or PBS, showing the beneficial effect of adding maleated PHBHH to the blend (Chikh et al. 2016; Thirmizir et al. 2017). On the other hand, the REx of poly(3-hydroxybutyrate) (PHB) and a peroxide can be used to alter the crystallization behavior to improve melt spinning (Fink 2013).

9.4 Factors Affecting Grafting

Graft copolymerization is a common technique to modify a polymer's properties with minimal degradation. The type and extent of the changes depend on many factors, the most important being the polymer type, the reagent concentration, the type of monomer, the mixing and processing parameters (Mani et al. 1999; Maharana et al. 2015). However, the efficiency of grafting cannot be improved by increasing only the concentration of the radical initiator or the monomer. Equally important is the proper mixing, and often, the inclusion of comonomers. In fact, grafting without a radical initiator is also possible and can be formed by shear-induced chain scission (Fink 2013).

In order to obtain a high grafting efficiency together with an effective suppression of the side reactions, it is necessary to transform the macroradicals on the backbone as much as possible into graft sites. In general, within reasonable limits, higher reaction temperatures, higher initiator levels and lower yield rates result in higher grafting efficiency (John et al. 1997a, Fink 2013).

Grafting is somewhat complicated by side reactions such as backbiting depolymerization, or hydrolysis, which leads to an undesirable Mw reduction, as shown for many systems such as MA-grafted PLA. However, this could be mitigated by some additives (chain extenders) that allow the relinking of chains. In addition, branching and/or crosslinking can also occur and depend on the same variables controlling grafting (Standau et al. 2019).

As the name suggests, melt-grafting is performed above the melting point of the polymer in question, typically in melt mixers or extruders. The method is quite generic, since it requires mixing the reagents before processing or melting the polymer first, followed by the addition of the reagent. This could be achieved using side feeders during extrusion. An important step for all polyesters is sufficient drying before processing to prevent degradation during melt processing (Mohanty and Nayak 2010; Muthuraj et al. 2015; Liu et al. 2017). Unreacted monomers and decomposition products can be removed by vacuum.

9.4.1 Initiators

Free radicals can be generated by several compounds. The selection of a grafting initiator during REx is mainly based on the initiator's half-life and solubility in the polymer (Fink 2013; Kučera et al. 2017). Peroxides are commonly used as initiators in graft copolymerization and can be divided into seven groups, providing a range of reactivity: diacyl peroxides, dialkyl peroxides, diperoxyketals, hydroperoxides, ketoneperoxides, peroxydicarbonates and peroxyesters (Takamura et al. 2008). Of these, diacyl peroxides such as benzoyl peroxide (BPO) and di-*t*-butyl peroxide (DTBP) are the most commonly used. To optimize the chemical compatibility or solubility of the peroxides, the organic character of these peroxides must be carefully chosen and peroxides which yield radicals with double bonds have higher grafting efficiency (Fink 2013).

The most important indicator for the activity of an initiator is its half-life ($t_{1/2}$), which is the time required to decompose half of the initial initiator content at a given temperature. For the first order decomposition, the half-life is given by Eq. 9.1:

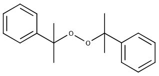
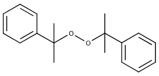
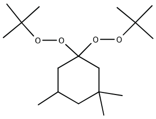
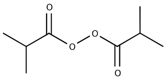
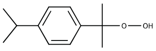
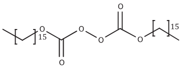
$$t_{1/2} = \ln 2 / k_d \tag{9.1}$$

where k_d is the constant of decomposition rate.

In general, when the residence time during REx is in the range of five times the half-life, the decomposition will be greater than 97%. However, if the half-life time is very short, the peroxide is decomposed mainly in the initial sections of the extruder, resulting in high concentrations of radicals in the polymer's backbone, which often results in an increase in crosslinking. Some examples of peroxide half-lives are shown in Table 9.2.

Based on the large difference between the types of peroxide, one can expect that their behavior and efficiency during grafting are also different, and as such, there are a large number of studies that have used different peroxide initiators, but few that directly compare their efficiency. The most studied polyester in light of peroxide

Table 9.2 Structures and half-life temperatures of some radical initiators

Compound	Structure	Initiator group	Half-life Temperature (°C)		
			10 h	1 h	1 min
DCP		Dialkyl peroxide	112	132	172
tert-butyl peroxybenzoate		Peroxyesters	103	122	160
1,1-di-(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane		Peroxyketal	85	105	148
Diisobutyryl peroxide		Diacyl peroxides	23	39	73
Di-isopropylbenzene-mono hydroperoxide		Hydroperoxides	129	154	207
Dicetyl peroxydicarbonate		Peroxydicarbonates	48	65	100

efficiency is PLA. Several peroxides have been used to control Mw and it has been shown that dialkanoyl peroxide, dialkyl peroxydicarbonate, diaroyl peroxide, peroxy acid and peroxy ester, which have carbonyl groups in the molecular structure, prevented excessive chain scission, while peroxides such as dialkyl and diaralkyl peroxide did not (Coltelli et al. 2010). Similar studies showed that peroxides with a short half-life only induced partial crosslinking of PLA, since the decomposition was fast and PLA was not yet completely molten. However, if the half-life is close to the residence time, a uniform crosslinking occurs (Standau et al. 2019).

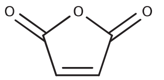
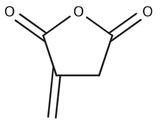
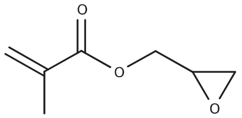
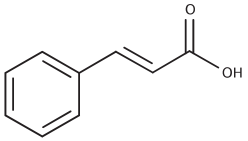
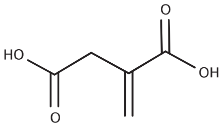
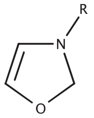
An alternative strategy to introduce free radicals for grafting are the so-called stable radicals, which are produced in two steps. A stable nitroxyl radical is grafted onto a polymer after which the grafted polymer of the first stage is heated in the presence of a monomer or oligomer at a temperature at which cleavage of the nitroxyl-polymer bond occurs and polymerization of the monomer is initiated in the polymer radical (Fink 2013). The benefit of this strategy is that the second step can be at a later stage, since the intermediate product can be stored for some time. Some examples of stable nitroxyl radicals can be 4-hydroxy-2,2,6,6-tetramethyl-piperidin-1-oxyl, 4-propoxy-2,2,6,6-tetramethyl-piperidin-1-oxyl, benzoic acid 2,2,6,6-tetramethyl-piperidin-1-oxyl-4-yl-ester and decanedioic acid bis(2,2,6,6-tetramethyl-piperidin-1-oxyl-4-yl) (Fink 2013).

9.4.2 Monomers

A wide variety of monomers have been grafted onto polyesters, the most important are listed in Table 9.3. Of these, MA is probably one of the most widely used reactive compatibilizers due to its good chemical reactivity, low toxicity and low homopolymerization potential. It is mainly chosen for its ability to react or interact with other polymers when the graft polymer is used as a compatibilizer in blends, especially polymers with functional groups such as -COOH, -NH_2 or -OH (Maharana et al. 2015; Standau et al. 2019).

Itaconic anhydride (IAH) has its double bond located outside of the anhydride ring, which makes it more reactive then MA and could also be bioderived (da Silva and Galland, 2013; Petruš et al. 2016). Alternatively, maleate esters such as dibutyl maleate or diethyl maleate have lower toxicity and volatility compared to MA, although they are also less reactive (Fink 2013). MA and IAH typically also lead to significant chain scission, while grafting GMA has been shown to increase viscosity, inferring that less chain scission occurred (Kim et al. 2004).

Table 9.3 Functional groups commonly grafted onto polyesters

Type	Functional group	Chemical name	References
Anhydride		MA	Pascente et al. (2008) Raquez et al. (2008b) Signori et al. (2011) Haque et al. (2012) Maharana et al. (2015) Puteh et al. (2015) Petruš et al. 2016 Standau et al. (2019)
		IAH	
Epoxy		Glycidyl methacrylate (GMA)	Kim et al. (2004)
Carboxylic acid		Cinnamic acid	Signori et al. (2011)
		Itaconic acid	Krivoguz et al. (2003) Isiklan et al. (2010) da Silva and Galland (2013)
Oxazoline		2-oxazoline 3-oxazoline 4-oxazoline	John et al. (1998) Mani et al. (1999)

Itaconic acid presents an interesting opportunity for grafting. It has two ionizable groups, with different pKa values, which can form hydrogen bonds (Isiklan et al. 2010) allowing different compatibility strategies in polymer blends. On the other hand, oxazoline compounds can readily react with carboxylic acids, making them useful for chain extension and compatibilizers through amide-ester bonds (John et al. 1998).

9.4.3 Mixing and Residence Time

Grafting literature is mainly focused on reactions and processing conditions. However, it has also been shown that the mixture strongly influences the grafting process. The efficient mixing not only distributes the components to improve the overall grafting level, but high shear can also help the generation of free radicals. Mixing units, such as static or dynamic mixers instead of the regular extruder head, are a method to achieve this. Of these, a dynamic mixer is the most efficient (Fink 2013).

The screw configuration and the positioning of the mixing zones will have a significant impact on REx. This highlights that the residence time distribution (RTD) is not the only factor for determining the reactive progress. Screw design should thus be focused on a configuration with an optimal mix to maximize the degree of grafting. However, it must be remembered that mixing in an extruder is related to the degree of fill and the RTD. A good degree of fill can be achieved by selecting appropriate kneading blocks, such as a reverse-conveying kneading block with a narrow disc (Fang et al. 2008).

The rheology of the polymer, as well as the monomer and initiator solubilities also affect the mixture and can change the course of the reaction due to crosslinking and degradation (Fink 2013).

The most commonly used equipment for REx or grafting is co-rotating and intermingled twin-screw extruders. However, co-rotating, fully intermeshed, four parallel screw extruders, have been shown to have even better mixing. It has been suggested that these extruders have less dissipative heating, can prolong residence time and, due to the low-pressure and the release of volatiles are much more efficient (Calderon et al. 2019a).

The process is further complicated by some interactions between the mentioned variables, which may not be predictable when scaling up from batch processes. For example, during the production of PCL-*g*-MA, MA concentration is more important when an internal mixer is used, while for extrusion, the degree of grafting is more strongly influenced by the initiator concentration and reaction temperature (Morais et al. 2019).

The importance of mixing goes as far as the choice of the state of raw materials as well. By grafting PP with MA using extrusion, PP is fed as a powder or in granular form, where the latter is more successful due to a better initial mixing and less diffusional resistance.

The overall residence time is governed by throughput and can be adjusted by screw speed, screw design and extruder geometry. The peroxide lifetime/residence time ratio has been shown to affect the degree of crosslinking, where the initiators are broken down more rapidly, thus leading to a greater degree of crosslinking (Coltelli et al. 2010).

Higher screw speeds also promote better mixing, and therefore, the grafting is expected to increase. Nonetheless, this also leads to a reduction in residence time. In fact, for PCL grafting, where a significant variation in the degree of grafting was observed, grafting was shown to depends on the concentration of the initiator and screw speed (John et al. 1997b).

9.4.4 Polymer Structure

Grafting efficiency or the degree of grafting depends on the ease of hydrogen abstraction from the polymer chain by free radicals. For example, thermal decomposition of DCP forms cumyloxy radicals, which then abstract hydrogen from the polymer or undergo a dismutation (Lal et al. 1968). The higher abstraction rate (r_a)/ hydrogen dissolution rate (r_d) ratio, the greater the ease of hydrogen extraction. The rate of hydrogen abstraction also depends on the type of hydrogen atom: non-activated, activated by a double bond or activated by an ether group. It was shown that the grafting was lower for polyolefins with high propene content due to the difference between chemical structures (Fink 2013).

The different polyesters presented above also vary significantly, depending on the length of the aliphatic section. For example, the grafting efficiency of poly(propylene carbonate) (PPC) is much higher than for PBS because PPC has tertiary carbons that are more reactive and less stable than the secondary carbons in the PBS structure (Calderon et al. 2019b). PLA and polyesters related with low aliphatic hydrocarbon content are relatively less reactive against radical graft modification, providing a relatively low degree of grafting (Dawidziuk et al. 2018).

9.4.5 Reagent Concentration

During reactive processing, the main aim is grafting the monomer onto the polymer chain. However, chain scission, crosslinking and homopolymerization of the monomer are competing reactions. Changing reagent concentrations alters the relative magnitude of each of these reactions since none of these reactions can be optimized individually. The exact optimal concentration is rather specific to each case, and is best illustrated with different grafting systems.

The effect of reagent concentration has been extensively studied and most studies have used an empirical approach to assess the effect of monomer and initiator concentration on the degree of grafting. The consensus is that the degree of grafting depends largely on these two variables, but cannot be increased simply by increasing the concentration of either of them.

Increasing the initiator concentration generally leads to the formation of more free radicals formed through the decomposition of the initiator. A higher concentration of radicals results in a greater chain transfer to the polymer, and consequently, a higher degree of grafting. However, an increase in the initiator concentration can also reduce the Mw due to chain scission. Therefore, there is usually an optimal concentration that balances the grafting and chain scission (John et al. 1997a).

The degree of mixing or the processing method used (extrusion *vs*. batch mixing) also influences the degree of grafting and the reagent concentration cannot be considered in isolation (Fink 2013). Some authors have found that the effect of reagent concentration is different using a batch mixer instead of an extruder and that temperature is a dominant factor in the extruder. Grafting efficiency thus depends on the number of free radicals produced and their mobility (diffusion) and stability (Morais et al. 2019). Therefore, the optimization of the degree of grafting is first achieved by ensuring a high reaction temperature to induce the decomposition of free radicals, sufficient mixing to increase the probability of the monomer and radical species interacting and finally, by using an optimal amount of monomer and initiator to favor grafting instead of side reactions such as chain crosslinking and scission (Morais et al. 2019).

It has been shown that for grafting MA onto PCL, lower DCP concentrations result in a higher degree of grafting, independent of the monomer concentration, and an increase in the initiator concentration decreases the degree of grafting, which may be attributed to possible undesired reactions (Morais et al. 2019). Similarly, by grafting MA onto PPC and PBS, an increase in monomer concentration increased the degree of grafting, but it was accompanied by a significant reduction in Mw due to chain scission. It is also interesting to note that even at the same monomer and initiator concentration, the degree of grafting is very different for PPC and PBS (Calderon et al. 2019b).

Mani et al. (1999) grafted MA onto PLA, PBS and poly(butylene succinate-*co*-adipate) (PBSA). As expected, the degree of grafting increased with increasing initiator concentration up to a maximum of approx. 1 wt.%, after which a drastic drop was observed for PLA. In all cases studied, the intrinsic viscosity (i.e. Mw) decreased dramatically after that point as a result of chain scission. The increase in graft content was due to the increase in radical formation (initiator decomposition), and therefore, to a higher chain transfer to the polymer backbone. Although crosslinking is generally expected with an increase in initiator concentration, it was not observed for these systems. These authors suggested that the optimal grafting depends, therefore, on an optimal peroxide/monomer ratio, above which termination reactions become prevalent (Mani et al. 1999).

Grafting IAH onto PLA was extensively studied by Petruš et al. (2016) by varying monomer and initiator concentrations. These authors categorised the behavior into four classes of monomer to initiator concentration; low/low, low/high, high/low and high/high. An increase in the degree of grafting was observed with an increase in initiator concentration in the entire range (0.5–10 wt.% IAH) after the generation of PLA macroradicals, which was favored at a high initiator concentration (Petruš et al. 2016).

At a low/low ratio, the formation of PLA macroradicals is favored because of limited IAH-free radical interactions. A relatively high degree of grafting was observed, as well as relatively few side reactions. However, at a low/high ratio, the desired reaction between PLA and free radicals predominates over IAH-free radical interactions due to a high concentration of reactive species and the viscosity of PLA reduces the extent of IAH interaction with free radicals.

As the initiator concentration increased, the concentration of PLA macroradicals increased, which led to chain crosslinking, scission and branching, as well as other termination reactions of the initiator. When the ratio becomes high/low, recombination of free radicals is unlikely and the main grafting reaction is favored. However, the conversion is low due to large amount of unreacted monomer.

When the ratio is high/high, the reaction between IAH and free radicals generates low reactivity IAH radicals which can be homopolymerized, due to lack of solubility of IAH in PLA. Although the degree of grafting is relatively high, the formation of other products is also prevalent (Petruš et al. 2016). These findings were similar to other investigations in which have shown that the yield of grafted polymer decreases with increasing monomer and initiator concentration (Kučera et al. 2017). A higher degree of grafting is accompanied by a higher extent of β-scission due to reactive tertiary carbon of IAH grafted onto the PLA backbone. Kučera et al. (2017) also found that the optimal reagent concentrations are a low monomer concentration (< 1 wt.%) and a high initiator concentration (> 0.5 wt.%).

Considering the effect of monomer concentration alone, the degree of grafting increased with increasing monomer concentration for PBS and PBSA, while it was relatively constant for PLA. At the same time, the intrinsic viscosity decreased with increasing monomer concentration because of increased chain scission (Mani et al. 1999). Similar behavior was observed for PCL and PBAT grafted with MA where an increase in MA concentration led to an initial increase in the degree of grafting. At low concentration, the free radicals formed from PCL combined directly with MA. As the concentration increased, termination reactions became more prevalent and the degree of grafting decreased. It was suggested using PBSA as an example that even in the presence of crosslinking and other degradative pathways, the degree of grafting generally increased with increasing monomer concentration, suggesting that MA inhibits crosslinking (John et al. 1997a; Signori et al. 2011).

9.4.6 Temperature and Pressure

In general, temperature is of the utmost importance in any chemical reaction. The degree of grafting depends on the amount, mobility and stability of the radicals formed during the reaction. However, too high processing temperatures cause degradation reactions, and the initiator decomposition may be too fast to be effective (Mani et al. 1999; Isiklan et al. 2010; Puteh et al. 2015).

For grafting PCL with MA, an increase in temperature leads to complete decomposition of the initiator, producing a higher number of free radicals, resulting in a higher degree of grafting. Higher temperatures also reduce viscosity and increase diffusion, both beneficial for grafting. However, at higher temperatures, radical recombination becomes more prominent, reducing the degree of grafting. Based on this, a maximum was observed in the degree of grafting as a function of temperature for PCL, which depends on the type of initiator used (John et al. 1997a; Morais et al. 2019). Similar observations were recorded for grafting natural rubber with IA where initially the degree of grafting increased as a result of the rapid decomposition of the initiator, but crosslinking was more prevalent as temperature increased, thus reducing the degree of grafting (Puteh et al. 2015).

9.4.7 Inhibitors and Co-Monomers

Other additives are often included in the grafting system to inhibit side reactions such as crosslinking or to promote the grafting efficiency of the monomer. Amides, sulfoxides and phosphites are effective in reducing crosslinking and chain scission, which is attributed to their electron donating properties. However, grafting can also be inhibited by adding phenolic stabilizers. The efficiency of stabilizers depends on their solubility in the polymer and the monomer, and will not only inhibit the side reactions, but also can reduce the grafting efficiency (Fink 2013; Petruš et al. 2018). Conjugated furan co-agents (e.g. butyl-3-(2-furyl) propenoate) are effective in increasing the degree of grafting of MA onto PP and have been shown to limit degradation (Signori et al. 2011). Similarly, cinnamic acid and ethyl cinnamate are effective for improving MA grafting by forming a weak adduct with MA, which increases the reactivity of MA (Signori et al. 2011).

The function of the co-agents is to react quickly with polymer macro-radicals, generating resonance-stabilized macro-radicals, thus preventing polymer chain scission. For example, butyl 3-(2-furyl) propenoate can be used for controlling Mw during grafting of MA onto PP. Functional nitroxides are also effective in controlling radical crosslinking through a reversible nitroxide-carbon radical coupling reaction, e.g. the addition of 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO). It is effective due to the selectivity of TEMPO for radical termination with carbon-centered radicals instead of radical-initiated crosslinking. In another example, Petruš et al. (2018) found that 2,6-di-*tert*-butyl-4-methylphenol (BHT) was effective in preventing crosslinking and degradation in grafting IAH onto PLA. Similarly, Nerkar et al. (2014) and Standau et al. (2019) showed that multifunctional coagents, such as pentaerythritol triacrylate (PETA), triallyl isocyanurate (TAIC) and triallyl trimesate (TAM) reduce the PLA degradation and promote long chain branching.

Grafting with monomers such as MA and acrylic acid can be quite low and to overcome this, more than one monomer can be used to improve the overall grafting efficiency (White and Sasaki 2003). For example, styrene can be used as a co-monomer to obtain high graft efficiency, with the additional benefit of less degradation. The macroradicals formed onto the polymer backbone must react with the monomers before undergoing chain scission and if the primary monomer is not reactive enough towards the macroradicals, the benefit of the co-monomer is that it can react more quickly, thus preventing chain scission. However, the co-monomer must be easily copolymerized with the primary monomer to obtain the desired functionality of the graft-copolymer (Fink 2013).

9.5 Reaction Mechanisms

In this section, the mechanism *via* which free radical grafting occurs is discussed as an overview. The kinetics of these processes are examined in the subsequent section, which includes a detailed overview of potential side reactions.

9.5.1 Overall Mechanism

Free radical grafting occurs as a complex set of reactions occurring simultaneously, summarized as the following sequence (Fig. 9.3):

- Thermal decomposition of the initiator, generating primary radicals which can be further decomposed into secondary radicals.
- Formation of macroradicals through the hydrogen abstraction mainly from the tertiary carbon of the polyester backbone.
- Covalent bonding of the monomer onto the macroradicals.
- Termination of grafting by hydrogen donors.

Peroxides are commonly used as free-radical initiators. They decompose through homolytic scission, producing two free radicals, or primary radicals ($RO^{\bullet}$) and subsequently, hydrogen abstraction occurs from the polymer chain which allows the formation of macroradicals.

Primary radicals can also undergo β-scission to form secondary radicals. Secondary methyl radicals are more likely to participate in homopolymerization compared to bulky primary radicals. It is well known that the probability of abstraction depends on the polymer structure. Hydrogen abstraction typically occurs at the α-carbon with respect to the carbonyl group for saturated carboxylic acids and their derivatives because the radicals are stabilized due to their conjugation with the carbonyl group (John et al. 1997a; Mani et al. 1999). It has also been pointed out that the polymer structure could influence the grafting (Mani et al. 1999). For example, the degree of grafting in PPC was twice that of PBS using MA as a monomer. Calderon et al. (2019b) thought that the difference in grafting was due to the fact that the PBS only has secondary carbons, which are more stable than the tertiary carbons found in the chemical structure of PPC.

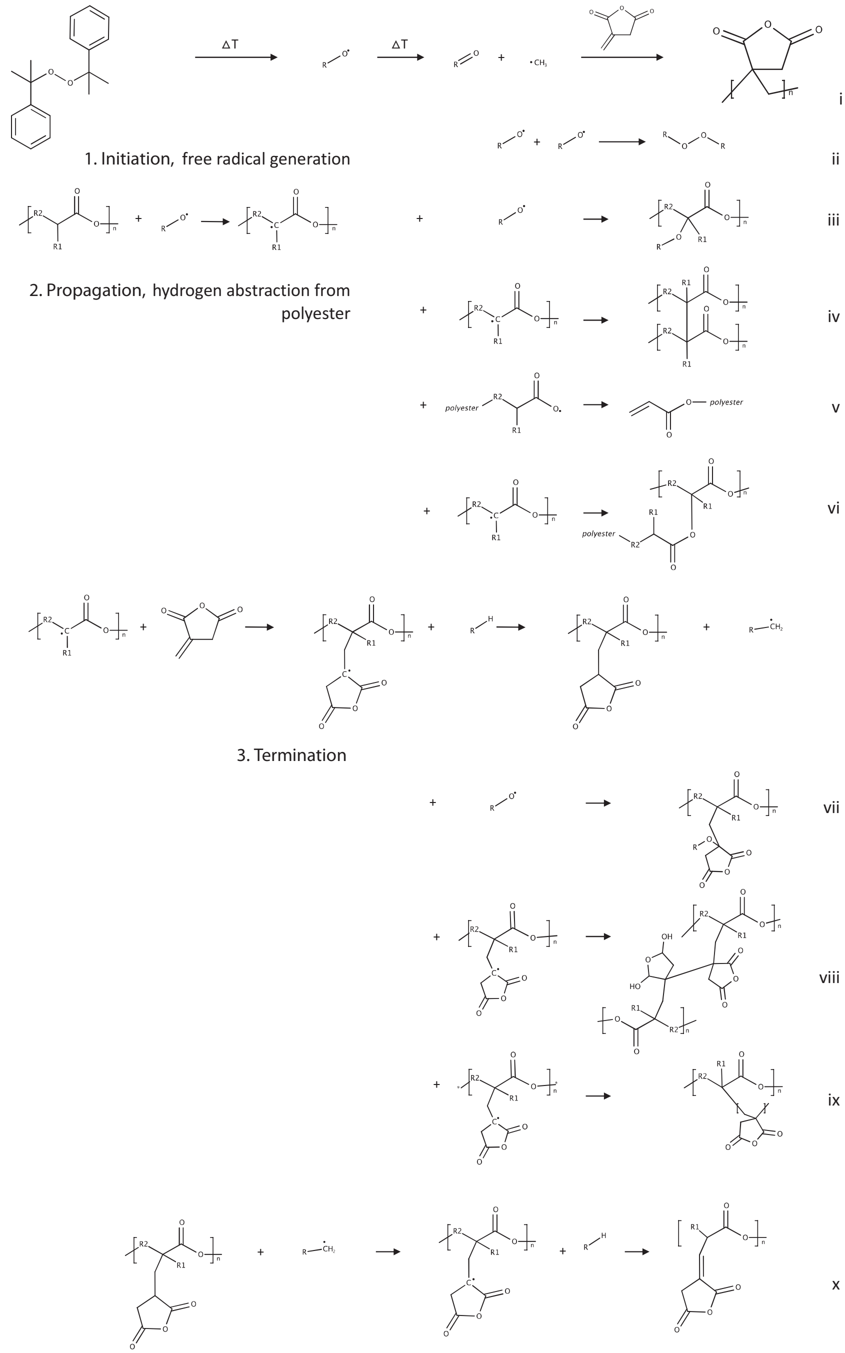


Fig. 9.3 Overall scheme of general reaction for grafting a monomer (IAH used as an example) onto a polyester. The main reactions are (1). Initiation, (2). Propagation and (3). Termination. Including side reactions, i to x

Propagation is the next step for generating a graft copolymer by a free radical mechanism which depends on the concentration of polymer radicals. This reaction continues until the initiator or the radicals have been consumed by the termination reactions. For the case of MA, the free radicals can abstract more hydrogens or combine with other free radicals (Kashani Rahimi et al. 2017) or alternatively the free radial can perform β-scission of the chain to produce a succinic anhydride end group. This typically occurs after the macro-radical has undergone a β-scission onto a radical chain end, as well as a vinyldine chain end (Mani et al. 1999).

Several authors have also suggested that MA could be grafted onto polyesters at the chain-end, based on the abstraction of the α-carbon hydrogen followed by β-scission and the formation of a vinylidene and macroradical chain end. The macroradical chain ends can then react with MA (Petruš et al. 2016; Kashani Rahimi et al. 2017; Morais et al. 2019).

During termination, when no more radicals are generated, the grafting slows down and eventually stops. To obtain a high degree of grafting, it is essential that the macro-radicals react with the monomers before undergoing side reactions. Grafting is accompanied by several possible side reactions, the extent of which depends on the reaction conditions (e.g. initiator and monomer concentration, radical reactivity, reaction temperature):

- Formation of secondary methyl radicals, which lead to the photopolymerization of monomers.
- Primary radicals can recombine, deactivating the free radical.
- Extinction of the active center by radical addition, or crosslinking, β-scission and branching.
- Addition of radicals onto grafted-chain macroradicals, which leads to the crosslinking of grafted chains.
- Hydrogen abstraction from the grafted polyester, which leads to β-scission.
- Non-radical side reactions, such as end-group reactions and polyester hydrolysis.

Several authors have proposed possible reaction mechanisms for PBAT (Kashani Rahimi et al. 2017; Muthuraj et al. 2017), PBS (Calderon et al. 2019b; Phua et al. 2012; Signori et al. 2011), PCL (John et al. 1997a; Mani et al. 1999; Kim et al. 2004; Morais et al. 2019), PLA (Ku Marsilla and Verbeek 2015b; Petruš et al. 2016) and PPC (Calderon et al. 2019b), all of which conform to the generalized mechanisms presented here. The only differences discussed in literature is the extent to which side reactions are taken into account. In general, homopolymerization of the monomer is not taken into account if grafting is performed about the ceiling temperature, however, it has recently been shown that this may have been an incorrect assumption (Petruš et al. 2016). In addition, the extent to which crosslinking occurs varies, depending on the system under consideration. For PLA, the first step, the formation of free alkoxy radicals, is the determining step for the degree of crosslinking. In the presence of radicals, PLA undergoes branching, crosslinking and chain scission, and reaction conditions are crucial for optimizing grafting (Standau et al. 2019). For example, primary *t*-butoxy radicals exhibit a high propensity for hydrogen abstraction, favorable for grafting. However, secondary methyl radicals tend to participate in homopolymerization, as shown for grafting IAH onto PLA. The high reaction temperature favors scission of primary radicals into secondary radicals, which makes melt grafting less efficient than solution techniques, if homopolymerization is to be avoided (Kučera et al. 2017).

The monomer used can also influence the extent of side reactions, as evidenced by the differences detected with grating glycidylmethacrylate (GMA) and MA onto PCL. Less chain scission occurred when GMA was grafted onto PCL compared to MA, however, the exact reason for this difference was not explained (Kim et al. 2004). Alternatively, when the reactivity of the monomer is low, co-monomers can be used to increase the degree of grafting, as explained above (Signori et al. 2011).

9.5.2 Kinetics

The kinetics of polymer grafting has been widely covered by White and Sasaki (2003) who have examined the kinetics: for the polymer grafting for natural rubber and polystyrene, and for REx of polyolefins and graft polymerization. More information on the kinetics of free radical modification for polyolefins in extruders can be found in the paper from Hamielec et al. (1991) and some other documents available for the kinetics of free radical grafting of PLA and other polyesters were recommended by Petruš et al. (2018).

First, the initiator must decompose to form the free radical which then attacks the respective polymer or monomer. For a compound to be an initiator it must have at least one bond with a low dissociation energy (100–200 kJ/mol) (Dossi et al. 2010). To produce a radical, the low dissociation energy bond (a single bond) is divided through homolysis (Dossi et al. 2010), so that each part produced retains one of the electrons in that bond. Thermal dissociation is the most common form, but redox initiation and photochemical initiation can also occur.

Redox or photochemical initiation are usually used in cases where the polymerization or grafting should be carried out at low temperature. Redox initiation is achieved by combining an initiator with a salt (e.g. ferrous) to produce the required radical. This can only work if the radical production rate is sufficiently fast to overcome the factors discussed above (e.g. the half-life). The photochemical option is also difficult, since it is activated very easily (Dossi et al. 2010).

Peroxide-based and azo-containing compounds typically undergo thermal decomposition according to Eq. 9.2. The velocity constant (k_d) is typically in the order of 10^{-4} -10^{-6} s^{-1} (Dossi et al. 2010) and can be described by an Arrhenius equation for temperature (Zhou and Zhu 1998).

$$I_2 \xrightarrow{k_d} 2R^{\bullet} \tag{9.2}$$

The start of the grafting reaction occurs when the radical produced attacks the monomer (e.g. MA) or polymer itself. Each pathway has an associated reaction rate. For a radical attack on the monomer. This is described as follows:

$$R^{\bullet} + M \xrightarrow{k_{i1}} RM^{\bullet} \tag{9.3}$$

where M represents the monomer.

If the radical attacks the polymer, the analogous equation is applied:

$$R^{\bullet} + P \xrightarrow{k_{i2}} P^{\bullet} + RH \tag{9.4}$$

where RH is the radical attached to the hydrogen it extracts from the polymer itself. Consequently, the polymer now becomes the reactive species and in turn reacts with the monomer.

$$P^{\bullet} + M \xrightarrow{k_{i3}} PM^{\bullet} \tag{9.5}$$

The result of any of these reactions is a highly reactive radical located on the monomer regardless of whether it is already bound to the polymer. Due to this free radical, propagation can occur causing an increase in Mw described below.

$$RM^{\bullet} + M \xrightarrow{k_p} RMM^{\bullet} \xrightarrow{k_p} RM_n^{\bullet} \tag{9.6}$$

$$PM^{\bullet} + M \xrightarrow{k_p} PMM^{\bullet} \xrightarrow{k_p} PM_n^{\bullet} \tag{9.7}$$

Finally, the reaction must end through one of the following three mechanisms. Graft formation is the desirable result (Eq. 9.8), where the monomer and polymer are joined, crosslinking (Eq. 9.9), where two reactive polymer chains are linked, or by the formation of homopolymers (Eq. 9.10), where two reactive monomers are joined.

$$\text{Graft formation} - PM_n^{\bullet} + RM_n^{\bullet} \xrightarrow{k_{t1}} PM_{(n+m)}R \tag{9.8}$$

$$\text{Cross linking} - PM_n^{\bullet} + PM_n^{\bullet} \xrightarrow{k_{t2}} PM_{(n+m)}P \tag{9.9}$$

$$\text{Homopolymer formation} - RM_n^{\bullet} + RM_n^{\bullet} \xrightarrow{k_{t3}} RM_{(n+m)}R \tag{9.10}$$

Below is a comparison of the grafting reactions for a conventional polyolefin grafted with MA and PLA grafting with IAH (Petruš et al. 2016). Both reactions begin with the decomposition of the initiator into a free radical, the abstraction of a hydrogen from the polymer and the addition of the respective MA or IAH monomer.

Table 9.4 Kinetics of graft polymerization without homopolymerziation

Steps	PP-*g*-MA
Radical formation	$I_2 \xrightarrow{k_d} 2R^\bullet$
Hydrogen abstraction from polymer	$R^\bullet + P \xrightarrow{k_{i2}} P^\bullet + RH$
Monomer addition	$P^\bullet + M \xrightarrow{k_{i3}} PM^\bullet$
Monomer extension	$PM^\bullet + M \xrightarrow{k_p} PMM^\bullet$
Links to another polymer chain	$PM_n^\bullet + PM_n^\bullet \xrightarrow{k_t} PM_{(n+m)}P$
In the case of no MA impurities, where there is no homopolymerization due to steric hinderance	$-\dfrac{d[M]}{dt} = \dfrac{k_g}{1+f} \bullet \sqrt{\dfrac{2 \bullet k_d}{k_t}} \bullet [I]^{\frac{1}{2}} \bullet [M]$
	$f = \dfrac{[PM^\bullet]}{[P^\bullet]}$

Source: White and Sasaki (2003)

Table 9.5 Kinetics of graft polymerization with homopolymerziation

Monomer of radical attacks	$R^\bullet + M \xrightarrow{k_p} RM^\bullet$
Reactive monomer reacts with another monomer (homopolymerization)	$RM_n^\bullet + M \xrightarrow{k_p} RM_{n+1}$
Termination occurs by reaction with another long chain of monomers	$RM_n^\bullet + R'M_m^\bullet \xrightarrow{k_p} RM_{m+n}R'$
Termination occurs by reaction with another polymer	$RM_n^\bullet + PM_m^\bullet \xrightarrow{k_p} RM_{m+n}P$
	$-\dfrac{d[M]}{dt} = k_g [M] \bullet [P'] + k_p [M] \bullet \left[[PM_n^{''}\right] + \left[RM_m^{''}\right]]$
	$-\dfrac{d[M]}{dt} = k_p \bullet \sqrt{\dfrac{2 \bullet k_d}{k_t}} \bullet [I]^{\frac{1}{2}} \bullet [M]$

Source: White and Sasaki (2003)

Both eventually end up with crosslinking *via* different mechanisms, but there is also the possibility of homopolymerization, which affects the reaction kinetics. Table 9.4 presents the case without homopolymerization. Table 9.5 shows the case with homopolymerization.

Homopolymerization occurs when the monomers are grafted repeatedly to form a long chain that can occur with or without the polymer as a substrate. Whether or not this reaction continues depends on the molecule that is grafted onto the polymer. For example, Cha and White (2001a) determined that MA was not homopolymerized when it is partially grafted onto polyolefins due to steric hindrance by a 1–2-disubstitution of double bonds. In this particular study, a low concentration of peroxide and MA was used and processed at 230 °C well above the ceiling temperature of 150 °C (Cha and White 2001a). Methyl methacrylate (MMA) behaved similarly with a single unit grafted onto the polymer due to steric hindrance (Cha and White 2003).

In line with this, Cha and White (2001b) analyzed grafting styrene onto polyolefins. These authors pointed out that there was competition between grafting and homopolymerization. This complicates the termination reactions and affects the kinetics of the system.

The competition between grafting *vs*. homopolymerisation of styrene, as determined Fourier transform infrared (FTIR) analysis showed that at low 2,5-dimethyl-2,5-bis-(*t*-butylperoxy) hexane (DBHA) contents both reaction conversions increased linearly with the increase in initial styrene content. However, by increasing the DBHA content at 4% addition of styrene, the grafting only improved with more DBHA (Cha and White 2001b), thus indicating that grafting can be promoted under the correct conditions.

The grafting kinetics of polyesters are very similar. The same kinetic equations were presented by Ku Marsilla and Verbeek (2015a) for PLA-*g*-IAH using DCP. By reordering the overall kinetic equation for grafting without homopolymerization, the effective velocity constant for the grafting of PLA-*g*-IAH was calculated for this case, using the slope of the initiation reaction rate *vs*. monomer concentration, dM/dt. From this, it was shown that the effective velocity constant is mainly affected by the initiator concentration (Table 9.6) and is relatively independent of temperature (Ku Marsilla and Verbeek 2015b).

$$\frac{k_g}{1+f\sqrt{k_t}} = \frac{\dfrac{d[M]}{dt}\left[\dfrac{1}{M}\right]}{\sqrt{2\cdot k_d}\,[I]^{\frac{1}{2}}} \tag{9.11}$$

PLA has a particularly complex reaction route (Table 9.7). If instead of the monomer extending the PLA-*g*-IA, it removes a hydrogen from the PLA polymer, this becomes the reactive species and two PLA molecules can interact directly and cross link without the IA molecule involved.

The kinetics of PLA grafting are much more complex, and the main grafting reaction is described as a function of the initial concentration of the monomer and PLA macroradicals (Table 9.8) (Petruš et al. 2016). The overall reaction conversion is represented by α, and K is the initial reaction rate. The remaining parameters were determined experimentally by Petruš et al. (2016).

Whether or not IA undergoes homopolymerization during reaction with PLA is somewhat debatable. Most work excludes homopolymerisation as processing occurs well above the ceiling temperature, which is very low, 90 °C. Most authors do not consider homopolymerisation to occur if processing above the ceiling temperature. However, a recent study suggests that homopolymerisation of IAH can

Table 9.6 Kinetic parameters determined by Ku Marsilla and Verbeek (2015a)

Effective velocity constant (1/mol s)$^{1/2}$	Initiator concentration (wt.%)	180 °C	200 °C
$\frac{k_g}{(1+f)\sqrt{k_t}}$	0.5	0.024	0.025
	1	0.027	0.03

Table 9.7 Reactions for PLA-*g*-IAH

$L101 \xrightarrow{k_d} 2R^{\bullet}$
$R^{\bullet} + PLA \xrightarrow{k_i} PLA^{\bullet} + RH$
$PLA^{\bullet} + IAH \xrightarrow{k_g} PLA\text{-}g\text{-}IA^{\bullet}$
$PLA\text{-}g\text{-}IA^{\bullet} + PLA \xrightarrow{k_{tr}} PLA^{\bullet} + PLA\text{-}g\text{-}IAH$
$PLA^{\bullet} + PLA^{\bullet} \xrightarrow{k_t} PLA\text{-}PLA$

Source: Petruš et al. (2016)

Table 9.8 Kinetic equations for PLA-*g*-IAH

$-\frac{d[IAH]}{dt} = k_g \cdot [PLA^{\bullet}] \cdot [IAH]$
$k_i \cdot [R^{\bullet}] = 2 \cdot f \cdot k_d \cdot \frac{[L101]}{[PLA]}$
$2 \cdot f \cdot k_d \cdot [L101] = k_t \cdot [PLA^{\bullet}]^2$
$\frac{d\alpha}{dt} = K \cdot (1-\alpha) \cdot [L101]^{1/2}$
$K = \sqrt{\frac{2 \cdot f \cdot k_d \cdot k_g^2}{k_t}}$

Source: Petruš et al. (2016)

occur at processing temperatures as high as 190 °C when initiated with L101 (Kučera et al. 2017).

9.5.3 Side Reactions

Crosslinking, thermal degradation, hydrolysis and other side reactions decrease the overall grafting achieved.

9.5.3.1 Peroxide Induced Crosslinking

Peroxides are also capable of inducing crosslinking in PE (Zhou an Zhu 1998), PLA and PP, which is often exploited during extrusion through low addition levels of peroxide (Takamura et al. 2008). This process consists of three steps beginning with the decomposition of the initiator to produce primary radicals. These then extract a radical from an available carbon on the polymer to produce a polymer radical. The polymer radicals can then recombine and crosslink the polymer itself without undergoing grafting according to the reaction below (Takamura et al. 2008):

Primary radical generation

$$\mathrm{RO\text{-}OR^{\bullet}} \rightarrow \mathrm{2RO^{\bullet}} \tag{9.12}$$

Hydrogen abstraction

$$\mathrm{RO^{\bullet}} + \mathrm{P} \rightarrow \mathrm{P^{\bullet}} + \mathrm{ROH} \tag{9.13}$$

Bimolecular recombination of polymer radicals

$$\mathrm{2P^{\bullet}} \rightarrow \mathrm{P\text{-}P} \tag{9.14}$$

Takamura et al. (2008) examined the effect of the type of peroxide (initiator), and these were classified according to their thermal decomposition rates. These authors showed that peroxides (lauroyl peroxide - LPO and BPO) are rapidly decomposed, which leads to higher Mw fractions and more gelling, indicating that faster decomposition rates lead to partial crosslinking. In comparison, moderate (tri-*n*-butyltin hydride - TBTH and *tert*-butylperoxy 2-ethylhexyl carbonate - TBEC) or slow initiators (DCP), lead to a uniform crosslinking capacity in molten PLLA, and the average Mw and degree of crosslinking were correlated with the ability of the peroxide to abstract a hydrogen from the polymer.

The reaction kinetics for crosslinking of PE using peroxide has been well established and discussed by Zhou and Zhu (1998). This study highlights that the concentration, the reaction temperature and the type of peroxide, all affect the crosslinking *via* the mechanism described. Most importantly, the termination of the polymer radicals is a diffusion-controlled process and that, consequently, not all radicals react. Some radicals remained detectable after several months (Zhou and Zhu 1998).

9.5.3.2 Chain Scission

Carlson et al. (1999) determined that during the grafting process of PLA with MA, an increase in the amounts of the initiator (L101 - peroxide), resulted in a higher melt flow index (MFI) (83.4 g/10 min at 0.50 wt.% L101 *vs*. 27.8 g/10 min at 0 wt.%) at the same addition level of MA (2 wt.%). This suggests that chain scission of PLA occurred as the viscosity decreased. This was similar to the behavior observed with PP. Chromatography also showed that when peroxide and MA are added, Mw decreased, suggesting an increase in chain scission corresponding to a decrease in intrinsic viscosity. These effects were worse at higher processing temperatures, suggesting that the degree of chain scission can be controlled between the initiator addition levels and the processing temperature.

Proposed mechanisms from this study include back biting and thermohydrolysis (Carlson et al. 1999). This is consistent with a previous study done by Carlson et al. (1998). Thermohydrolysis is a simple reaction in which free water at high temperature can cause the chain to spilt in two at the ester group (O-C=O), which leads to a molecule with a free hydroxyl group and a carboxylic acid (Fig. 9.4).

Backbiting occurs when a polymer which still contains a free radical rearranges and the radical attacks the group of esters, which leads to the same hydroxyl-containing molecule as before, but a cyclic molecule is produced instead of the carboxylic acid-containing molecule. Hydrolytic and thermal degradation along with backbiting can also occur in polymers that do not contain esters.

9.5.3.3 β-Scission

A reduction in viscosity has also been observed during grafting of PCL with MA when initiated by DCP. This is similar to the behavior of polyolefins, since it is believed that the peroxide initiates scission of the polymer backbone, thus creating smaller chains. Some control over the degree of scission can be achieved by controlling temperature and monomer concentration.

An increase in the MA content in this case favors grafting and with a higher concentration of MA, the occurrence of β-scission decreases as the macro radicals react immediately. Morais et al. (2019) demonstrated that β-scission was promoted

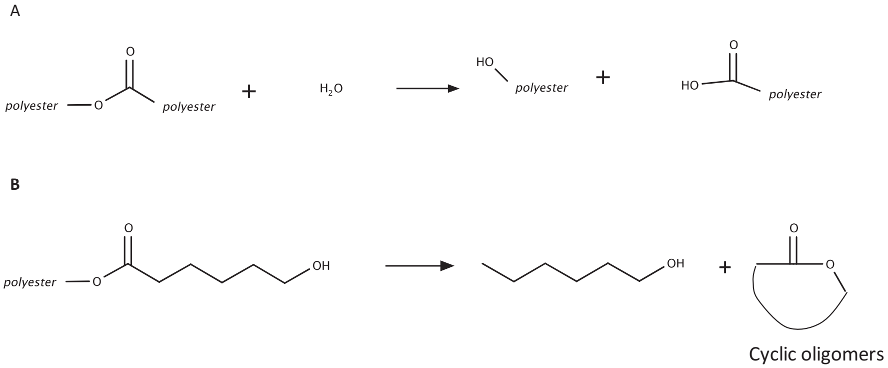


Fig. 9.4 Reaction mechanisms of chain scission by thermohydrolysis (**A**) and back-biting (**B**). Reproduced with permission from Carlson et al. (1999)

by high temperatures which initiated the decomposition of DCP. Signori et al. (2011) also suggested that β-scission can occur for PLA-*g*-MA.

All these degradation mechanisms can play a role during the processing of grafted polyesters. Al-Itry et al. (2012) discussed the exchange of between these mechanisms well, but noted that the velocity of a mechanism such as hydrolysis depends a lot on the water availability, the morphology of the polymer and the temperature. These authors also indicated that hydrolysis takes place between 150 and 215 °C which can directly compete with thermal degradation, which generally takes place above 180 °C, which can randomly break the polymer chain, thus leading to lower Mw chains. β-scission can also occur at this temperature. They also noted that for PLA cyclic oligomers are formed through backbiting (trans-esterification mechanism), while for PBAT, benzene rings are produced (Al-Itry et al. 2012). A reduction in Mw and melt strength for malleated PBAT has also been observed (Nabar et al. 2005).

9.5.4 Material Properties of Grafted Polyesters

This section outlines the changes in thermal behavior, rheology and mechanical properties which arise due to grafting. It mainly focuses on polyesters, however, some examples based on polyolefins are included for comparison.

9.5.4.1 Thermal Behavior

The addition of another component through grafting can affect the degree of crystallinity, the crystallization rate, the glass transition temperature (T_g) and melting temperature (T_m). It is common that grafting decreases the T_g and T_m values compared to pure polyester. This has been observed for PBS (Teramoto et al. 2005), PLA (Hassouna et al. 2011) and PLLA (Hwang et al. 2012) systems, which have been grafted with MA. Sometimes, these changes are minor, as with PLA grafted with MA in the presence of Lupersol, which caused a reduction in both T_g and T_m of only 0.5 °C (Hassouna et al. 2011). However, grafting also affects chain arrangement and increased the melting enthalpy by 3 J/g. Interestingly, for a combination of PLA + 10% MAG-PLA, the T_g and T_m were 0.5 °C higher than pure PLA alone, although the melting enthalpy coincided with pure PLA (Hassouna et al. 2011).

A similar decrease in T_g for grafted PLLA was also observed by Hwang et al. (2012) when grafted with MA using DCP. The addition of MA caused a decrease in T_g from 54.9 °C to 49.9 °C when 30 phr was added. A corresponding decrease in crystallinity also occurred from 13.0% to 10.2%. This was attributed to chain branching of MA onto PLLA, which causes a decrease in the regularity of the polymer and hinders the crystalline growth of PLLA. Thermal stability was also affected with a decrease in Mw for PLLA-*g*-MA samples due to the addition of MA (small Mw). Despite the differences in the thermal behavior of the PLLA-*g*-MA samples, there was only a small variation in the mechanical properties of compression molded films from this material (Hwang et al. 2012).

Differential scanning calorimetry (DSC) analysis of PBS modified with IAH or MA in the presence of 1,4-butanediol and SA showed a very different thermal behavior to pure PBS (Teramoto et al. 2005). The most notable change was the decrease in melting enthalpy by increasing the itaconate or maleate content. The incorporation of these lower Mw units decreased the thermal stability of the material, reducing the degradation temperature from 389 °C to 377 °C and 373 °C for 15 mol % IAH and MA, respectively. T_g and T_m values were also reduced with MA, having a greater affect than IAH.

The effect of grafting on crystallinity and crystallization behavior has been examined in depth by You et al. (2013) by producing long-chain branched PLA *via* radical grafting. This was produced by grafting PLA with PETA using DCP. Through radical grafting the fraction of comb-like chains, as well as the number of arms was increased. A decrease in the crystallization temperature was observed as the branching level increased and the crystallization rate constant increased with PETA-*g*-PLA due to the presence of chain clusters which helped nucleation. This increased the crystallinity upon cooling from 0.94% (PLA) to 13.0% for a material produced from 0.3% DCP, 3% PETA and 0.2% antioxidant.

9.5.4.2 Rheology

Until recently, grafting of compounds such as IAH and MA onto polymers was focused on the addition of these groups to PE or PP. PP is naturally linear, has a low melt strength and has no strain hardening properties, making it unsuitable for applications such as blow molding and foaming where extensional forces occur.

A high melt strength polypropylene (HMSPP) can be obtained by free radical grafting in a two-step process. Initially, MA is grafted onto isotactic PP in a melt state to achieve PP-*g*-MA, before reacting with an epoxy to increase the branch length (Tang et al. 2008). The HMSPP produced *via* this method has a low MFI and sags less when stretched. The addition of epoxy chains also increased the degree of crystallinity and crystallization temperature. Similar results were observed when grafting is used to crosslink PE. The MFI of the material was also reduced, and the mechanical properties were affected with improved impact strength and creep resistance, while a reduction in ε_b values as reported from Tamboli et al. (2004) by Ku Marsilla and Verbeek (2015b).

In comparison, the grafting of MA onto PLA has been shown to affect the MFI of the material depending upon the temperature at which it is grafted. Carlson et al. (1999) evaluated the effect of the initiator Lupersol 101 at concentrations of 0–0.5 wt.%. Minor differences in the degree of grafting were detected between T_m of 180 °C (approx. 0.65% grafting) and 200 °C (0.672%), with 0.5% Lupersol, but a significant change in MFI occurred from approx. 85 to 135 (g/10 min). A corresponding change in intrinsic viscosity and Mw of the material also occurred and it is thought that this could have arisen through β-scission, back biting and/or thermohydrolysis. This same study also highlighted the increase in melt viscosity, when only peroxide was used, or the reduction in melt viscosity in the presence of MA and a peroxide, was different from what occurs with polyolefins. For PE, the addition of peroxide alone or in combination with MA causes branching and gelation and for PP chain scission arises. Carlson et al. (1999) thought that the decrease of Mw in this case occurred due to competition between branching and grafting of MA.

It is important to understand the Mw changes due to these mechanisms. Kim et al. (2004) studied PCL systems grafted with MA and GMA. The increase in the polydispersity index (PDI) indicated that chain scission did not occur during grafting with GMA, instead chain extension/crosslinking occurred. In comparison, the grafting of MA onto PCL resulted in a decrease in Mw as the MAH content increased. Without BPO to initiate the grafting reaction, a decrease in Mw occurred; and there was also chain scission, which was promoted by higher processing temperatures (Kim et al. 2004).

9.5.4.3 Mechanical Properties

Free radical grafting with different monomers is widely used to improve the compatibility of the blends, e.g. PP/low density poly(ethylene) (LDPE) blends (1.3–2.7 °C) (Krivoguz et al. 2006), as well as some polyester blends. The grafted PLA can be used to make the PLA compatible with starch. For PLA-*g*-MA initiated by 2,5-bis(*tert*-butylperoxy)-2,5 dimethylhexane, the σ_m values increased from 61.6 MPa ± 3.8 for pure PLA to 63.4 MPa ± 1.6 for PLA-*g*-MA and the ε_b values remained constant: 5.2% ± 0.5% (Zhang and Sun 2004). Once starch was added to the blend, the best σ_m value was 53.9 ± 2.1 MPa. However, this is an improvement in the blend which did not contain PLA-*g*-MA which was reportedly 30.0 MPa ± 2.6.

In comparison, an optimal amount of MAH-*g*-PLA was observed by Zhang et al. (2017) to occur in PLA/wood fiber composites at 30%, where the σ_m values increased up to this point from 43.5 MPa to more than 47 MPa, and ε_b values from 3.35 to 3.95%. The increase in PLA-*g*-MAH further decreased these properties until 50% of PLA-*g*-MAH was comparable to the absence of PLA-*g*-MAH in σ_m value and only a small improvement in ε_b value (3.65%).

PLA grafting with MA has also been explored by Yu et al. (2013) as an option to improve the melt strength of PLA for foaming applications. However, consistent with the other studies reported here, according to other results reported there, the production of PLA-*g*-MA decreased the melt strength together with Mw. This was attributed to the fact that the low Mw components produced by decomposition of PLA by peroxide can act as plasticizers, thus decreasing the melt strength. For foaming applications, the grafted PLA leads to broken cells on the surface of the foam beads and an open cell structure connected in the center. Overall, this study concluded that PLA-*g*-MA, which was linear in structure, could not resist elongation forces during cell growth. The result is a foam structure similar to foams produced at high temperature (Yu et al. 2013).

According to Jin et al. (2000), when maleic groups are incorporated into PBS together with SA and 1,4-butandiol (BD), a decrease in the ε_b values occurred from 58.1 to 52.2% or from 24 to 7%, depending on the ratio of the components SA/BD/MA (50/45/5) and (50/40/10), respectively (Jin et al. 2000). The ε_b values decreased as a result of the introduction of MA units into PBS. However, the ε_b and σ_m values were greatly improved by the chain extension when BPO was added through a solution-based method. PBS grafted with MA without BPO remained highly biodegradable with 12% degradation in 25 days compared to <2%.

The flexural and tensile properties, and impact strength for PBS, PBS-*g*-MA, and PBS/PBS-*g*-MA blends were examined by Muthuraj et al. (2015) together with composite samples containing miscanthus (grass) produced using DCP as an initiator. Regardless of the performance of the composite material, the tensile properties of PBS-*g*-MA and a PBS/PBS-*g*-MA blend in a 95/5 wt.% ratio was comparable to pure PBS (approx. 40 MPa). However, the YM of the PBS-*g*-MA was marginally greater than that of pure PBS and the addition of 5% PBS-*g*-MA produced a comparable value of 0.08 GPa, indicating that only a small addition was required to achieve comparable results. All three samples were comparable in flexural strength in this study, but the notched impact strength of pure PBS-*g*-MA was significantly higher but also more variable (64 J/m) which was attributed to partial crosslinking, which was produced during grafting (Muthuraj et al. 2015). Similar results were observed by Phua et al. (2013) for PBS-*g*-MA.

John et al. (1997a) indicated that the tensile properties of PCL-*g*-MA change very little compared to pure PCL, which had a σ_m of 550 N and an ε_b of >850%. Once grafted, regardless of whether it was performed in batch or by extrusion, the σ_m values oscillated between 589.5 and 640 N and the ε_b between 882 and 1070%. The authors attributed this to the minor changes in Mw and intrinsic viscosity.

John et al. (1998) also grafted two grades of PCL (787 and 767) with oxaline groups which were then compression molded to make traction bars. These authors reported that for 787 samples the σ_m values were inversely proportional with a decrease in ε_b values due to grafting. However, in the case of PCL 767, a decrease in both mechanical properties were observed. The difference in the properties of these materials grafted with PCL was attributed to changes in intrinsic viscosity and Mw. No change was observed for PCL 787, but a slight increase in Mw was observed for PCL 767.

9.6 Conclusions

Polymer grafting is a practical way to improve the properties of conventional polymers and is an emerging field as a mechanism for improving biobased or biodegradable polyesters for application in polymer blends. This chapter discussed polyester grafting in light of conventional grafting methods and technologies, focusing on REx.

It can be concluded that grafting of polyesters is better be optimized empirically. The influencing aspects of monomer and initiator concentration must be balanced with the appropriate temperature profile, mixing, processing conditions, the rheology of the polymer and the possibility of side reactions. All of which can change during processing.

This chapter also highlighted recent changes in the field, including whether or not homopolymerization should be considered during grafting above the ceiling temperature, which was previously not thought to occur.

In general, this chapter provided an overview of the important aspects to consider for anyone looking to functionalize a bio-polyester to improve compatibility with other materials, petrochemical or not, or to manipulate the mechanical properties of these materials for a particular application.

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Conflicts of Interest The authors declare no conflict of interest.

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