Reactive Compatibilization of Plant Polysaccharides and Biobased Polymers: Review on Current Strategies, Expectations and Reality

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Abstract

Our society is amidst a technological revolution towards a sustainable economy, focused on the development of biobased products in virtually all sectors. In this context, plant polysaccharides, as the most abundant macromolecules present in biomass represent a fundamental renewable resource for the replacement of fossil-based polymeric materials in commodity and engineering applications. However, native polysaccharides have several disadvantages compared to their synthetic counterparts, including reduced thermal stability, moisture absorption and limited mechanical performance, which hinder their direct application in native form in advanced material systems. Thus, polysaccharides are generally used in a derivatized form and/or in combination with other biobased polymers, requiring the compatibilization of such blends and composites. In this review we critically explore the current status and the future outlook of reactive compatibilization strategies of the most common plant polysaccharides in blends with biobased polymers. The
chemical processes for the modification and compatibilization of starch and lignocellulosic based materials are discussed, together with the practical implementation of these reactive compatibilization strategies with special emphasis on reactive extrusion. The efficiency of these strategies is critically discussed in the context on the definition of blending and compatibilization from a polymer physics standpoint; this relies on the detailed evaluation of the chemical structure of the constituent plant polysaccharides and biobased polymers, the morphology of the heterogeneous polymeric blends, and their macroscopic behavior, in terms of rheological and mechanical properties.

1. Introduction

Bioplastics have been in the focus of academic and industrial research and development efforts for more than two decades now. Their global production reached 4 million metric tons in 2015 and keeps sharply increasing. The robust growth of this emerging field of industry is driven by multiple factors including environmental awareness and changing consumer preferences, new policies and legislation as well as product development. Nevertheless, the estimated market share of bioplastics still has not exceeded 1% of the global plastics production (European Bioplastics & nova-Institute, 2017). Increasing the market share of bioplastics plays a crucial role in reducing the dependence on fossil-based resources towards the transition to a bio-based society, lessening the environmental impact of polymeric materials and achieving a circular economy. This, however, requires the overall improvement and careful tailoring of the performance of existing materials as well as the development of novel biopolymer grades.

Physical blending, i.e. the simple mixing of thermoplastics in the melt state, is a convenient and cost-efficient route to create new polymeric materials with the desired set of properties. The compatibility of most polymer pairs, however, is not sufficient to ensure the satisfactory performance of their blends – biopolymers are no exception. In our present publication, we review the techniques developed in order to improve compatibility in biopolymer blends by reactive methods. In a recent paper (Imre & Pukánszky, 2013), we already emphasized the importance of the proper, and preferentially quantitative analysis of miscibility-structure-properties correlations. Following the same approach, here we also aim to explore the chemistry of the process in more
detail. We also limit our study to the blends of plant polysaccharides with other biopolymers, for several reasons. Polysaccharides such as starch and cellulose represent the most abundant natural polymers in the biosphere, and therefore have a considerable market share. However, due to their inherently less favorable characteristics, such as high hydrophilicity and lack of thermoplasticity, they are in most cases applied in combination with other polymeric materials. The unique chemical structure of polysaccharides, and the abundance hydroxyl moieties in particular, also enables a wide range of reactive compatibilization techniques.

In the following sections, we discuss some commonly used – and often misused – definitions of the field, such as those of natural, biobased and biopolymers as well as miscibility and compatibility. This is followed by the review of compatibilization strategies in polysaccharide blends, both from a chemical perspective and according to more pragmatic considerations regarding the implementation of such strategies. Finally, we aim to provide a practical guide for the compatibilization of heterogeneous polymeric materials based on plant polysaccharides and biobased polymers.

2. Biopolymers, natural and synthetic biobased polymers

What exactly do we mean when we talk about bioplastics and biopolymers? At present, these terms are applied to describe several different classes of materials, depending on the background and field of expertise of the user. Common usage covers natural, bio-based and biodegradable macromolecules as well as biocompatible polymers for biomedical applications. From an environmental point of view, the origin of raw materials and degradability are the most critical factors. Based on these, polymers fall into four overlapping categories, as illustrated by Fig. 1a that also lists the most significant examples in each category.

The European standard CEN/TR 15932:2010 (“Plastics - Recommendation for terminology and characterisation of biopolymers and bioplastics,” 2010) aims to address the ambiguity regarding the definitions in this field, while taking into consideration both public perception and the current use of biopolymer-related terms. According to the standard, the polymeric materials generally labelled as biopolymers (or bioplastics) fulfill the criteria of one or more of the below categories.
- Biobased polymers: Polymers with constitutional units that are totally or in part from biomass origin. Natural (synthesized by living organisms) and synthetic biobased polymers (whose monomers derive from renewable resources) both belong to this category.

- Biodegradable polymers: A polymeric item that can be biodegraded (according to the relevant standards, e.g. EN 13432 (“Packaging - Requirements for packaging recoverable through composting and biodegradation - Test scheme and evaluation criteria for the final acceptance of packaging,” 2000) and EN 14995 (“Plastics - Evaluation of compostability - Test scheme and specifications,” 2006). Biodegradability is linked to the structure of the polymer chain; it does not depend on the origin of the raw materials.

- Biocompatible polymers: Polymers that are compatible with human or animal tissues and suitable for medical therapy. The polymer does not harm the body or its metabolism in any way while fulfilling the expected function.

As the above classification reflects, the standard essentially affirms the current practice by acknowledging ‘biopolymer’ as an umbrella term for a rather wide range of polymeric materials. The guide also emphasizes the need to use specific terms whenever possible. Naturally, listing the complete terminology exceeds the scope of this review. Instead, we turn our attention to two specific groups of biopolymers, i.e. synthetic biobased polymers and plant polysaccharides. The latter group belongs to the family of natural polymers and accounts for the largest fraction of all biomass, therefore representing the main renewable resource for biofuel and materials production (Field, Behrenfeld, Randerson, & Falkowski, 1998; Martínez-Abad, Ruthes, & Vilaplana, 2016). Here, we focus our attention to the most significant representatives of plant polysaccharides, namely cellulose, hemicelluloses and starch. The industrial application of starch and lignocellulosic biomasses is growing rapidly due to the abundance, low cost and renewable nature of these feedstocks. Nevertheless, few studies have been published on the global availability of biomass resources and most of these focuses on fuel and electricity production without considering other applications. Some recent publications aim to fill this gap, providing a detailed analysis of starch (Marques, Moreno, Ballesteros, & Gírio, 2018) and lignocellulosic materials (Alzagameem, El Khaldi-Hansen, Kamm, & Schulze, 2018; Tye, Lee, Wan Abdullah, & Leh, 2016), respectively.
In lignocellulosic biomass, cellulose microfibrils are the main structural component, embedded within a matrix of hemicelluloses, pectins, and polyphenolic lignins (Burgert & Keplinger, 2013; Cosgrove & Jarvis, 2012). The cellulose macromolecule itself consists of (1→4)-linked β-D-glucopyranosyl units that form long, linear polymeric chains, which aggregate in partially crystalline microfibrils of few nanometers in diameter. The term hemicellulose comprises several different classes of plant polysaccharides that vary substantially in composition and primary molecular structure not only between plant species but also between tissues and developmental stages within the same species. Hemicelluloses are structurally-complex glycan copolymers (xylans, mannans, xylglucans, and mixed-linkage β-glucans), sharing with cellulose a similar backbone of β-(1→4)-linked monosaccharides (mainly glucose, mannose or xylose), decorated with a wide pattern of neutral sugar and uronic acid substitutions. Starch consists of two types of polysaccharides based on α-D-glucose monomers (Q. Chen et al., 2015). Amylose is typically the minor component; it is a linear polymer with a molar mass in the range of $10^5$-$10^6$ g/mol. Amylopectin, on the other hand, has a hyperbranched structure with a molar mass of ca. $10^8$ g/mol. The starch industry is currently growing, and about 180 million tons of starch and starch derivatives are expected to be produced worldwide by 2022 (Marques et al., 2018).

A common feature of plant polysaccharides is their rather recalcitrant structure due to strong intra- and intermolecular interactions, and in some cases a high degree of crystallinity. The large number of highly polar hydroxyl groups present in these natural polymers plays a crucial role in both these characteristics, by enabling the formation of H-bonds. Therefore, plant polysaccharides are not intrinsically thermoplastic, i.e. they cannot be processed in the melt state without chemical modification and/or plasticization. Plasticizers, however, have a tendency of migrating to the surface, resulting in unstable mechanical characteristics over time, and various other issues during application. Thermoplastic starch is also prone to slow recrystallisation after processing, which leads to the embrittlement of the material (Huneault & Li, 2007). Another consequence of their rather polar, hydrophilic nature is the moisture sensitivity of plant polysaccharides. Therefore, they generally contain a considerable amount of water, depending on environmental conditions such as temperature and humidity. This, in turn can lead to considerable hydrolysis and molar mass decrease during processing and to unstable properties during application.
The above issues can and often are addressed by blending the polysaccharides with more hydrophobic matrices. Due to environmental concerns and practical considerations, these latter commonly belong to the family of biobased or biodegradable polymers, resulting in fully biobased and/or degradable compositions. According to data collected by European Bioplastics (European Bioplastics & nova-Institute, 2017), the market share of degradable starch-based blends alone added up to almost a fifth of the global production of biobased and degradable polymers (Fig. 1b). Moreover, this figure does not contain non-degradable grades and a range of other polysaccharide-based materials such as wood plastic composites. The development of such blends and composites with satisfactory performance profiles – according to the desired application – depends on the control of structure and interfacial adhesion in order to facilitate stress transfer between the respective phases. This, however, is seldom achievable without the implementation of a range of physical or chemical modification techniques commonly referred to as compatibilization.
**Fig. 1** Biobased and degradable polymers; **a)** the classification of biopolymers; **b)** global production capacities of bioplastics in 2017 according to European Bioplastics (European Bioplastics & nova-Institute, 2017); degradable grades (fossil- or biobased): PLA – poly(lactic acid), PBAT – poly(butylene adipate-co-terephthalate, PBS – poly(butylene succinate), PHAs – polyhydroxyalkanoates; biobased, non-degradable grades: PE – polyethylene, PA – polyamide, PET – poly(ethylene terephthalate).
3. Compatibilization of heterogeneous polymeric compounds

3.1 Miscibility and compatibility in polymer blends

Although several papers discuss the distinction between miscibility and compatibility (Imre & Pukánszky, 2013; Koning, Van Duin, Pagnoulle, & Jerome, 1998; J.-B. Zeng, Li, & Du, 2015), these two terms are still often confused. Miscibility (Koning et al., 1998; Olabisi, Robeson, & Shaw, 1979) describes the number of phases as well as the composition thereof upon blending two polymers. It is determined by thermodynamic factors, namely the free enthalpy of mixing:

\[ \Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix} \]  

(1)

The resulting blend is homogeneous (i.e. the respective polymers do not form separate phases) only in case the free enthalpy of mixing (\( \Delta G_{mix} \)) is negative. Since the entropy contribution (\( \Delta S_{mix} \)) is largely negligible when blending high molar mass polymers, the resulting morphology is in a great part determined by the change of enthalpy (\( \Delta H_{mix} \)). The extent of the latter, on the other hand, depends on the intra- and intermolecular interactions between the blend components. Due to the lack of specific interactions, complete miscibility rarely occurs in practice (Koning et al., 1998). The great majority of polymer pairs are partially miscible at most, i.e. their blends consist of two distinct phases, both being rich in one polymer, while containing a fraction of the other blend component. The extent of mixing on a molecular level is, however, negligible in most cases, thus it does not affect properties to a significant degree.

Compatibility is essentially a technical term that concerns the property profile of a blend in connection with a certain application. Although mechanical characteristics are generally in the focus of attention when assessing compatibility in a multi-component polymeric material, a multitude of other properties such as processability, transparency, permeability, surface quality or degradability might also be taken into consideration. Improving the compatibility of its components alters the property profile of a heterogeneous system in order to better fit the requirements of a certain application. One should keep in mind, though, that the enhancement of some characteristics is often accompanied by the deterioration of others.
The rule of mixtures estimates the properties, e.g. the tensile strength of polymer blends ($\sigma_b$) as the linear combination of the respective properties of the components ($\sigma_1$ and $\sigma_2$) multiplied by their volumetric fraction ($f$) in the blend:

$$\sigma_b = f\sigma_1 + (1 - f)\sigma_2$$  \hspace{1cm} (2)

The properties of homogeneous blends tend to follow this hypothetical correlation relatively well. The mechanical behavior of materials based on immiscible polymeric components, on the other hand, generally deviate from the rule of mixtures, due to their more complex morphology and the resulting micromechanical deformation processes. In Fig. 2, we compare two typical examples. PLA and thermoplastic starch (TPS) are largely incompatible, thus the relative tensile strength of their blends ( ) is well below the 100 % value suggested by the rule of mixtures across the whole composition range. PLA and poly(methyl methacrylate) (PMMA) ( ), on the other hand, form strong interactions, and are in fact partially miscible. This is also reflected by the SEM micrographs that reveal well-dispersed, submicron sized PMMA particles in the PLA/PMMA blend, while the large starch particles are easy to observe in PLA/TPS even at 10× lower magnification. Thus, the relative tensile strength of the PMMA-based material even exceeds 100 %. Therefore, it is considered a blend of compatible polymers. The successful compatibilization of a blend or composite of incompatible components is sometimes attributed to reaching or exceeding the values predicted by the rule of mixing for a certain characteristic. Although the correlation indeed serves as a convenient threshold, in practice the requirements of the application determine the success or failure of any compatibilization effort.
Fig. 2 The relative strength of two PLA blends, ( ) PLA/TPS and ( ) PLA/PMMA; SEM micrographs: PLA/TPS – 10 vol% TPS, 500× magnification; PLA/PMMA – 30 vol% PMMA, 5000× magnification (Imre, Renner, & Pukanszky, 2014; Müller et al., 2016).

Miscibility and compatibility are of course not fully independent terms. As mentioned above, most polymer pairs are immiscible, their blends having a heterogeneous morphology. In general, compatibility in such polymeric systems can be considered a function of structure and interfacial adhesion. Interfacial adhesion is governed by the strength and number of interfacial interactions; the chemical structure of the respective polymer chains plays a crucial role in determining both. Some polymeric materials, e.g. polyolefins, are only capable of weak Van der Waals-type secondary interactions. The presence or absence of functional groups capable of specific interactions (induced dipole, dipole-dipole interactions and hydrogen bonding) as well as the nature and arrangement of such functional groups are decisive in terms of not only miscibility but also com-
compatibility of immiscible polymer pairs. Naturally, the number of interfacial interactions correlates with the number of the functional groups at the interface connecting the phases, but also with the specific surface area of said interface. In short, good compatibility requires the formation of a large number of strong interactions across an extensive interface.

Aside from a few exceptions, such as reactor blends, most polymer blends are prepared by melt mixing. While the composition of the phases can be estimated solely based on miscibility, blend morphology shows a great degree of variety and complexity as a function of polymer characteristics and processing conditions. Besides blend composition and interactions, temperature, shear rate as well as the viscosity and elasticity of the phases also must be considered. During the melt mixing of two immiscible polymers, shear forces tend to break up larger drops of one phase that in turn becomes dispersed in the other phase, i.e. the matrix. This process continues until an equilibrium particle size is reached. The equilibrium particle size may vary to a large extent, from tens of nanometers to several micrometers, depending on a number of factors. Higher shear rates and stronger interfacial interactions, for instance, facilitate finer phase dispersion. The effect of the viscosity ratio of the two polymers is more diverse, depending on the mechanism of drop formation and coalescence during processing (J. M. H. Janssen & Meijer, 1993; Koning et al., 1998; S. Wu, 1987).

A finely dispersed morphology has several advantages in terms of optical properties and permeability, among other characteristics. More importantly, it results in an increased specific surface area of the dispersed phase, thus in a more effective interfacial adhesion, and improved mechanical properties (consider the morphology and relative strength of PLA/PMMA blends in Fig. 2. Consequently, compatibility can be improved up to a certain point simply by optimizing processing conditions. The improvement achievable with this approach is, however, rather limited. In order to considerably enhance the performance of a polymer blend, a wide range of modification strategies is available that are commonly referred to as compatibilization.

Most compatibilization techniques involve the introduction of an additive – i.e. compatibilizer – that exerts its activity at the blend interface in order to facilitate interfacial adhesion. In the case of non-reactive compatibilization, pre-made amphiphilic compounds are used. Such molecules
are able to interact with the respective polymers in both phases. The most common representatives of non-reactive compatibilizers are block-copolymers (Cai, Wan, Bei, & Wang, 2003; Duquesne, Rutot, Degee, & Dubois, 2001; Na et al., 2002; Vilay, Mariatti, Ahmad, Pasomsouk, & Todo, 2010), one constitutive end or block of which is miscible with one blend phase (Phase A), while the other with the second phase (Phase B). Macromolecules with various structures can be used for this purpose, e.g. diblock, triblock or graft copolymers, as illustrated in Fig. 3. The compatibilization effect is most commonly associated with the formation of an interphase facilitating interfacial adhesion as well as a finer morphology with reduced average diameter of the dispersed particles (Koning et al., 1998). Amphiphilic low-molar mass compounds (Yokesahachart & Yoksan, 2011), ionomers (Landreau, Tighzert, Bliard, Berzin, & Lacoste, 2009) or third polymers – at least partially – miscible with both components (Parulekar & Mohanty, 2007) work in a similar manner.

**Fig. 3** The effect of compatibilization on the morphology of polymer blends due to the activity of amphiphilic polymer structures at the interface. Image drawn using inspiration from (Koning et al., 1998).

In the case of reactive methods, amphiphilic structures form *in situ* during blending. This can be achieved through the addition of low molar mass (Jang, Shin, Lee, & Narayan, 2007; Jun, 2000; P. Ma et al., 2014; Piming Ma, Hristova-Bogaerds, Schmit, Goossens, & Lemstra, 2012; N.
Wang, Yu, & Ma, 2007; J.-F. Zhang & Sun, 2004), oligomeric (Al-Itry, Lamnawar, & Maazouz, 2012; Quiles-Carrillo, Montanes, Sammon, Balart, & Torres-Giner, 2018) or polymeric (Avella et al., 2000; Detyothin, Selke, Narayan, Rubino, & Auras, 2015; Huneault & Li, 2007; Jang et al., 2007; Kumar, Mohanty, Nayak, & Rahail Parvaiz, 2010; Li & Huneault, 2011; Ren, Fu, Ren, & Yuan, 2009; Shi et al., 2011; C.-S. Wu, 2003; J.-B. Zeng et al., 2011) reactive compounds that act as coupling agents, forming covalent bonds between the phases. Another type of reactive compatibilization involves the formation of graft or block copolymers from their monomers (Don, Chung, Lai, & Chiu, 2010; Philippe Dubois & Narayan, 2003; Lai, Sun, & Don, 2015; Lönnberg, Larsson, Lindström, Hult, & Malmström, 2011), the respective chain sections of which are miscible with different phases of the blend. Throughout this review we focus our attention to such reactive techniques, for several reasons. First of all, although physical compatibilization strategies are also commonly applied, reactive methods prove to be more efficient in general (Imre & Pukánszky, 2013; Koning et al., 1998). Furthermore, the large number of available hydroxyl moieties on polysaccharide chains offers a convenient site for reactive modification.
4. Reactive compatibilization strategies in polysaccharide-based compositions

The rich palette of carbohydrate chemistry offers almost unlimited possibilities for the modification and substitution of hydroxyl groups in polysaccharides (Q. Chen et al., 2015; Heinze & Liebert, 2001; Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998; Söderqvist Lindblad & Albertsson, 2004; Vilaplana, Zou, & Gilbert, 2018). Therefore, in the following sections we focus our attention to reactive compatibilization methods. Typically, this can be implemented through oxidation, esterification or etherification. Depending on the chemical structure of the reagents and the resulting products one can differentiate graft copolymerization, coupling and crosslinking reactions, as discussed in more detail below. The common aspect of these methods is the in-situ formation of a block or graft copolymer, the respective blocks of which are miscible with different blend phases.

4.1 Substitution with monofunctional reagents

The substitution of hydroxyl groups of plant polysaccharides has a long history. Cellulose acetate (CA), for instance was first described by Schutzenberger (Schützenberger, 1865) as early as 1865, while studies on the chemical modification of starch have been performed in the early 1940s (Q. Chen et al., 2015). In the case of cellulose acetate, the main purpose of this modification is the thermoplasticization of cellulose. The substitution of starch -OH groups with more hydrophobic moieties, however, often aims to decrease the moisture absorption of this natural-based material, thus the properties of starch become more stable. Nevertheless, the chemical modification also affects the structure and morphology of the native polysaccharides, as well as their mechanical characteristics, transition temperatures and thermal stability. The origin of the polysaccharide substrate, methods, conditions and types of reagents all have a significant effect on the outcome of the modification. The products are often characterized by their degree of substitution (DS). In the case of starch and cellulose, for instance, this value ranges from 0 to 3, a DS of 3 meaning that on average all three hydroxyl groups of the anhydroglucose repeating units have been substituted.
One of the most commonly applied chemical modifications of polysaccharides is the substitution of their hydroxyl groups by esterification. The reaction can be performed using acids, acid chlorides (Aburto et al., 1999; Fang, Fowler, Sayers, & Williams, 2004) or anhydrides (Chi et al., 2008; Lopez-Rubio, Clarke, Scherer, Topping, & Gilbert, 2009; R. Shogren, 1996; R. L. Shogren, 2003; Y. X. Xu, Miladinov, & Hanna, 2004). With the increasing proportion of acetyl moieties (Jiang, Qiao, & Sun, 2006; M. Tupa, Maldonado, Vázquez, & Foresti, 2013; M. V. Tupa, Ávila Ramírez, Vázquez, & Foresti, 2015; Y. X. Xu et al., 2004; Liming Zhang, Xie, Zhao, Liu, & Gao, 2009) or longer nonpolar side-groups (Di Filippo et al., 2016; Miladinov & Hanna, 2000; Namazi, Fathi, & Dadkhah, 2011; M. Tupa et al., 2013), besides itself becoming more hydrophobic, starch also loses its original, highly crystalline granular structure (Fig. 4a). Due to the disruption of inter- and intra-molecular hydrogen bonds induced by the progressive replacement of -OH groups, the surface of the particles first starts to show increased roughness (Fig. 4b). Finally, the complete disruption of the granular structure and the fusion of the particles might also occur (Fig. 4c and d).

![Fig. 4](image-url) The morphology of a) native corn starch compared with its propionylated counterparts having a DS of b) 0.05; c) 0.13; and d) 1.59, respectively. SEM images, 1000× resolution (Di Filippo et al., 2016).
In terms of compatibilization of heterogeneous polymeric materials, the effect of substituting the hydroxyl groups of polysaccharides with rather hydrophobic, monofunctional reagents is not easy to interpret. While this type of modification decreases inter- and intramolecular interactions within the polysaccharide phase, it also leads to less interaction between the blend or composite components, i.e. less adhesion at the interface. Thus, it is not surprising that in many cases such modification was found to result in a strongly phase separated morphology with no specific interactions between blend components, nor any improvement in mechanical properties compared with unmodified starch (Jiang et al., 2006; Koenig & Huang, 1995; Lianlai Zhang, Deng, Zhao, & Huang, 1997), or even a deterioration thereof (Koenig & Huang, 1995).

There are studies, however, that claim to have achieved improved compatibility in starch-based blends by this method (Wokadala, Emmambux, & Ray, 2014; S. Zeng, Wang, Xiao, Han, & Meng, 2011), as in their view, the hydrophilic nature of thermoplastic starch hinders compatibility with more hydrophobic polymers (Wokadala et al., 2014). There is some truth to that claim, although the complete picture is a little more complex than that. As discussed above, esterification and etherification generally hinder interfacial interactions, which is undesirable from a compatibilization point of view. By decreasing intra- and intermolecular interactions within the polysaccharide phase, however, such modifications can drastically alter blend or composite morphology, leading to decreased particle size and a more homogeneous dispersion of the dispersed phase. This, in turn equals increased interfacial area and the development of a more homogeneous stress-field under deformation, thus potentially leading to higher tensile strength. Therefore, it is well understandable that such behavior was mostly observed in heterogeneous materials based on non-plasticized starch (Wokadala et al., 2014; S. Zeng et al., 2011), in which the polysaccharide essentially acts as a filler. As Fig. 4 also suggests, the properties (e.g. thermoplasticity) and especially the morphology of native starch changes drastically as an effect of substitution, resulting in the improved composite morphology and mechanical characteristics described earlier. In the case of thermoplastic starch, the change in blend morphology due to such modifications is much subtler and is to a great extent governed by other factors, e.g. plasticizer content, therefore real compatibilization due to substitution with monofunctional reagents is rarely observed in such materials.
4.2 Coupling

4.2.1 Coupling with small molecules

By the term coupling we mean the establishment of chemical bonds between the respective phases of a heterogeneous polymeric material. It is a rather common and conventional form of reactive compatibilization, as it involves the in-situ formation of amphiphilic compounds, in this case typically block and graft copolymers, in order to facilitate interfacial adhesion. As Fig. 5a illustrates, one way to achieve this is the introduction of small molecules with at least one functional group being able to react with one phase, and another being able to react with the other phase. Naturally, these two moieties can be identical, and they very often are. The application of such compounds can also lead to crosslinking in one or both polymer phases, in case both functional groups react with one polymeric component. Excessive crosslinking, on the other hand, might lead to the formation of a polymer network, and thus thermoset behavior, i.e. the material can no longer be brought into the melt state. Thus, in order to preserve the thermoplastic nature of the blend or composite, coupling agents are applied in limited concentrations.

Due to their numerous hydroxyl groups, numerous bifunctional compounds can form covalent bonds with polysaccharides. These include organic bi- and trifunctional acids (Olivato, Grossmann, Bilck, & Yamashita, 2012), maleic (J. M. Raquez et al., 2008; Stagner, Dias Alves, Narayan, & Beleia, 2011; Tomasik, Wang, & Jane, 1995) and succinic anhydride (J. S. Bao, Xing, Phillips, & Corke, 2003; Bhosale & Singhal, 2006; Hui, Qi-he, Ming-liang, Qiong, & Guo-qing, 2009; Shih & Daigle, 2003; R. L. Shogren, 2003; Tomasik et al., 1995) as well as silane compounds (Jariyasakoolroj & Chirachanchai, 2014) and diisocyanates (Karagoz & Ozkoc, 2013; Schwach, Six, & Avérous, 2008). Finding appropriate reagents that are able to react with the other, typically more hydrophobic polymer tends to be more challenging, and the low number – or complete lack of – available functional groups limits the effectiveness of this type of modification.
Fig. 5 Compatibilization strategies: a) coupling with bifunctional reagents; b) coupling with reactive polymers; c) graft copolymerization with bifunctional or cyclic monomers.

In the cases where the coupling reaction between the two phases could be confirmed, significant improvement in the mechanical properties was observed (Jariyasakoolroj & Chirachanchai, 2014; Quiles-Carrillo et al., 2018). Still, mechanical performance is often limited by the inherent properties – e.g. low tensile strength – of the dispersed polysaccharide phase (Karagoz & Ozkoc, 2013), among other things as discussed in Section 6.3. Potential side-reactions represent another challenge; we have already mentioned possible cross-linking in the polysaccharide phase. In a rather elaborate paper, Schwach et al. (Schwach et al., 2008) compare different methods for the compatibilization of PLA/TPS blends. One technique discussed by the authors involves the use of a bifunctional reagent, 4,4'-methylenebis(phenyl isocyanate) (MDI). As the authors also note, the limited success of compatibilization might well be explained by the numerous side reactions diisocyanates can participate in plasticized starch blends. Besides the hydroxyl groups of PLA
and starch, such compounds can react with any traces of moisture as well as the hydroxyl-rich plasticizer forming low molar mass ureas and urethanes.

Due to the availability, low price, high reactivity and relatively benign nature of this unsaturated acid derivative, maleic anhydride (MA) has also been considered for the compatibilization of polysaccharide-based blends (Jang et al., 2007; J.-F. Zhang & Sun, 2004), with moderate success. The anhydride moiety can form covalent bonds with the available hydroxyl groups in the reaction mixture. Due to its double bond, MA can also radically react with the aliphatic chain of matrix polymers such as PLA in the presence of a peroxide initiator (J.-F. Zhang & Sun, 2004).

Several studies have also shown promising results regarding the use of poly(carboxylic acid)s – e.g. citric, malic and tartaric acids – as environmentally benign, non-toxic and non-volatile alternatives to MA. Moreover, these organic acids are inexpensive due to their abundance, since they can either be extracted from fruits and vegetables, or can be synthesized by microorganisms (Sailaja & Seetharamu, 2008). Similarly to anhydrides, poly(carboxylic acid)s participate in esterification and transesterification reactions, resulting in the formation of reactive side-groups and cross-links between the polysaccharide chains and other polymers with appropriate reactive groups, e.g. the hydroxyl or amine end-groups of polyesters and polyamides, respectively. The effect of these agents on the properties of polymer blends is rather complex. Besides their compatibilization effect, and thus improved tensile strength, they can also exert a plasticizing effect and facilitate the acid hydrolysis of polysaccharide chains (Martins & Santana, 2016; Olivato, Müller, Carvalho, Yamashita, & Grossmann, 2014; Reddy & Yang, 2010). Nevertheless, the consequent disruption of the granular structure of starch results in reduced viscosity, improving processing characteristics and the homogeneity of the material.

### 4.2.2 Reactive polymers

One way to overcome the challenge represented by the lack of available functional groups in most hydrophobic matrix polymers is the introduction of such reactive moieties to the macromolecule by using peroxide initiators. MA-grafted polymers have been used for decades for the compatibilization of polyolefin blends and composites that contain hydrophilic compounds such
as lignocellulosic fibers (Danyadi et al., 2007; Klason, Kubat, & Gatenholt, 1992; Renner, Móczó, & Pukánszky, 2009) or starch (Bikiaris et al., 1998; Bikiaris & Panayiotou, 1998; Senna, Hossam, & El-Naggar, 2008; Shujun, Jiugao, & Jinglin, 2005; S. J. Wang, Yu, & Yu, 2005, 2006). The same concept has since been applied with success to polyesters (Arbelaiz, Fernández, Valea, & Mondragon, 2006; Hwang et al., 2013; Muthuraj, Misra, & Mohanty, 2017; Nabar, Raquez, Dubois, & Narayan, 2005), and among them biobased and biodegradable polymers such as poly(lactic acid) (Detyothin et al., 2015; Hwang et al., 2013; Raghu, Kale, Raj, Aggarwal, & Chauhan, 2018).

In contrast to using a combination of a peroxide and the anhydride for the in situ coupling of a polysaccharide with the matrix polymer (J.-F. Zhang & Sun, 2004), the reactive polymers introduced in this section are synthesized in a separate process step, similar to the one described in detail by Detyothin et al. (Detyothin, Selke, Narayan, Rubino, & Auras, 2013) for the preparation of MA-grafted PLA by reactive extrusion. In a second step, this reactive compatibilizer is mixed with the other blend components during melt processing, forming graft copolymers by mainly reacting with polysaccharide hydroxyls through its anhydride moieties, according to Fig. 5b. Other moieties such as acrylic acid, oxazoline, and glycidyl methacrylate can also be grafted to confer reactivity to otherwise non-reactive polymers; however, MA grafting is generally preferred due to MA’s easier handling, low toxicity and because it does not tend to homopolymerize during conventional free-radical melt-grafting conditions (Huneault & Li, 2007).

The polymer backbone of the reactive compatibilizer is typically identical with that of the matrix (Philippe Dubois & Narayan, 2003; Huneault & Li, 2007), but this is not necessarily the case. Nevertheless, it is of critical importance that the long chains of the reactive polymer should be miscible with the matrix. The entanglements thus formed ensure the effective stress transfer during deformation between the covalently bonded matrix and dispersed phase. There are more complex approaches as well, such as the one described by Akrami et al. (Akrami, Ghasemi, Azizi, Karrabi, & Seyedabadi, 2016). In this study, a reactive compatibilizer is prepared by first reacting MA with poly(ethylene glycol) (PEG) in solution, followed by the addition of starch, thus forming PEG-starch copolymers with free carboxylic groups. Once mixed with a blend of PLA and TPS, the carboxylics are anticipated to react with the hydroxyl moieties present in both
blend components. Unfortunately, the reactions taking place during compatibilization were not analyzed in detail, which is a common deficiency of many studies in this field.

This approach (Akrami et al., 2016) resulted in a slight increase in tensile strength. This latter characteristic is a convenient and common measure of the success of compatibilization, as discussed in more detail in Section 6.3. Changes in blend or composite structure can also provide information on the effectiveness of a certain modification technique. Decreased particle size and a more homogeneous dispersion of the dispersed phase as a result of compatibilization are often reported. Improvements in mechanical performance, on the other hand, tend to be more moderate (Huneault & Li, 2007).

Here, we must once more draw attention to the limiting effect of the inherently low strength of many plant polysaccharide materials on the mechanical performance of the blend or composite as a whole. Reactive polymers were successfully implemented for the compatibilization of lignocellulosic fillers with various polymer matrices (Plackett, 2004), resulting in significantly improved tensile properties. Nevertheless, in the case of strong interfacial adhesion between the phases, the dominating micromechanical deformation process was found to be the fraction of the fibers, limiting the ultimate strength of such composites (Faludi et al., 2014). Consequently, beyond ensuring strong interfacial adhesion, and effective stress transfer between the phases by compatibilization, one should also aim to modify the inherent properties of plant polysaccharide-rich materials, such as starch, hemicelluloses, cellulose or lignocellulosic fillers, in order to create biobased structural materials with a competitive set of properties.

4.3 Graft copolymerization

The amphiphilic copolymer structures acting as compatibilizer can also be synthesized via the graft copolymerization of various bifunctional and cyclic monomers initiated by the hydroxyl groups of plant polysaccharides, according to Fig. 5c. Such modifications are often referred to as “grafting from” as opposed to the “grafting to” approach discussed in Section 4.2. The advantage of this technique is that amphiphilic copolymer structures can be achieved in one step, often via
reactive processing, while the easily accessible end-groups of the side-chains formed by graft copolymerization enable further reactive modification steps, if necessary.

4.3.1 Bifunctional monomers

Numerous studies have been published on the grafting of bifunctional monomers onto plant polysaccharides. Acrylate monomers (Hebeish, ElRafie, Higazy, & Ramadan, 1996; Higazy, Bayazeed, & Hebeish, 1987; Jyothi, Sajeev, & Moorthy, 2010; Zou et al., 2012) have been the focus of research for many decades, aiming the synthesis of copolymer structures for various applications. Lately, biobased and/or degradable side-chains gained considerable importance, and thus novel monomers appeared, such as lactic acid (Ambrosio-Martín, Fabra, Lopez-Rubio, & Lagaron, 2015; Hafren & Cordova, 2007). In spite of a few exceptions (Ambrosio-Martín et al., 2015; Lai et al., 2015), bifunctional monomers never gained significant practical importance in the compatibilization of heterogeneous polymer systems, mostly due to the convenience of ring-opening polymerization (ROP) techniques using cyclic monomers, as presented in section 4.3.2. Therefore, we refrain from discussing them in much detail. The main drawback of many bifunctional monomers is the formation of low molar mass side-products (typically water) during their polymerization. These latter need to be constantly removed from the reaction mixture by vacuum or other means in order to shift the equilibrium towards the formation of the polymer. Nevertheless, achieving high molar masses still tends to be a challenge.

4.3.2 Ring-opening polymerization

Unlike the polycondensation of bifunctional compounds (e.g. hydroxy acids), the ring-opening polymerization of cyclic monomers proceeds without the accumulation of side-products, thus promoting the formation of high molar mass polymers and enabling the modification of polysaccharides via reactive processing. Nevertheless, proper drying protocols of the raw materials need to be set up to minimize moisture content that might lead to the hydrolysis of the growing side-chains. Another – generally undesirable – side reaction is the homopolymerization of the cyclic monomers initiated by water or other proton donors, such as hydroxyl-containing plasticizers, being present in the reaction mixture.
There are numerous cyclic organic compounds that can be used as monomers in ROP; the majority of them – at least those that have significant practical importance – belong to the family of cyclic esters, i.e. lactones. **Fig. 6** shows the schematic representation of the ring-opening polymerization of a cyclic ester. The most commonly applied monomers for compatibilization purposes in polysaccharide blends and composites are ε-caprolactone (CL) and lactide (LA). The grafting of these compounds onto starch is typically carried out under anhydrous conditions either in bulk (P Dubois, Krishnan, & Narayan, 1999; Rutot-Houze et al., 2004; Yu et al., 2008), in organic solvents (L. Chen et al., 2005; Rutot-Houze et al., 2004; Sugih, Picchioni, Janssen, & Heeres, 2009) or in ionic liquids (Q. Xu, Kennedy, & Liu, 2008). Although similar reactions have been reported also in aqueous media (Choi, Kim, & Park, 1999; Gong, Wang, & Tu, 2006), these techniques never gained much significance. The ROP reactions discussed above are almost without exception (I. Kim & White, 2005) catalyzed by Lewis-acids, among which tin (II) 2-ethylhexanoate (L. Chen et al., 2005; P Dubois et al., 1999; Philippe Dubois & Narayan, 2003; Lönnberg et al., 2011; Yu et al., 2008) and various aluminum alkoxides (P Dubois et al., 1999; Philippe Dubois & Narayan, 2003; Sugih et al., 2009) are most commonly applied.

In two similar studies, Schwach et al. (Schwach et al., 2008) and Dubois et al. (Philippe Dubois & Narayan, 2003) both compare different compatibilization strategies in polyester/starch blends. One such strategy in each case is the ex-situ synthesis of polyester-graft polysaccharides, PLA-graft amylose and PCL-graft dextran, respectively, followed by the incorporation of these copolymers into starch blends in the melt state. Strictly speaking, these modifications should be classi-
fied as physical compatibilization, of course. Nevertheless, we discuss them here, as in both cases the synthesis of the compatibilizer is in focus, and from a chemical point of view it is very similar to reactive compatibilization techniques based on graft copolymerization. In both cases, only moderate improvement could be achieved due to the addition of the compatibilizer. As Dubois et al. (Philippe Dubois & Narayan, 2003) note, in addition to the time-consuming synthesis of the graft-copolymer, improved mechanical performance was obtained only when the compatibilizer was first precipitated onto the surface of starch granules in order to ensure they are localized at the interface. The in-situ graft-copolymerization of CL onto starch proved to be a much more favorable process that lead to considerably improved mechanical characteristics, highlighting the efficiency of reactive modification techniques.

As we discuss in more detail in Section 5.2, reactive processing – and reactive extrusion (REX) in particular – is a highly convenient technique for the ROP-synthesis of polyesters, both poly(ε-caprolactone) (PCL) (Balakrishnan, Krishnan, Narayan, & Dubois, 2006; B. J. Kim & White, 2003; Machado et al., 2008) and poly(lactic acid) (PLA) (Jacobsen, Fritz, Degée, Dubois, & Jérôme, 2000; Jacobsen, Fritz, Degée, Dubois, & Jérôme, 2000). This method can also be applied for the in-situ formation of polyester-graft polysaccharides (Számel, Domján, Klébert, & Pukánszky, 2008; Vidéki, Klébert, & Pukánszky, 2005; Warth, Mühlaupt, & Schätzle, 1997).

The use of silylated substrates, as reported in several studies (Philippe Dubois & Narayan, 2003; Sugih et al., 2009), also deserves mentioning. Such modifications involve a pre-treatment step, in which some of the polysaccharide hydroxyls are substituted with silicon reagents, resulting in their respective silyl ethers. Besides enhancing the hydrophobicity and thermal stability of the polysaccharide, silylation has the additional benefit of “protecting” some of the -OH groups, thereby reducing the number of proton donors acting as initiators during the ROP of cyclic monomers. As a result, fewer but longer polyester side-chains form on the remaining free polysaccharide hydroxyls, potentially leading to more efficient compatibilization due to entanglement with the matrix polymer.
5. Implementation of compatibilization strategies

5.1 Bulk and solvent-based methods

Compatibilization by substitution and graft copolymerization reactions is commonly performed in bulk or in solution, especially at the laboratory scale. However, in case there are multiple polymeric components present in the reaction mixture, e.g. the coupling of two polymers with small molecules or reactive polymers, such techniques prove less convenient and melt processing techniques are favored even at smaller scales. A major challenge for synthesis in bulk is to maintain effective mixing and dissipate the excess heat arising due to the increasing molar mass, and thus increasing viscosity of the products.

Performing the reaction in a solvent, such as organic solvents (L. Chen et al., 2005; Rutot-Houze et al., 2004; Sugih et al., 2009), ionic liquids (Q. Xu et al., 2008) or water (Choi et al., 1999; Gong et al., 2006), to some extent helps dealing with these problems, while also presenting new challenges. On the one hand, solution-based techniques make viscosity- and temperature-control more easily manageable, while they also enable the purification of the product. However, the removal – and eventual recycling – of the solvent requires the introduction of additional process steps making such techniques costly and time-consuming compared to the melt processing methods discussed in the following section. Consequently, such methods are often difficult to scale up for industrial production (J.-M. Raquez, Narayan, & Dubois, 2008).

5.2 Reactive processing

Extrusion is a thermo-mechanical process that is based on the action of one or two screws spinning in a tight barrel equipped with temperature control. The resulting high shearing forces between the plastic melt, the screw and the barrel lead to elevated temperature and pressure along the extruder. Two main categories of extrusion devices can be distinguished: single-screw and twin-screw extruders. The screw of single-screw extruders tends to be composed of one single piece, while twin-screw type devices often comprise shorter sections, i.e. screw elements that are selected and assembled according to the processed material and requirements regarding the
product. These latter are referred to as modular extruders. There are three main types of screw elements that can be used: conveying screws, kneading blocks and reverse screws. Due to their different shape they affect the viscoelastic melt differently, facilitating material transport, mixing or shearing. The overall screw profile is one of the most crucial factors in extrusion processing. Additionally, twin-screw extruders can be classified as counter-rotating or co-rotating (Duque, Manzanares, & Ballesteros, 2017; Erdmenger, 1957; Kohlgrüber & Bierdel, 2008). In co-rotating devices, the shearing and plasticizing effect is axial (the maximum velocity being achieved at the intermeshing zone), while in counter-rotating twin-screw extruders, the effect is radial (highest velocity being achieved at the screw tips).

The ultimate goal of materials design and development is to obtain new materials or to enhance the properties of existing ones to meet the requirements of specific applications. By means of extrusion-compounding and reactive extrusion, a wide range of tailor-made polymer blends and composites can be produced. Due to their excellent mixing characteristics, intermeshing and co-rotating twin screw extruders are particularly suitable for this purpose. As opposed to single-screw extrusion, which produces mainly a distributive mixing and where the process throughput is dependent on the screw speed and the pressure profile, twin screw extrusion allows the adjustment of several independent process variables, including feed flow rate, screw rotation speed and temperature profile along the screw axis. This leads to a high process flexibility and optimization potential (Uitterhaegen & Evon, 2017).

Reactive extrusion (REX) describes a special process in extrusion technology in which individual components are chemically modified during melt processing. Twin-screw extruders are typically used for REX purposes, due to their excellent control of mixing and residence time distribution (J.-M. Raquez, Narayan, et al., 2008). The stoichiometric ratio of the components needs to be ensured by using highly accurate feeders, while surplus reaction heat is dissipated through the barrel wall. One of the most common goals of REX is the compatibilization of heterogeneous polymeric materials, and polysaccharide-based ones among them. As illustrated by Fig. 7, the process involves the in-situ formation of amphiphilic structures, and thus covalently bonding the phases in the melt state, according to one of the chemical routes discussed in Section 4.
**Fig. 7** The compatibilization of polysaccharide-based polymer blends and composites in the melt state by reactive extrusion.

REX is a convenient and cost-effective technique for the esterification of polysaccharides using anhydride reagents (Hanna & Fang, 2002; Miladinov & Hanna, 2000; J.-M. Raquez, Nabar, Narayan, & Dubois, 2008; J. M. Raquez et al., 2008; Rudnik, Matuschek, Milanov, & Kettrup, 2005; Rudnik & Zukowska, 2004; Tomasik et al., 1995; L. F. Wang, Shogren, & Willett, 1997), the coupling of blend components using bifunctional reagents (Schwach et al., 2008) or reactive polymers (Philippe Dubois & Narayan, 2003; J.-M. Raquez, Nabar, et al., 2008) as well as for the in-situ formation of graft-copolymers by ROP (Számel et al., 2008; Vidéki et al., 2005; Warth et al., 1997). Reactions that would otherwise require heavy equipment, such as batch reactors, can be performed more efficiently in a continuous manner by REX. Moreover, extruders are far more capable of dealing with the dramatic change of viscosity due to the increasing molar mass of one or more components of the reaction mixture during polymerization (Brown & Orlando, 1998; J.-M. Raquez, Narayan, et al., 2008; Tzoganakis, n.d.). One should keep in mind that unlike in the case of solvent-based methods, there is no practical solution for the purification of materials produced by reactive extrusion. Thus, catalysts, unreacted monomers and other reagents as well as side-products formed during the process cannot be removed from the finished
product. Depending on their concentration, such chemical species might affect the characteristics of the material, and even prohibit its use in certain areas, e.g. food and medical applications.

The rheological behavior of polysaccharide-based blends is strongly affected by the blend composition, the properties of the components (viscosity ratio and elasticity ratio), the volume fractions, as well as by the morphology and interactions between phases (Biresaw & Carriere, 2001). It should also be noted that rheological characteristics play a significant role during reactive processing in the melt state, regardless the reactivity of the components. Through melt viscosity and relative viscosity of the components, rheological properties affect residence time distribution (RTD) inside the extruder, shear viscosity in the screw channels and die as well as the dynamics of post-extrusion phenomena, e.g. die-swell. In polymerization processes carried out by reactive extrusion, the percentage monomer conversion has been found to be proportional to mean residence time and thus on RTD (De Graaf & Janssen, 2000; Poulesquen, Vergnes, Cassagnau, Gimenez, & Michel, 2001).

In general, the processing properties of polysaccharides and synthetic biobased polymers differ considerably. The viscosity of polysaccharides is much higher than that of conventional polymers, while the majority of biobased polymers, and aliphatic polyesters in particular, tend to form relatively low viscosity melts, often leading to difficulties with processing such blends. The complexity of the rheological behavior of thermoplastic starches and other polysaccharides further complicates melt processing: rheological properties depend on the botanical origins of the natural polymers (molar mass, and amylose/amylopectin ratio in the case of starch). The effect of chemical modifications such as esterification as well as the amount and type of plasticizers needs to be considered. Thermoplastic starch, for instance, was reported to behave similarly to a high molecular weight viscoelastic polymer at high amylopectin contents, while lower amylopectin/amylose ratios result in gel-like behavior. In both cases, plasticizer content only affected the viscosity of the polymer melt, but not its inherent rheological behavior (Della Valle, Buleon, Carreau, Lavoie, & Vergnes, 1998).

It is well known that the precise control of such processes is rather challenging, due to the non-Newtonian behavior and high viscosity of polymer melts, the consequent high shear stresses oc-
curring during extrusion, and the complex reactions taking place between the blend components
during reactive extrusion. All these parameters affect the structure of the compatibilized blend to
a high degree, therefore also influencing its macroscopic properties. Therefore, the study of rheo-
logical behavior during REX process, i.e. rheokinetics, is essential in modeling and optimizing
processing conditions (X. Bao et al., 2018).

In any case, despite reactive extrusion certainly being an important way to modify and develop
novel polymeric systems, it is a rather complex process that involves many interacting variables.
Reactions in the melt state are governed by local flow conditions (residence time, temperature,
mixing), while also affecting flow conditions through changes in molar mass, viscosity as well as
temperature due to reaction heat. Moreover, the geometry and the kinematics of a twin-screw
extruder are often rather complex, compared to a batch reactor. Therefore, the optimization of
such processes is a highly challenging task (Jongbloed, Kiewiet, Van Dijk, & Janssen, 1995).
Consequently, studies generally focus either on the determination of general, theoretical correla-
tions, or providing practical tools for the optimization and control of specific reactive extrusion

5.3 Catalysts

The substitution of the hydroxyl groups of plant polysaccharides with more hydrophobic moi-
eties through esterification is a well-described in the literature (Simon, Müller, Koch, & Müller,
1998; Whistler, 1945). The acylation reaction can be catalyzed by a wide range of organic and
inorganic compounds including acids (Cheng, Dowd, Selling, & Biswas, 2010), bases (Whistler,
1945), halogens (Biswas et al., 2008) or even enzymes (Alissandratos & Halling, 2012). The
formation of polyester chains through ROP is most commonly catalyzed by one family of metal-
organic compounds, namely metal alkoxides ranging from aluminum (P Dubois et al., 1999;
Philippe Dubois & Narayan, 2003) to lanthanide alkoxides. The efficiency of these Lewis-acid
type catalysts is based on the in-situ formation of alkoxides with an alcohol or other protic impuri-
ties present in the reaction medium (Kowalski, Duda, & Penczek, 1998). Accordingly, polysac-
charides containing free hydroxyl groups such as starch (P Dubois et al., 1999), dextran (Philippe
Dubois & Narayan, 2003) or cellulose and its derivatives (Hatakeyama, Yoshida, & Hatakeyama,
can be grafted with cyclic esters by this method conveniently. Among the metal alkoxides discussed above, tin(II) bis(2-ethylhexanoate), or stannous octoate \([\text{Sn(Oct)}_2]\), is by far the most commonly applied. Its extensive use is mainly due to the fact that it is accepted by the American Food and Drug Administration (FDA) for polymer coating formulations in contact with food. Moreover, \text{Sn(Oct)}_2 is less sensitive towards water and other protic impurities than aluminum alkoxides, which facilitates its use in the laboratory and in industry as well (Lecomte & Jérôme, 2011). Despite the FDA approval, the health and environmental effects of tin catalysts are rather ambiguous, as Hege et al. (Hege & Schiller, 2014) discuss in some detail. Therefore, numerous other metal-organic compounds such as Li, Mg, Ca, Zn, Fe and Zr alkoxides have been considered as more environmentally benign catalyst in ROP syntheses (Kundys, Plichta, Florjańczyk, Frydrych, & Żurawski, 2015). Due to their very low toxicity, iron compounds are often used as alternatives for the catalysis of ring-opening polymerization (Dobrzynski, Kasperczyk, Janeczek, & Bero, 2002; Kundys et al., 2015; O’Keefe, Breyfogle, Hillmyer, & Tolman, 2002; Stolt et al., 2005), with varying degrees of success. Among them, iron(III) acetylacetonate \([\text{Fe(AcAc)}_3]\) (Dobrzynski et al., 2002; Kundys et al., 2015) has shown much promise, resulting in polymers with molar masses similar to those prepared with \text{Sn(Oct)}_2.

Organocatalysis is another concept that aims to reduce the environmental effect of catalysts (Domínguez de María, 2010) used for the esterification of polysaccharides (M. Tupa et al., 2013) or the ROP of lactones (Casas, Persson, Iversen, & Córdova, 2004; Hafrén & Córdova, 2005; Persson, Schröder, Wickholm, Hedenström, & Iversen, 2004). Although the term originally comprises all reactions catalyzed by metal-free organic compounds, it is often applied to nontoxic, small organic molecules such as hydroxy (lactic, tartaric) and amino (proline, alanine) acids. These latter have been claimed to act as ‘minimal hydrolyses’ catalyzing reactions in a biometric fashion, thus being highly selective (Persson et al., 2004) and active under relatively mild conditions (Domínguez de María, 2010). Nevertheless, as chemical catalysts, they are able to withstand high temperatures and remain active under strongly basic or acidic conditions as well. Some of these claims, however, might be somewhat too optimistic. As studies show, in many cases high catalyst concentrations and elevated temperature are necessary for such catalysts to be efficient (M. V. Tupa et al., 2015). Another considerable drawback of such compounds is that
their application for reactive processing purposes is questionable. Due to their acidic nature, besides catalyzing esterification and polymerization reactions, they might also facilitate the hydrolysis of certain polymeric components, in particular polyesters and polyamides.
6. Evaluation of the efficiency of compatibilization

6.1 Rheology

The viscoelastic behavior of polymer blends or composites plays a crucial role in the optimization of processing conditions as well as the development of phase morphology and macroscopic properties. Depending on the processing and/or testing conditions, the viscosity of heterogeneous polymeric materials in the melt state can deviate either in a negative or positive direction from the additive rule, this is, the logarithmic combination of the viscosities of its respective components. In general, a negative deviation indicates weak interfacial interactions, while the opposite behavior can be observed in the case of strong interactions. Thus, an increase in viscosity due to the addition of a compatibilizer suggests that the additive exerts interfacial activity, a prerequisite for successful compatibilization. Although discussing the complex relation between compatibilization and rheological behavior exceeds the scope of this paper, this topic is examined in detail in the excellent review of Koning et al. (Koning et al., 1998).

Plant polysaccharides and most synthetic biopolymers are thermodynamically dissimilar in nature, and hence are incompatible unless a compatibilizer is used (Maliger, McGlashan, Halley, & Matthew, 2006). This latter is often added in the melt state, considerably affecting the rheological properties of the blend. Although many studies report the effect of compatibilizers on blend morphology and mechanical properties, much less attention has been paid to their effect on rheological properties (Démé, Peuvrel-Disdier, & Vergnes, 2014).

As Van Puyvelde et al. (Van Hemelrijck, Van Puyvelde, & Moldenaers, 2006; Van Puyvelde, Velankar, & Moldenaers, 2001) point out, the presence of surface-active copolymers as compatibilizers significantly affect the rheological characteristics of blends. Nevertheless, rheological characterization is seldom considered for the determination of compatibilization efficiency. This is largely due to the complex nature of rheological processes that make the prediction of macroscopic properties challenging. Nevertheless, improved compatibility has been reported for modified polysaccharide blends based on the increased complex viscosities of the blends (F Xie, Yu, Liu, & Dean, 2006; Fengwei Xie et al., 2007; J. Xu & Finkenstadt, 2013). One should consider
such claims with caution, since the viscosity and rheological behavior of polysaccharide blends depend on numerous factors besides compatibilization, including plasticizer content, changes in molar mass due to polymerization or degradation caused by the compatibilizer (Li & Huneault, 2011) or residual humidity (Mittal, Akhtar, & Matsko, 2015), and even the order of mixing the components (Ali Nezamzadeh, Ahmadi, & Afshari Taromi, 2017).

### 6.2 Morphology

The mixing of miscible polymers results in a homogeneous, single-phase system, the properties of which largely depend on those of the components and the volumetric ratio thereof. In immiscible blends, on the other hand, it is commonly accepted and experimentally confirmed that the size and distribution of the dispersed particles are the result of a competitive process between breakup and coalescence phenomena. Interfacial interactions, the shear rate of mixing, as well as the viscosity ratio of the blend components are all key parameters determining the degree of dispersion (Van Hemelrijk et al., 2006; Van Puyvelde et al., 2001). Heterogeneous blends are labeled as compatible in case their property profile fits the requirement of a certain application; in general, strong adhesion between the respective phases at the interface is necessary to achieve this. As discussed earlier, interfacial interactions can be improved by the addition or in-situ formation of compatibilizers that also substantially affect the morphology of the blends, resulting in reduced average particle size of the dispersed phase (see Fig. 8a and b) as well as improved mechanical properties (Huneault & Li, 2007; Imre & Pukánszky, 2013; Martins & Santana, 2016). This latter can be a consequence of both/either stronger interfacial interactions and/or the increased surface area of the interface due to morphological changes. One should keep in mind, however, that the purpose of compatibilization is never the conversion of immiscible blends into fully miscible ones, but the proper control of blend morphology and the enhancement of interfacial adhesion in order to tailor mechanical properties.

In most cases, the major component of the blend forms the continuous phase, whereas the minor component is the dispersed phase (Shujun et al., 2005). Depending on the volume fraction of the blend components, phase inversion takes at a certain composition at which the two phases switch their functions (Steinmann, Gronski, & Friedrich, 2001). This occurs when both polymers are
present in approximately equal amounts or at high concentrations of the minor phase (Schwach & Avérous, 2004). A wide range of different morphologies can be obtained by melt mixing, such as spherical, lamellar, fibrillar, and even co-continuous (Rodriguez-Gonzalez, Ramsay, & Favis, 2003; Steinmann et al., 2001). Co-continuous microstructures are distinguished by the mutual interpenetration of the phases (Galloway & Macosko, 2004). This morphology is particularly interesting because both components can contribute fully to the properties of the blend, resulting in a synergistic improvement of the final properties.

The mechanical properties of heterogeneous polymeric materials are strongly related to their morphology. Consequently, the structure of polysaccharide blends should be closely monitored in order to determine the effect of compatibilization and tailor mechanical performance. Zhang and Sun (J.-F. Zhang & Sun, 2004) and Jang et al. (Jang et al., 2007) both studied the morphology and mechanical performance of PLA/non-plasticized starch composites in the presence or absence of MA-based reactive compatibilizers, namely MA (Jang et al., 2007; J.-F. Zhang & Sun, 2004), MA-g-TPS (Jang et al., 2007) and MA-g-PLA (J.-F. Zhang & Sun, 2004). Since the polysaccharide component is not thermoplastic, it acts as a filler in the heterogeneous compositions, thus its average particle size does not change noticeably during processing. Nevertheless, one can still observe the effect of compatibilization based on the morphology of the materials.
The effect of reactive compatibilization on the morphology of thermoplastic and granular starch-based materials; PLA/TPS blends (43 wt% starch): a) no compatibilization; b) coupling the phases with MA-grafted PLA (Huneault & Li, 2007); PLA/starch composites (30 wt% starch): c) without compatibilizer, d) in presence of 3 phr of MA and e) 15phr of MA-grafted TPS (Jang et al., 2007).

These studies suggest that MA is an efficient compatibilizer both applied as an in-situ reactive agent (Jang et al., 2007; J.-F. Zhang & Sun, 2004), and grafted onto a PLA chain (J.-F. Zhang & Sun, 2004). MA-g-TPS, on the other hand is not as effective for PLA/starch blend systems (Jang et al., 2007). While sharp edges and large cavities can be observed around the starch granules in the unmodified composites (Fig. 8c), the SEM micrograph taken on the fracture surface of MA-compatibilized indicate stronger interfacial adhesion (Fig. 8d). The morphology of the samples prepared with MA-g-TPS strongly depend on the compatibilizer content: the interface between starch and the biopolymer matrix still has some cavities at rather low MA-g-TPS concentrations, while increasing copolymer contents (15 parts per hundred rubber (phr), Fig. 8e) result in a morphology similar to that of MA-compatibilized blends. The efficiency of MA as a compatibilizer might be in part explained by its plasticizing effect: as discussed by Wang et al. (H. Wang, Sun, & Seib, 2002), good wetting at interface is needed to achieve strong adhesion. Thus, reducing the
surface tension of starch due to the absorption of MA, and the lower viscosity of the PLA phase due to its plasticizing effect might be beneficial.

### 6.3 Mechanical properties

The effect of compatibilization is often reported based on morphological analysis (Philippe Dubois & Narayan, 2003; Jang et al., 2007) without discussing mechanical properties. This is from our standpoint insufficient, since the improvement of the mechanical properties is often the most common goal of such modification techniques. Another common claim is to report improved compatibility based on increased Young’s modulus (Hwang et al., 2013). Compatibilization most commonly aims to improve interfacial adhesion between the respective components. However, modulus, or stiffness, is determined at very low deformations, under which conditions the phases do not separate at the interface. Accordingly, this characteristic does not provide sufficient information on the strength of interfacial adhesion. The parameters that determine the stiffness of a heterogeneous polymeric material are the properties and volumetric ratio of its constituents, and the structure and morphology of the blend. Since compatibilization changes the composition of the material and often results in structural changes (e.g. reduced particle size of the dispersed phase), it can affect stiffness as well. This correlation, though, is hardly direct, and at the same time it is rather complex. Side-reactions, plasticization or crystallization due to the addition of a compatibilizer also have a similar effect. Consequently, the Young’s modulus of a polymer blend or composite is not a proper indicator of compatibility.
Fig. 9 Mechanical property profile of polysaccharide blends and composites with ( ) and without ( ) compatibilization: a) granular starch in PCL, PCL-g-starch compatibilizer (Philippe Dubois & Narayan, 2003), b) wood fibers in plasticized PLA, MDI compatibilizer (Adriana Gregorova, Sedlarik, Pastorek, Jachandra, & Stelzer, 2011), c) TPS in PLA, MDI compatibilizer (Schwach et al., 2008), d) almond shell fibers in PLA, MA-g-linseed oil compatibilizer (Quiles-Carrillo et al., 2018), e) TPS in PLA, MA-g-PLA compatibilizer (Detyothin et al., 2015) and f) cellulose microfibers in PCL, MAGMA-g-PCL compatibilizer (Haque, Errico, Gentile, Avella, & Pracella, 2012).
A direct consequence of successful compatibilization is the enhanced tensile strength of the blend or composite in question. Consequently, numerous studies (Arbelaiz et al., 2006; Avella et al., 2000; Detyothin et al., 2015; Philippe Dubois & Narayan, 2003; A. Gregorova, Hrabalova, Wimmer, Saake, & Altaner, 2009; Adriana Gregorova et al., 2011; Haque et al., 2012; Huneault & Li, 2007; Jariyasakoolroj & Chirachanchai, 2014; Karagoz & Ozkoc, 2013; Li & Huneault, 2011; Lönnberg et al., 2011; Muthuraj et al., 2017; Quiles-Carrillo et al., 2018; Raghu et al., 2018; Schwach et al., 2008; C.-S. Wu, 2003) consider this characteristic when evaluating the efficiency of various compatibilization strategies. To get a more complete picture on the effect of compatibilization, however, it is worth investigating the mechanical property profile of a material as a whole, including tensile strength, elongation-at-break as well as Young’s modulus. In Fig. 14 we present such property profiles of starch- (left column in blue) and lignocellulose-based (right column in green) blends and composites before ( ) and after compatibilization ( ). The relative values listed in the diagrams reflect the change of each mechanical characteristic compared to the non-compatibilized material (100 %).

The first three examples in Fig. 9a, b, and c show a rather similar increase in both modulus and strength accompanied by a slight decrease of deformability, indicating that all these materials became more rigid as a result of reactive compatibilization. As discussed above, increased modulus is often related to phenomena not directly related to increased interfacial adhesion which is the main purpose of such modifications. This seems to be the case here as well. In Fig. 9a PCL chains are grafted to granular starch by ROP to improve the properties of PCL/starch blends. However, the relatively short grafted chains have a tendency to crystallize, leading to the observed change in mechanical characteristics. Detyothin et al. (Detyothin et al., 2015) also point out that molar mass of the compatibilizer or that of the macromolecules forming during reactive compatibilization can be a significant factor limiting the efficiency of such modifications. Despite the large number of studies investigating MA-grafted polymers for the compatibilization of polysaccharide-based blends and composites, the molar mass of the reactive polymer is seldom considered, aside from a few exceptions (Mani, Bhattacharya, & Tang, 1999). Such compatibilizers are typically synthesized by reactive extrusion using peroxide initiators. According to Detyothin et al. (Detyothin et al., 2015), the molar mass of MA-g-PLA, and therefore its intrinsic viscosity, decreases gradually as a function of grafting degree due to chain scission reactions,
which phenomenon also affects the macroscopic properties of the materials compatibilized in this manner.

The reason for the similar mechanical behavior presented in Fig. 9b and c, showing the property profile of wood fiber-reinforced plasticized PLA, and PLA/TPS blends, respectively, is somewhat different. The compatibilizer in both cases is an isocyanate, MDI. This latter reacts with any active hydrogen-containing groups in the reaction mixture, such as the -OH moieties of cellulose, starch, and PLA, coupling the phases in order to improve interfacial adhesion. Nevertheless, it also reacts with the respective plasticizers (poly(ethylene glycol) in PLA, and glycerol in TPS) forming polyurethanes and thus increasing the overall stiffness of these heterogeneous materials.

Fig. 9d, e and f, on the other hand, show the effect of successful compatibilization, resulting in both enhanced strength and deformability, while modulus remains largely unaffected in each case. The observed tendencies are rather similar despite the different modification techniques, matrices and dispersed phases. A typical example for the compatibilization of TPS-based blends is the introduction of MA-grafted polymers synthesized in a separate step (Detyothin et al., 2015; Huneault & Li, 2007) or in-situ during reactive extrusion (N. Wang et al., 2007). Moderately enhanced mechanical performance compared to the unmodified blend was reported in such cases, as it can be observed in Fig. 9e, due to stronger interfacial adhesion and a more homogeneously dispersed morphology. The increase in strength, however, seems to be much more pronounced in lignocellulose-based composites (Fig. 9d and f). One reason for this might be the different compatibilization approach applied in these cases. MA-g-PLA (Fig. 9e) is essentially assumed to react with one phase (TPS), while its polyester chain promotes stress transfer through entanglements by mixing with the matrix polymer. Unlike maleated PLA, MA-g-linseed oil (Fig. 9d) and MA/glycidyl methacrylate-grafted PLA (MAGMA-PCL, Fig. 9f) contain multiple reactive sites, being able to form covalent bonds with both phases. Furthermore, the presence of glycerol as a plasticizer in the TPS/PLA blend possibly leads to side-reactions, further limiting the effectiveness of compatibilization.
As Fig. 10 suggests, there is a general tendency, according to which the mechanical performance of polysaccharide-based composites (−, ···) can be enhanced to a far greater extent than that of thermoplastic starch blends (−, ···). In the figure we collected the relative tensile strength of various polysaccharide-based heterogeneous materials compared to the respective non-modified system. From each study reviewed (Arbelaitz et al., 2006; Avella et al., 2000; Detyothin et al., 2015; Philippe Dubois & Narayan, 2003; A. Gregorova et al., 2009; Adriana Gregorova et al., 2011; Haque et al., 2012; Huneault & Li, 2007; Jariyasakoolroj & Chirachanchai, 2014; Karagoz & Ozkoc, 2013; Li & Huneault, 2011; Lönntberg et al., 2011; Muthuraj et al., 2017; Quiles-Carrillo et al., 2018; Raghu et al., 2018; Schwach et al., 2008; C.-S. Wu, 2003), we only included the highest values at a certain polysaccharide content, regardless of the type and amount of compatibilizer used. Most available data have been published on compatibilization using reactive polymers (···), followed by small molecules (−, ···), while modification of the polysaccharide fraction by ROP (−, ···) is relatively rarely considered. The results seem to justify this tendency: the former two techniques tend to provide better results, especially if one takes into consideration their relative simplicity. As noted earlier, compatibilization tend to affect the strength of composites more than that of blends, and this difference only increases as a function of polysaccharide content, as the highlighted curves illustrate. The higher the filler content, the higher the tendency of fillers in a composite material to aggregate, thereby deteriorating mechanical properties. Compatibilization can help resolve this issue, resulting in a considerable increase of tensile strength over the unmodified material. In blends such as TPS/PLA, this phenomenon does not play a role. Moreover, strong interfacial interactions due to compatibilization can lead to the break-up of starch granules during processing, leading to smaller dispersed particle size, i.e. more favorable morphology (Starch/PCL). This is not likely to take place in a lignocellulose-reinforced composite (Flax/PCL), due to the much higher inherent strength of the dispersed fibers.

This latter characteristic, however, might limit the performance of plant polysaccharide-based compositions in some cases, as Faludi et al. (Faludi et al., 2014) point out in an elaborate study performed on PLA/lignocellulose composites. As the authors conclude, contrarily to most claims
published in the literature, interfacial adhesion between filler and matrix is rather strong in such composites. Therefore, the dominating micromechanical deformation mechanism is the fracture of the dispersed fibers, thus determining also the macroscopic strength such heterogeneous materials. Consequently, enhancing the intrinsic strength of the dispersed phase might be the way to further improve the mechanical properties of polysaccharide-based blends and composites.

The above examples highlight that evaluating the efficiency of compatibilization solely based on mechanical properties is not always sufficient. Although tensile strength is a characteristic of significant importance from a practical point of view, this one value does not reveal the reasons behind the success or failure of a given compatibilization strategy. In order to tailor the properties of polysaccharide blends or composites, detailed analysis of their chemical structure, morphology and mechanical behavior, including micromechanical deformation processes, need to be performed, thus the factors limiting their performance can be identified.
Fig. 10 The relative strength and of compatibilized (blue) starch- and (green) lignocellulose-based \((\ldots)\) blends and \((\ldots)\) composites; compatibilization technique: \((\ldots)\) grafting-to, \((\ldots)\) coupling with small molecules, \((\ldots)\) coupling with reactive polymers; the relative values indicate the change in mechanical characteristics compared to the non-compatibilized material with a similar composition (Arbeloaiz et al., 2006; Avella et al., 2000; Detyothin et al., 2015; Philippe Dubois & Narayan, 2003; A. Gregorova et al., 2009; Adriana Gregorova et al., 2011; Haque et al., 2012; Huneault & Li, 2007; Jariyasakoolroj & Chirachanchai, 2014; Karagoz & Ozkoc, 2013; Li & Huneault, 2011; Lönnberg et al., 2011; Muthuraj et al., 2017; Quiles-Carrillo et al., 2018; Raghu et al., 2018; Schwach et al., 2008; C.-S. Wu, 2003).
4. Conclusions

Due to their unique properties as well as environmental concerns, plant polysaccharides have been in the focus of research for many decades. Their application for materials purposes, however, is seldom feasible without modification. Thus, polysaccharides are generally used in a derivatized form and/or in combination with other polymers, requiring the compatibilization of such blends and composites. Throughout the paper, reactive compatibilization techniques have been considered due to their efficiency and feasibility in polysaccharide-based compositions. It is difficult to draw general conclusions regarding the most successful strategies currently available. Nonetheless, one can conclude with some certainty that coupling reactions involving either reactive polymers or low molar mass reagents show much promise due to their efficiency and versatility. The substitution of polysaccharide hydroxyls by either monofunctional compounds or longer side-chains through the ROP of cyclic monomers, on the other hand, seems to be more suitable for tailoring the intrinsic properties of polysaccharide substrates rather than for compatibilization purposes. Similarly to other efforts targeting the reactive modification of polymers, melt processing techniques, and most importantly reactive extrusion continue to gain attraction for the compatibilization of polysaccharide blends and composites as well, due to being highly cost-effective, versatile and easily upscalable. Finally, it should be emphasized that the efficiency of compatibilization techniques can be evaluated based on numerous indicators such as processability, morphology and mechanical performance. Nevertheless, the development of successful strategies requires the detailed analysis of the chemical structure, morphology and mechanical behavior of these heterogeneous systems.

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