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6

Polymeric Blends with Biopolymers

Hero Jan Heeres, Frank van Mastrigt, and Francesco Picchioni

6.1

Introduction

The future scarcity of oil sources and the current strong awareness of sustainability issues in society are two of the main drivers behind the interest, at both academic and industrial levels, in the use of biopolymers (defined here as “polymers that involve living organisms in their synthesis process”) in a variety of consumer products [1]. Biopolymers are in general characterized by relatively low costs and a large spread in geographic availability. However, they usually display (when taken alone) rather unsatisfactory mechanical properties (e.g., tensile properties in thermoplastic starch) and the variability of the feed on a (macro)molecular level (e.g., different amino acid compositions in proteins) is also a serious issue. In this respect, blending of biopolymers with commercial ones (e.g., polyesters) is the most common route for the production of bioplastics. Such blending processes are often aimed at overcoming the disadvantages outlined above while at the same time exploiting production technologies (e.g., extrusion) that are well established in the plastic industry [2].

Possible markets for bioplastics [3], as envisioned by the European Commission in 1998, include mainly packaging applications and the use as plastic bags. The total production levels were estimated to be 1 145 000 ton in the first decade of the new century. Almost 15 years later, these expectations are fulfilled and bioplastics have found applications in the foreseen application areas. In addition, the total volume is even considerably higher (1 145 000 ton/year as predicted in 1998 versus 1 500 000 ton/year estimated in 2009) [4]. By looking at these numbers, one might be tempted to consider the bioplastic industry a large one indeed. However, when comparing the bioplastic volumes with those of fossil-derived plastics (more than 30 000 000 ton/year in Europe only), it is clear that the bioplastics industry is in reality only in a state of infancy [1]. This is probably a consequence of the fact that many scientific/technological issues concerning the use of biopolymers in bioplastics have been only partially addressed and solved. Among these, the selection of a given biopolymer for a certain application is still a major issue in the design of new chemical products. Blends of commercial polymers with alginat

[5], starch [6], gluten [7], carboxymethyl cellulose [8–10], soya proteins [11,12], wood flour [13,14], and natural fibers [15,16] have been extensively studied and reported in the open literature. Generally, a plasticizer must be added to the biopolymer to be able to process it using conventional processing equipments such as extruders [17]. However, in some cases biopolymers have been used as simple solid fillers [18–20]. The situation is further complicated by the fact that within every class of biopolymers (e.g., soya proteins) further variations in the (macro)molecular structure as a function of the (botanical) origin (and in some cases even of the harvested region) are possible.

In this chapter, we will not consider all possible blends of biopolymers and synthetic plastics but focus on starch (St) and chitosan (Cht). These two materials were selected as they have already a broad application range, are produced in large volumes, and are considered as good examples of the advantages and disadvantages associated with the use of biopolymers in bioplastic materials.

Starch is considered one of the most promising candidates for use in bioplastics because of its wide availability (although from different sources) and relatively low cost. The monomeric unit of this biopolymer consists of D-glucose, which is arranged in a simple linear (amylose) or branched fashion (amylopectin) [21]. Starch is generally a semicrystalline polymer where crystallinity is the result of organization of amylopectin in the granules while, amylose constitutes the main part of the amorphous phase. Starches from different sources are in principle characterized by a different molecular weight as well as amylopectin/amylose ratio.

The large availability of starch makes this material a popular choice for a wide variety of products [22,23]. Moreover, besides commercial polymers, starch can be blended easily with other biopolymers such as chitosan [24,25], gluten [26,27], and lignin derivatives [28]. In general, starch blends and composites have found applications for packaging purposes, for foam production [29–34], and for tissue engineering [35,36] and biomedical applications in general [37–42]. In many cases, the main objective of starch addition to other polymers is the necessity to reduce feedstock costs while at the same time preserving/conferring a biodegradable character to the end product [43–47]. Furthermore, in some cases St is simply added to other polymeric systems as a filler [48–54].

Besides simple melt mixing processes, other routes to starch blends have been explored. Blending in solution is a widely studied possibility [55–59]; however, the use of less environment-friendly solvents is a serious drawback. *In situ* blends can also be prepared by chemically grafting a polymeric chain on the starch [60–62] or vice versa [63]. However, also in this case, the use of organic solvents renders the process less attractive from an industrial point of view and actually is only convenient when the product has a high-value specialty type of application, for example, in the biomedical industry [64].

Starch is, generally speaking, a hydrophilic polymer in which hydrogen bonding is mainly responsible for the intermacromolecular interactions. The latter must be overcome to render starch processable, usually by addition of a plasticizer, for example, glycerol or other polyols [65]. The same intermacromolecular interactions are actually also responsible for the low miscibility of starch with many commercial polymers, for

example, polyesters and hydrophobic ones in general [66,67]. This incompatibility between starch and other polymers may be overcome by two strategies: either by the addition of a compatibilizer [68] or by the use of a (chemically) modified starch [69]. In both cases, the employed strategy has often consequences for the biodegradability of the blends. The system is further complicated when considering that often additional components are employed to the blends to fine-tune the mechanical properties. Such component could be another (commercial) polymer [70–73] or even a filler in the form of fibers, for example, natural ones such as cotton [74–76]. The influence of the additional components on the biodegradability should be carefully assessed [75,77]. This property is determined using standardized procedures involving assessment of the mechanical properties of the blends as a function of time [78,79] upon exposure to typical degradation conditions, for example, soil burial. In this chapter, we will limit the discussion to the synthesis and mechanical/rheological properties of starch- and chitosan-based blends and not to biodegradability as this topic has been recently reviewed [80].

From the above discussion, it is clear that starch may indeed represent a paradigmatic example for the scientific/technological issues relevant to biopolymer blends. The incompatibility at molecular level (thus the necessity of modification or compatibilization), the variability in the macromolecular structure (linear versus branched chains), the necessity to use a plasticizer (e.g., glycerol), and sensitivity to moisture and temperature are all factors that render starch an excellent representative of a biopolymer. However, due to the lack of variation in the chemical structure at monomer level in starch (the only functional groups being the hydroxyl ones), we decided to also include chitosan-based blends in this chapter. Chitosan is the second most abundant biopolymer in nature consisting of repeating 1,4-linked 2-amino-2-deoxy- β -D-glucan units [81]. As such, it is the only naturally occurring carbohydrate source with an amine functionality.

As seen for starch, chitosan needs to be used in combination with a plasticizer for processability [82] and is mostly incompatible with commercial polymers [83]. It finds application, in its pure form as well as in blends with other biopolymers (such as St, cellulose and derivatives, proteins, etc.), mainly in the food (packaging) industry [84–93]. It is very similar to St and it is not surprising if one takes into account the very similar chemical structure of these two polymers, which differ only by the presence on the C₂ of an –OH group for starch and an –NH₂ group for chitosan. Such slight variation in the chemical structure of the monomeric unit is, however, responsible for relevant differences in properties. Indeed, the presence of an easily ionizable (e.g., by protonation) amino group (responsible also for the antibacterial activity of this material [94,95]) along the backbone renders Cht-based blends particularly interesting for application in biomedical products (e.g., in tissue engineering and drug delivery) [96–105], in conductive materials [81,95,106,107], and in metal complexation resins [108–113].

In Sections 6.2 and 6.3, we will discuss starch- and chitosan-based blends by critically reviewing the scientific literature on the subject published in the past 15 years. In Section 6.4, we will provide a short summary of the more general concepts and a short outlook to future possibilities for both biopolymers.

6.2 Starch-Based Blends

In this section, we start by providing an overview of the most studied starch-based blends with synthetic polymers. The choice of the polymer to be blended with the starch and the physical form (e.g., as solid or as thermoplastic (TPS) material) and structural properties (e.g., amylose intake) of the latter are then discussed. Finally, general trends in terms of mechanical behavior for uncompatibilized and compatibilized blends are presented.

Blends of starch with a variety of polymeric materials have been widely studied and reported in the open literature. Figures 6.1 and 6.2 report the chemical

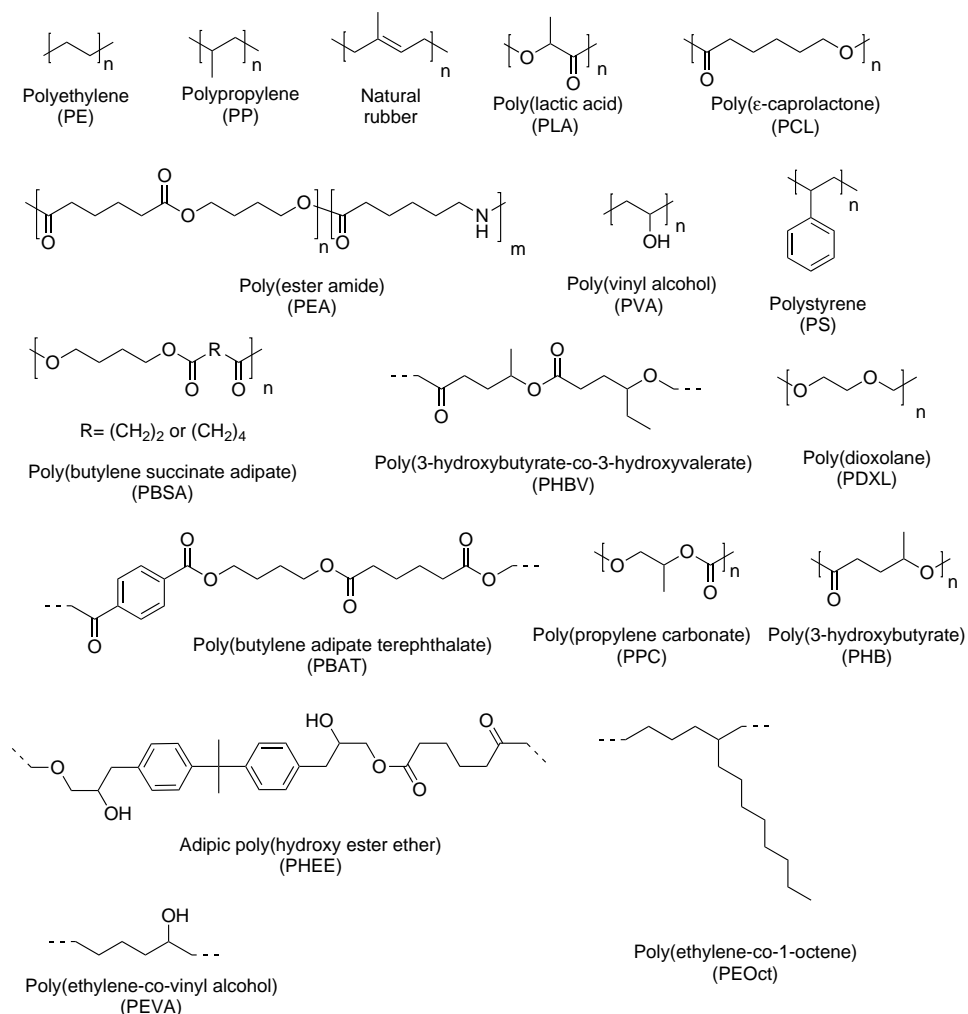


Figure 6.1 Chemical structures and full names of the most common polymers blended with starch.

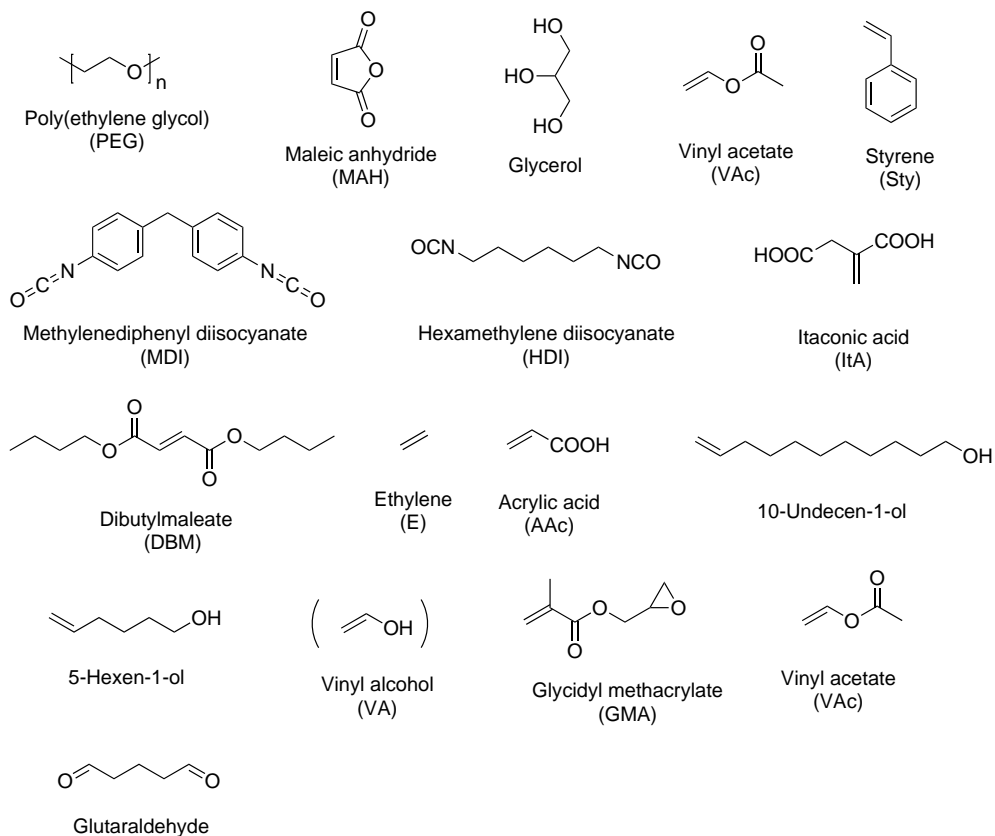


Figure 6.2 Chemical structures of the most common monomeric units and low molecular weight compounds used as additives for St-based blends.

structures and full names of the most important polymers and additives used in St-based blends.

An overview of the most popular starch-based blends together with the type of starch, its physical form (i.e., as solid or as thermoplastic material, with the corresponding plasticizer), and eventually the compatibilizer is reported in Table 6.1.

6.2.1

Polymer Selection for Starch Blending

The choice of the polymer to be blended with starch depends on many factors: mechanical and thermal behavior, biodegradability, and compatibility. By taking a general look at the most popular polymers (Table 6.1), it is quite difficult to define a generic framework for polymer selection. A suitable methodology may be based on

Table 6.1 Overview of St blends with synthetic polymers.

Polymer	Starch	Additives	Reference
LDPE	Maize (S)	PEG	[114]
LDPE	(Modified) sago (S)	—	[115]
LDPE	Sago (TPS, glycerol)	PE-g-MAH	[116]
LDPE	(Modified) potato (TPS, glycerol)	—	[117]
LDPE	Rice and potato (TPS, water)	—	[118]
LDPE	Corn (TPS, glycerol)	PE-g-MAH	[119]
LDPE	Corn (S)	PE-g-MAH	[120]
LDPE	Not specified	PE-co-10-undecen-1-ol, PE-co-5-hexen-1-ol	[121]
LDPE	Tapioca (TPS, glycerol, and water)	PE-g-DBM	[122]
LDPE	Potato (S)	PE-g-MAH	[123]
LDPE	Tapioca (TPS, glycerol)	PE-g-MAH, PE-g-AAc	[124]
LDPE	Corn (S)	PE-g-MAH	[125]
LDPE	Corn (S)	PE-g-(sty-co-MAH)	[126]
LDPE	Corn (S)	PE-g-GMA	[127]
LDPE	Wheat (S) and (TPS, glycerol)	PEVAc	[128]
LDPE	Corn (TPS, glycerol)	—	[129]
LDPE	Not specified	—	[130]
LDPE	Banana (S)	PE-g-MAH	[131]
LDPE	Wheat (TPS, water, and glycerol)	—	[132]
LDPE	Tapioca (TPS, water, and glycerol)	PEVA	[133]
LDPE	Corn (TPS, glycerol)	—	[129]
LDPE	Corn and rice (S)	—	[134]
LDPE	Rice (TPS, glycerol)	PE-g-MAH	[135]
LDPE	Corn (S)	PEAAc	[136]
HDPE	Tapioca (TPS, water, and glycerol)	HDPE-g-MAH	[137]
PE	Corn (TPS, glycerol)	PE-g-ItA	[138]
PEOct	Corn (S)	PEOct-g-MAH	[139]
PEOct	Corn (S)	PEOct-g-AAc	[140]
PLA, PHEE	Corn (S)	—	[141]
PP-g-MAH	Corn (TPS, glycerol)	—	[142]
PLA	Wheat (S)	MDI	[143]
PLA	Corn (S)	St-g-PLA	[144]
PLA	Corn (TPS, glycerol)	PLA-g-MAH	[145]
PLA	Corn (S)	—	[146]
PLA	Corn (S)	PVA	[147]
PLA	Wheat (TPS, glycerol, and sorbitol)	PLA-g-MAH	[148]
PLA	Corn (TPS, glycerol)	—	[149]
PLA	Maize (S, amylopectin only)	PEVA	[150]
PLA	Corn (TPS, glycerol)	—	[151]
PLA	Corn and tapioca (TPS, water, and glycerol)	—	[152]
PLA	Wheat (TPS, glycerol)	PCL	[153]
PLA	Wheat (TPS, glycerol)	Several compatibilizers	[154]
PLA	Wheat	MDI	[155]

PLA	Corn (S)	PLA-g-AAc	[156]
PLA	Corn (S)	PLA-g-AAc	[157]
PHB	Potato (water solution)	St-g-VAc	[158]
PHB	Corn (S)	—	[159]
PHB	Maize (TPS, water, and glycerol)	—	[160]
PHBV	Not specified	—	[161]
PHBV	Corn (TPS, water, and glycerol)	—	[162]
PHBV	Maize (S)	—	[163]
PHBV	Corn (TPS, acetyl tributyl citrate)	St-g-GMA	[164]
PEA	Wheat (TPS, glycerol)	—	[165]
PCL	Corn	HDI	[166]
PCL	Wheat and potato (TPS, glycerol)	—	[167]
PCL	Starch formate	—	[168]
PCL	Corn (S)	St-g-PCL	[169]
PCL	Sago (S) and (TPS, water, and glycerol)	—	[170]
PCL	Corn (S) and (TPS, glycerol)	—	[171]
PCL	Corn (S) and (TPS, glycerol)	PEG	[172]
PCL	Corn (TPS, water)	PCL-g-AAc	[173]
PCL	Wheat (TPS, glycerol, and/or water)	PCL-g-MAH	[174]
PCL	Tapioca (S)	PDXL	[175]
PCL	Corn (S) and (TPS, glycerol)	—	[21]
PCL	Corn	—	[176]
PCL	Corn (TPS, glycerol)	—	[177]
PCL	Corn (S)	PCL-g-GMA, PCL-g-DEM	[178]
PCL	Potato (TPS, glycerol)	—	[179]
PCL	Corn (S)	PCL-g-AAc	[180]
PCL	Not specified	PCL-g-MAH	[181]
PCL	Corn (S)	—	[182]
PP	Amylose	Modified amylose	[183]
NR	Corn (TPS, glycerol)	—	[184]
NR	Cassava (S)	NR-g-MAH	[185]
PS	Not specified	St-g-PS	[186]
PBS	Corn (TPS, glycerol)	—	[187]
PBSA	High-amylose starch	—	[188]
PBSA	Corn (S)	—	[189]
PEVA	Acetylated tapioca (TPS, glycerol)	—	[190]
PEVA	Corn (S)	—	[191]
PVA	Sago (S)	—	[192]
PVA	Corn (TPS, glycerol)	—	[193]
PVA	Potato	Glutaraldehyde	[194]
PVA	Cassava	—	[195]
PPC	Corn (S)	—	[196]
PPC	Corn (S)	—	[197]
PDXL	Corn (S)	—	[198]

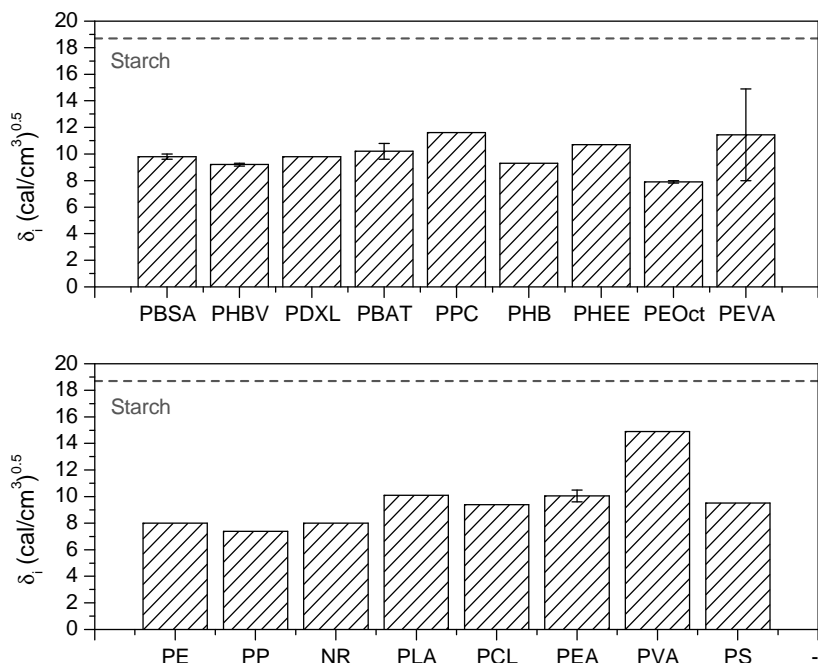


Figure 6.3 Solubility parameters for all polymeric materials in Table 6.1. Error bars take into account, for copolymers, changes in the chemical composition.

differences in solubility parameters between starch and the second polymer in the blend. The solubility parameter (δ), calculated using a group contribution approach [199], for all reported systems is given in Figure 6.3.

For all polymers, the δ_{polymer} is smaller than δ_{starch} , thus clearly indicating that the main idea behind blending is actually to attenuate the hydrophilic character of the starch component. However, in some cases (e.g., LDPE or PS), the selected polymer is not biologically degradable. This is not necessarily a major issue since, even when using commercial polymers that are in principle poorly biodegradable, the starch component is easily degraded and this also has a positive effect on the subsequent degradation rate of the second polymer [200]. In some cases, the final blend needs to be biodegradable rapidly and this puts constraints on the choice of the second polymer. In general terms, the higher the amount of St in the blend, the faster the degradation process [201,202].

6.2.2

Starch Structure

The starch source is also a variable and allows tuning of the properties of the starch-polymer blend. The amylose/amylopectin ratio, the moisture content, and the kind

and amount of plasticizer used are known to affect the mechanical behavior of the blends.

The botanical origin of the starch, resulting in a.o. differences in the amylose/amylopectin ratio, has a strong influence on the properties of pure TPS [203]. This is also, although slightly, reflected in St-based blends with several different polyesters [204]. Inspection of blend morphology indicates that the starch phase becomes more finely dispersed as the amylopectin content in the blend increases. This leads to changes in tensile strengths, though a clear trend is absent. The same authors, working at a fixed starch intake of 70 wt% in blends with polyolefins, observed that the morphology is a clear function of the amylopectin/amylose ratio. This is not surprising if one takes into account the fact that the same ratio results generally in different viscosities of the St phase. Because of differences in the morphology, one would expect related differences in the mechanical behavior for blends containing starch at different amylose intakes. This has been only partially confirmed [205] and it is still a point of debate in the open literature.

The physical nature of the St phase (either as solid or as TPS) also has a clear influence on the final properties and rheological behavior [21]. Virgin starch gives plastic behavior in blends with PCL, while gelatinized starch results in brittle behavior with relatively high stress [137]. Ishiaku *et al.* [170] studied PCL blends with sago starch and found that the ultimate strength and elongation at break decrease with the starch intake; however, TPS performs better than normal starch. The overall inferior performance of TPS is explained by the formation of water (and thus voids after evaporation) in the molding stage. This does, however, not constitute a general concept since in other cases no differences are observed between solid St and TPS [128]. It must be stressed here that these discrepancies are more rule than exception, thus strongly suggesting that the influence of the plasticizer in general terms is strongly dependent on the system under examination.

The amount of water initially present in the starch source seems to have little effect on the final properties for blends with PLA, the only exception being the water uptake of the blends [146]. This has been confirmed by other researchers [206–209] and in particular by a systematic study on blends of sago starch with PCL [210]. Here, St is used in various states: native, predried, as TPS (20 wt% glycerol), and granules obtained by “powderizing” TPS. Elongation at break of the blends comprising of native and thermoplastic starches decreases almost linearly with the St volume fraction, whereas nonlinear dependences were observed for predried and thermoplastic starch granules (Figure 6.4). Except for blends containing native starch, the tensile strength was found to decrease linearly with the St volume fraction. One may conclude that in all cases, the tensile properties decrease almost linearly with the St volume fraction up to a maximum of around 0.6.

In successive research, the authors showed that predrying of the starch has a positive effect on properties and the drop rate as function of starch intake is reduced [211].

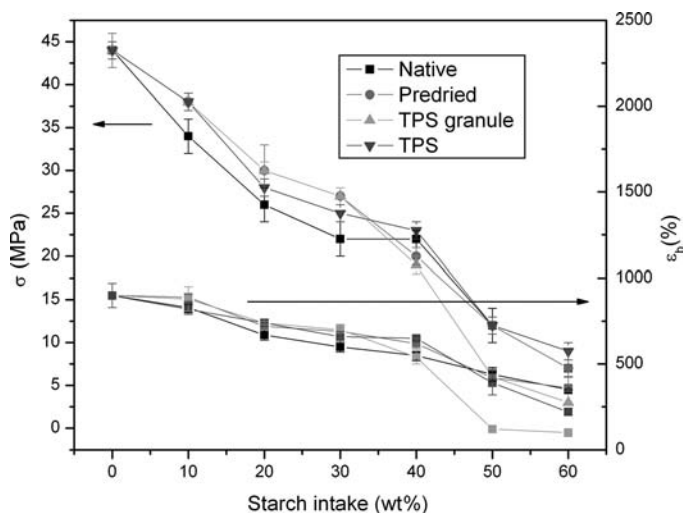


Figure 6.4 Mechanical properties versus ST intake as a function of the physical form of the St phase.

6.2.3

Uncompatibilized Blends

For blends in which St is the main component (i.e., the matrix), the addition of a second polymer (dispersed phase, for example, PEA) often results in an improvement in the mechanical properties (tensile strength, modulus, and elongation [165]). The opposite trend is generally observed when starch represents the minor component. For blends in which St is the dispersed phase, for example, with PPC [197], generally an increase in modulus [212] and a decrease in tensile strength with the St intake are observed. This is in agreement with semiempirical equations for composites with uniformly distributed (also in size) spherical particles [213]. Here, the decrease in tensile strength when the starch volume fraction (ϕ) increases can be described theoretically by

$$\sigma_C = \sigma_0(1 - 1.21\phi^{2/3}), \quad (6.1)$$

where σ_C and σ_0 are the tensile strength of the blend and the matrix, respectively, and ϕ is the volume fraction of the filler (starch in this case). For the modulus, a theoretical equation may be derived and this was shown to be a good model for the experimental trends:

$$E_C = E_0 \left[1 + \left(\frac{\phi}{1 - \phi} \right) \left(\frac{15(1 - \nu)}{8 - 10\nu} \right) \right], \quad (6.2)$$

where E_C and E_0 are the modulus of the composite and the matrix, respectively, ϕ is the volume fraction of the filler (starch in this case), and ν is the Poisson ratio for the matrix [214]. These trends clearly indicate that starch acts as rigid component in

the blends (increase in modulus, and decrease in tensile strength and elongation). This decrease in tensile strength and elongation at break (with respect to the pure components) as a function of the St intake is often perceived as a serious issue from an application point of view and hampers the use of larger amount of St in the blend without significant reductions in the mechanical properties.

It is clear that the morphology (i.e., the average particle size and particle size distribution of the minor component in the blend) and the chemical composition determine the final properties of the material. The first attempt to relate the blend morphology to the properties of the individual components has been proposed and is based on surface energy considerations [215]. For example, Biresaw and Carriere [216] reported surface energy measurements on St blends with PS, PCL, PHBV, PLA, PBAT, and PHEE. The surface energy of the solids and subsequently the interfacial adhesion was calculated. The surface tension of a liquid or solid is expressed as

$$\gamma_S^{\text{TOT}} = \gamma_S^{\text{D}} + \gamma_S^{\text{P}} = \gamma_S^{\text{D}} + 2(\gamma_S^+ \gamma_S^-), \quad (6.3)$$

where S is the solid, either starch (St) or polymer (Po), γ^{TOT} is the total surface energy, and γ^{D} is the contribution due to dispersive forces and γ^{P} due to polar ones, the latter being split into contributions for electron/H bonding donor (γ^+) and acceptor (γ^-) ability. The interfacial tension between starch and the polymer in the liquid phase ($\gamma_{\text{St/Po}}$), as determined from contact angle measurements for the individual components, is estimated by

$$\gamma_{\text{St/Po}}^{\text{TOT}} = (\sqrt{\gamma_{\text{St}}^{\text{D}}} - \sqrt{\gamma_{\text{Po}}^{\text{D}}})^2 + 2(\sqrt{\gamma_{\text{St}}^+ \gamma_{\text{St}}^-} + \sqrt{\gamma_{\text{Po}}^+ \gamma_{\text{Po}}^-} - \sqrt{\gamma_{\text{St}}^+ \gamma_{\text{Po}}^-} - \sqrt{\gamma_{\text{Po}}^+ \gamma_{\text{St}}^-}). \quad (6.4)$$

The results [216] show the absence of a clear correlation between the estimated interfacial tensions and the mechanical properties. This suggests that other factors, besides interfacial properties, also determine the mechanical behavior. Indeed, the morphology is also influenced by the processing conditions. A typical example is given for PCL/St blends. The rheological behavior of the individual components [167] as a function of the shear rate differs significantly. For instance, the viscosity of PCL follows the Carreau–Yasuda model:

$$\eta = \frac{\eta_0}{[1 + (\lambda \dot{\gamma})^a]^{(1-n)/a}}, \quad (6.5)$$

with η_0 the viscosity at zero shear rate, λ the relaxation time, $\dot{\gamma}$ the shear rate, n the pseudoplasticity index, and a the Carreau–Yasuda fitting parameter. On the other hand, the viscosity of TPS generally follows a power law model:

$$\eta = K \dot{\gamma}^{n-1}, \quad (6.6)$$

with K being the consistency index. In the above-mentioned example [167], such differences in viscosity behavior have direct consequences for the processing of the blend. Between 1 and 100 s⁻¹, the viscosity of TPS decreases with the shear rate while it is at a Newtonian plateau for PCL. As a result of the nonmiscibility and

differences in viscosities ($\eta_{\text{TPS}} \gg \eta_{\text{PCL}}$), different morphologies (i.e., different average St particle sizes) are accessible by simply controlling the shear rate inside the processing equipment.

The fact that both interfacial tension between starch and the other polymeric material and the rheological properties of both have a clear influence on the morphology of the blends (and thus on the final properties) is not surprising when taking into account the general theories for morphology development in the melt [217]. Indeed, when mixing a given polymer with TPS (taken here as example of dispersed phase), the presence of shear causes breakup of the TPS droplets, thus in principle leading to a finer dispersion of the latter in the matrix (Figure 6.5b), while coalescence of the TPS droplets leads to a higher average particle size (thus to a coarse dispersion).

The balance between these two phenomena is the governing factor for morphology formation and it usually expressed in terms of the Weber number (We):

$$We = \frac{\eta_d Gr}{\gamma}, \quad (6.7)$$

where G is the velocity gradient in the system (a function of the kind of mixing equipment used and the kind of flow), r is the droplet radius, and γ is the interfacial tension between the two liquid polymers. For a given droplet to break up, the Weber number must be higher than a critical value (We_{cr}), which is in turn a function of the kind of flow during mixing (e.g., shear or elongational) and of the viscosity ratio (Figure 6.5a) between dispersed and continuous phases (η_d/η_c). From these theoretical considerations, it is clear that both the interfacial tension between the polymers (directly affecting the We values) and the rheological behavior (affecting the We_{cr} values) must be taken into account when trying to gain a more fundamental understanding of the relationship between the blend morphology and the properties of the individual components.

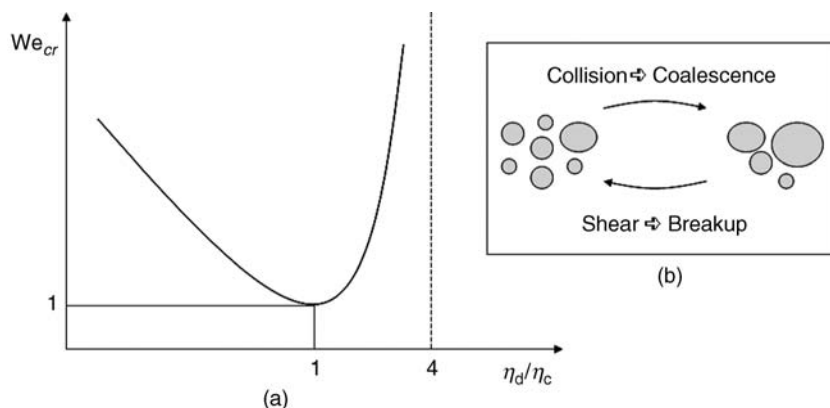


Figure 6.5 (a) Critical Weber number (We_{cr}) as a function of the viscosity ratio between dispersed phase (η_d) and continuous one (η_c) for shear flows. (b) Schematic representation of droplet breakup and coalescence during melt mixing.

6.2.4

Compatibilization

To overcome the trends in mechanical properties discussed above (namely, a decrease in tensile strength and elongation at break especially at higher St intakes in the blend), compatibilization of the blends is often perceived as a necessity. A compatibilized blend is characterized in general by a lower interfacial tension between the components (thus resulting in higher We values, see above) and also better interfacial adhesion. In this respect, two main strategies for compatibilization have been developed for starch-based blends. The first consists of starch modification with hydrophobic chains, while the second involves the use of a functionalized polymer (e.g., PE-g-MAH) to be used in combination with the virgin one (e.g., PE). In this case, the intention is to graft the starch on the compatibilizer *in situ*, that is, during processing. In both cases, the general idea is to improve the affinity of the St with the other polymer and in particular the interfacial adhesion between the St particles and the matrix.

The first strategy comprises the use of modified starch, usually with hydrophobic chains (see above) [218–223] in combination with native St. Starch can be modified before blending with hydrophobic polymers such as LDPE. In particular, the reaction with (long-chain) anhydrides (Figure 6.6) should theoretically result in improved compatibility with apolar polymers [115].

Indeed, the presence of hydrophobic chains (even for a one-carbon chain as in starch formate [168,224]) grafted on St results in general in a better compatibility [190,225] and better mechanical properties (particularly a higher modulus). Tensile strength and elongation at break still decrease with the St intake but to a lesser extent with respect to blends containing unmodified starch. It is postulated that the presence of aliphatic chains on the St increases the interfacial adhesion with the other polymer and ultimately favors the stress transfer mechanism between the two phases [115,117]. This approach has one drawback, besides the necessity of an extra processing step for the St modification, and this involves biodegradability. Modified starch displays usually a lower biodegradation rate (the effect being more relevant as the length of the grafted chains increases) with respect to the unmodified one [226].

The second strategy involves a chemical reaction between one of the two components (usually St) with a compatibilizer precursor (e.g., polymers grafted with MAH). In some special cases, the compatibilizer precursor is also generated

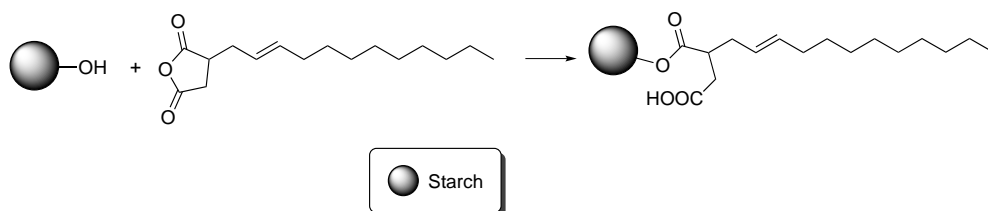


Figure 6.6 Modification of starch with dodecen-1-yl-succinic anhydride.

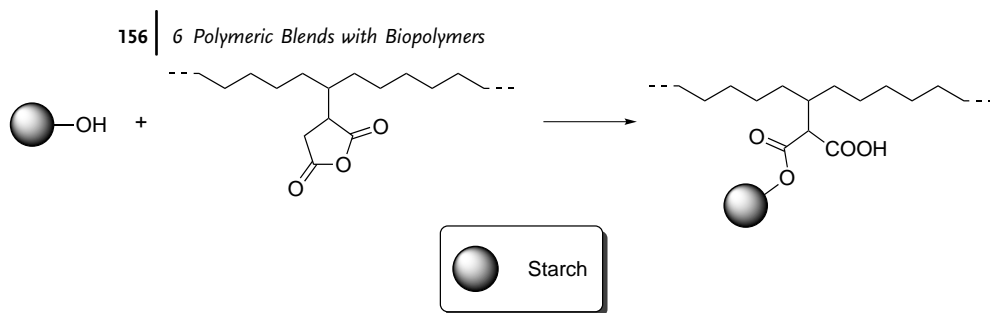


Figure 6.7 Schematic reaction between -OH groups on the surface of the ST particles (S) or droplets (TPS) and the MAH groups on PE-g-MAH (taken here as example).

in situ directly by addition of a peroxide and MAH to the St blend [227–231]. Independently of the way in which the maleated polymer is added (either directly or generated *in situ*), a chemical reaction is supposed to take place between the -OH groups on the starch and the anhydride group on the compatibilizer (Figure 6.7).

Confirmation of the occurrence of this reaction has been obtained in many studies, mainly by spectroscopic methods (e.g., FTIR) [119,232–234]. The disappearance of the peaks assigned to the anhydride (typically around 1850 , 1780 , and 1720 cm^{-1}) in FTIR spectra of the blend and the appearance of those typical of esters and acid groups (at 1730 and 1710 cm^{-1} , respectively) is often considered as proof of the reaction. This is, however, not entirely correct when using plasticized starch in the blend. Typical plasticizers for starch are polyols (e.g., glycerol and sorbitol) as well as water, that is, molecules containing -OH groups as in the starch. As a consequence, the possibility that the observed trends in the FTIR spectra are actually due to the reaction of the plasticizer with MAH may not be excluded. The occurrence of such side reaction has been demonstrated in binary blends of functionalized polymers with St. Kim *et al.* [235] studied PCL-g-GMA blends and observed a decrease in gel content (PCL-g-GMA acts as cross-linker for St) as the glycerol intake increases. The possible competition of St and the plasticizer with the reactive groups of the compatibilizer represents a very important factor and determines the properties of the ultimate blends. This was also illustrated by Taguet *et al.* [236], when studying blends of TPS (wheat, glycerol) with HDPE compatibilized by PE-g-MAH. The average particle size for uncompatibilized blends decreased with the glycerol content, while an increase with the PE-g-MAH intake at relatively high glycerol content was observed for compatibilized blends. The authors attributed the first effect to the differences in TPS viscosity as a function of the glycerol intake. The second effect is explained by the formation of two different TPS phases during mixing: a glycerol-rich one on the outside and a starch-rich one on the inside. This is governed by the spreading coefficient ($S_{\text{St/Gly}}$):

$$S_{\text{St/Gly}} = \gamma_{\text{St/HDPE}} - \gamma_{\text{Gly/HDPE}} - \gamma_{\text{St/Gly}}, \quad (6.8)$$

with $\gamma_{i/j}$ being the interfacial tension between component i and j . St and glycerol have about the same surface energy but starch has a much higher average molecular weight. Thus, it can be readily assumed that $\gamma_{\text{Gly/HDPE}}$ will be significantly smaller

than $\gamma_{St/HDPE}$ and that $\gamma_{St/Gly}$ will be very low, as typical for a partially miscible mixture. Thus, the spreading coefficient of glycerol/starch is most probably a positive number. This would lead to the spontaneous formation of a thin glycerol-rich layer during melt mixing at the TPS/polyethylene interface to reduce the overall surface free energy of the system. This layer is expected to hinder the interaction between St and PE-g-MAH, probably through reaction of the glycerol itself with the compatibilizer precursor. As a result, at relatively high glycerol content, the reaction between St and PE-g-MAH is hindered, the compatibilizer (PE-g-St) is not formed, and thus the particle size, as observed experimentally, does not decrease with respect to the uncompatibilized blend.

A critical comparison, besides empirical ones [154], of the two compatibilization strategies (see above) is very difficult, not in the last place due to the rather long and time-consuming synthetic steps needed for the preparation of well-defined compatibilizers [237,238]. Moreover, some authors preferred a combined approach to the problem, for example, by using modified starch as the main component together with a compatibilizer precursor [239–241] or the use of modified starch as the compatibilizer precursor [242]. This renders the rationalization of the observed effects very difficult to achieve.

When selecting a compatibilization strategy, not only the chemistry of the system should be taken into account, but also the effect on the melt viscosity (crucial in determining the blend morphology) should be considered. When aiming for relatively low melt viscosities, the use of compatibilizer precursors (as in a maleated polymer) is an advantage with respect to premade compatibilizers, since the latter cause a significant increase in the melt viscosity [243].

Generally, both compatibilization strategies are effective. The decrease in tensile strength and elongation at break at higher St intakes is attenuated when the blend is compatibilized. However, in almost all studied systems, such attenuation is only partial and the mechanical properties (e.g., tensile strength and elongation) of the pure polymer (e.g., PCL) remain in almost all cases unattainable.

6.2.5

Composites

Compatibilization of blends is generally not sufficient to improve (see above) the mechanical properties to the desired values, especially at relatively high starch contents. The use of inorganic fillers is a very attractive route to further improve product properties. Among all possible fillers, clays in general [244–247] and montmorillonite in particular are the most popular choices [248,249]. This is likely due to the “nano” size of the filler particles, which ultimately results in a large increase in the stiffness of the end product [250,251]. Arroyo *et al.* [252] recently reported nanocomposites of TPS (wheat, water, and glycerol) with PLA (possibly grafted with MAH, PLAG) and montmorillonite. The authors found that TPS can intercalate the clay, the latter being mostly present in the starch phase. Clay composites with TPS, PLA, and/or PLA-g-MAH show very similar mechanical behavior, with rather similar values of E , σ , and ε (see Figure 6.8 for modulus values).

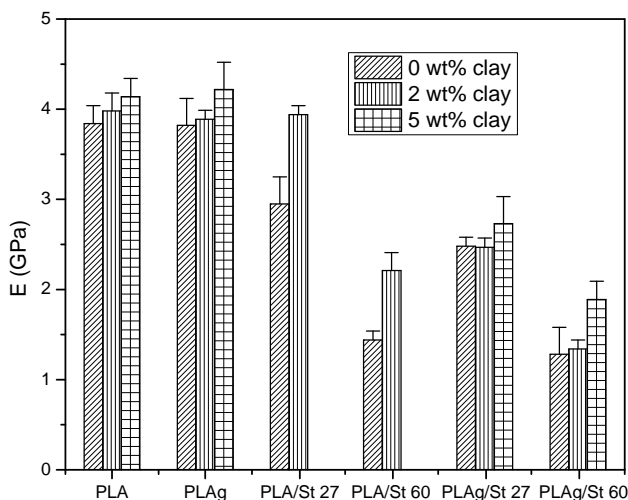


Figure 6.8 Tensile modulus as a function of composition. The number in the sample code indicates the TPS wt% in the blend.

Besides clays, carbon nanotubes were also used as nanofiller in St-based blends. In this case, besides improvements in mechanical behavior, a less pronounced moisture sensitivity of the final product is usually observed [253]. Also, inorganic salts such as CaCO_3 may be used to prevent swelling of St-based blends [254].

6.3

Blends with Chitosan (One Amino Group Too Much . . .)

Based on the close resemblance in chemical structure between chitosan and starch, the only difference being an amino group instead of a hydroxyl one in the chemical structure of the monomeric unit, one might anticipate similar blending behavior. However, this is actually not the case and the presence of amino groups results in specific interactions between the Cht chains. These must be overcome upon blending to obtain good dispersions [255]. However, as generally observed for polymeric systems, fully miscible blends are more exception than rule [199]. In the case of chitosan, full miscibility has been reported with hydroxypropyl cellulose and a few other polymers [256,257]. In most cases, as for St-based blends, immiscibility remains a common issue. Despite the general immiscibility, Cht has often been blended with commercial polymers to combine its positive properties (e.g., conductivity and antibacterial activity) with favorable properties of the other component. Correlo *et al.* [258] studied blends of Cht with several different polyesters (PBS, PCL, PLA, PBSA, and PBTA) and determined relevant mechanical properties as a function of the chemical composition. The mechanical properties of Cht/PBS blends over a wide range of compositions from pure PBS up to 70 wt% Cht are given in Figure 6.9.

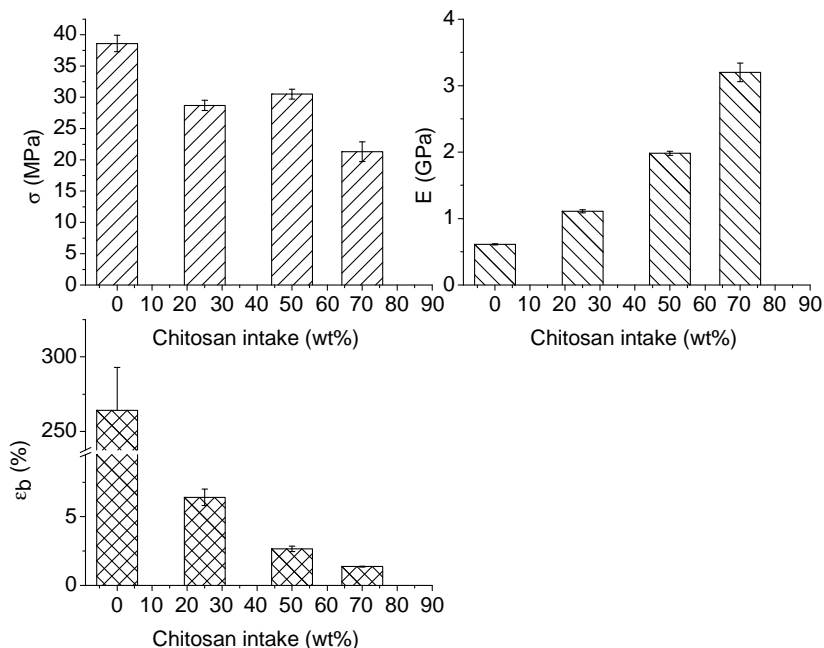


Figure 6.9 Mechanical properties for PBS/Cht blends.

The addition of Cht results in a reduction in tensile strength and elongation at break and a higher modulus. As for St (see above), these trends are easily explained by the lack of compatibility between the components and are in agreement with semiempirical relations. At relatively high Cht intakes (>50 wt%), aggregates can be formed, which further lower the stress value at which the materials fails. These trends are also valid for blends with different polyesters (Figure 6.10).

The elongation at break decreases dramatically for all blends except the one with PLA. This may be rationalized when considering that PLA is the only polyester with a T_g above room temperature, thus showing brittle behavior.

The results discussed above clearly point out the necessity for Cht-based blends for compatibilization. The use of diisocyanates is a promising option [259]. The relatively higher reactivity of the $-\text{NH}_2$ groups with $-\text{NCO}$ groups [260] compared to hydroxyl groups renders this possibility even more attractive for Cht than for St. However, the difficulties associated with diisocyanate synthesis, mainly based on the use of phosgene, as well as the necessity for a controlled reaction (isocyanates being extremely reactive), make this strategy not widely popular. The use of a modified polymer as compatibilizer is a more convenient route. Wu [261] studied blends of PEOct compatibilized by PEOct-g-AAc and found similar effects as described for starch (see above). The main action of the compatibilizer is an attenuation in the decrease of tensile strength and elongation at break at higher biopolymer intake. Deviations from this trend have, however, already been reported. For example, Johns and Rao [262] used MAH (as monomer) for the compatibilization of Cht/NR blends.

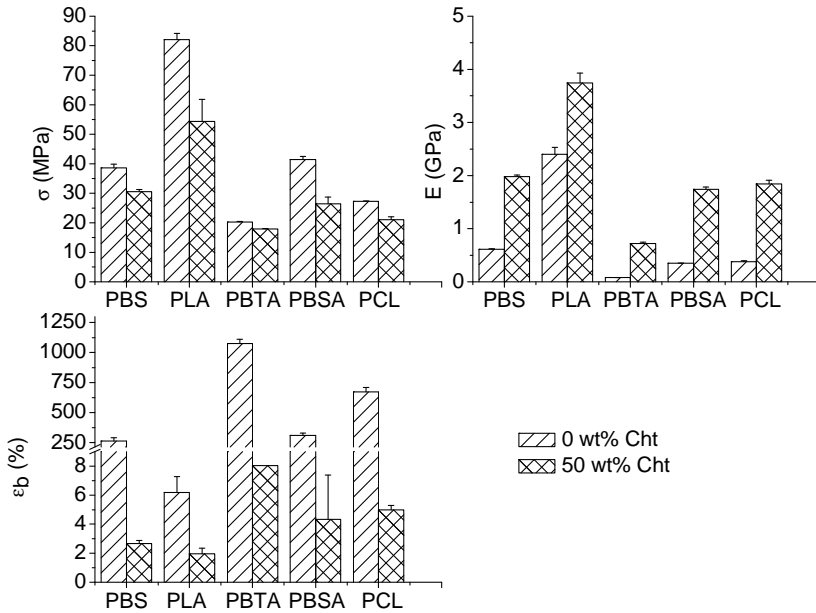


Figure 6.10 Mechanical properties of Cht-based blends with different polyesters.

The authors assumed that MAH is grafted on the NR chains and that the corresponding NR-g-MAH chains react successively with the amino groups of Cht to yield the desired block copolymer (Figure 6.11), the effective compatibilizer for this system.

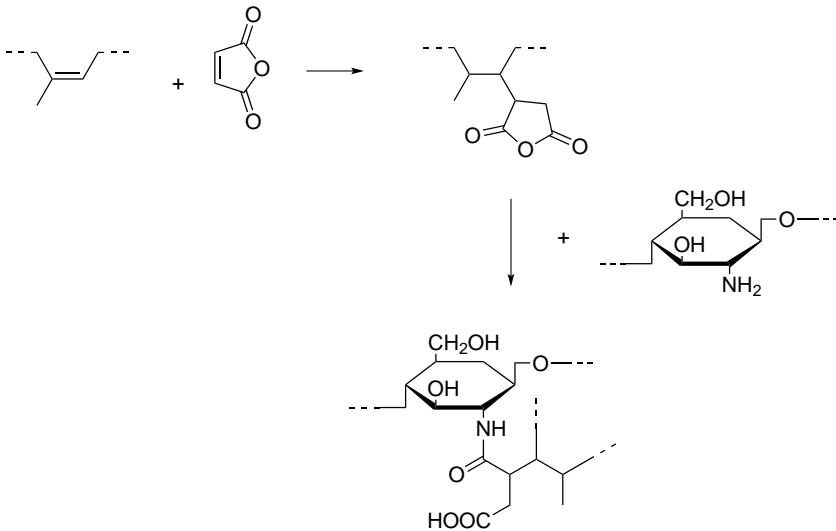


Figure 6.11 Grafting of MAH on NR and reaction of NR-g-MAH with chitosan.

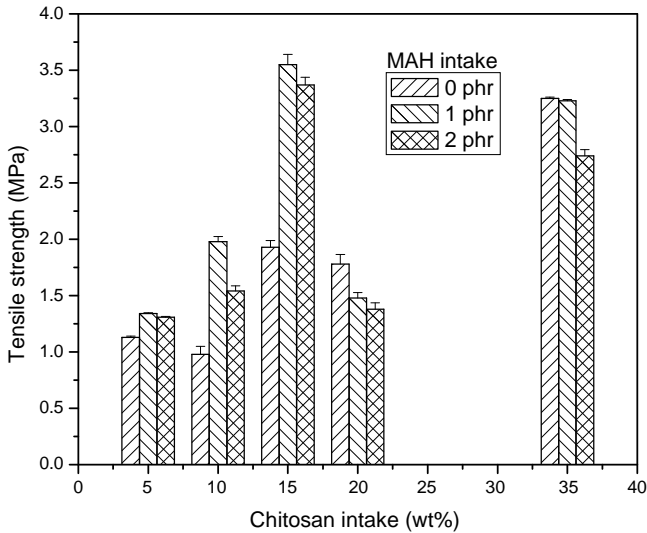


Figure 6.12 Tensile strength as a function of Cht intake for blends with NR.

When looking at the tensile strength as a function of composition (Figure 6.12), the modulus and elongation are not shown for brevity since the trends closely resemble the one of σ , and a strong negative effect of this compatibilization strategy is observed.

Both the σ and ε_b decrease with the MAH and Cht intake in the blends, the only exception being the tensile strength of the blend containing 15 wt% Cht. The authors attributed this lack of effect to a delicate balance between compatibilization and the plasticization of the blend, the latter due to unreacted MAH. The observed trends remain, however, at least peculiar when considering the general behavior of compatibilized blends based on St and Cht, that is, a decrease in tensile strength at higher biopolymer intake [83].

6.4

Future Perspectives

The above discussion clearly points out the existence of a number of general strategies for the preparation of biopolymer-based blends with good product properties. These can be extrapolated to improved routes for these materials.

6.4.1

Biopolymer Plasticization

The use of a plasticizer (like polyols) is in most cases an absolute necessity for processing of biopolymers and biopolymer-based blends. This is a direct result of the specific interactions in the materials as well as their sensitivity to relatively high

temperatures. The plasticizer (both structure/functionality and intake) has a clear influence on the rheological properties of the biopolymer and in turn on the morphology and end properties of the blends. The use of mixed plasticizer systems, as shown for St [263], allows fine-tuning of the rheological behavior and can be seen as a tool for the design of improved processes for these materials. The use of new plasticizers is also a possibility. In particular, the use of supercritical CO₂ (scCO₂) represents a “green” option in this respect. Indeed, it has already been demonstrated that scCO₂ can induce starch gelatinization [264] in combination with water. Besides the necessity to work at relatively high pressure (>80 bar), the inert nature of scCO₂ and the possibility to remove it by simple degassing of the system constitute clear advantages for this system over more classical ones. Furthermore, the possibility to recycle the CO₂ stream, to use relatively low processing temperatures, and to integrate the plasticization process with, for example, a foaming one renders this approach even more attractive. The addition of “plasticizer enhancers” [265], such as citric acid for starch [266], is also a viable option to modify the product properties of the blends. Citric acid aids rupture of the St granules and was shown to improve the TPS dispersion in blends of corn St with LDPE. The mechanical properties were better than St alone and in some cases similar to those of pure LDPE [267].

6.4.2

Blend Morphology and Compatibilization

The morphology of a polymeric blend is in general a function of the composition (volume fractions) and the viscosity and surface energies of the individual components. Blends of biopolymers do not constitute in this respect an exception to the rule. Process and product design must therefore take into account and when necessary comprise all of these aspects. From a scientific point of view, this requires a multidisciplinary approach. However, to the best of our knowledge, such studies are not known in the open literature.

The strong differences in polarity of many biopolymers with respect to commercial ones render the blends almost always immiscible and not compatible. The use of a compatibilizer is often needed to obtain the desired thermal and mechanical behavior. The use of diisocyanates represents a popular choice even if this is not completely in line with the “green” and “sustainable” character of these materials. The use of compatibilizers’ precursors (e.g., maleated polymers) represents a viable option. The relatively lower reactivity of the anhydride groups with respect to the isocyanates is in this case compensated by the commercial availability of the polymers (e.g., PE-g-MAH) or in any case by the easiness of their production process. From a purely scientific point of view, the use of premade block or graft copolymers is most useful to gain a better understanding of the compatibilization mechanism as well as of compatibilizer effects on the thermal and mechanical behavior of the blend. This means that synthetic routes should be available for well-characterized grafted polymers (e.g., St-g-PCL). However, the use of a biopolymer (e.g., starch) together with a monomer (e.g., styrene) and initiator generally results in grafting efficiencies on the order of 30% [268] because of the fact that the reaction

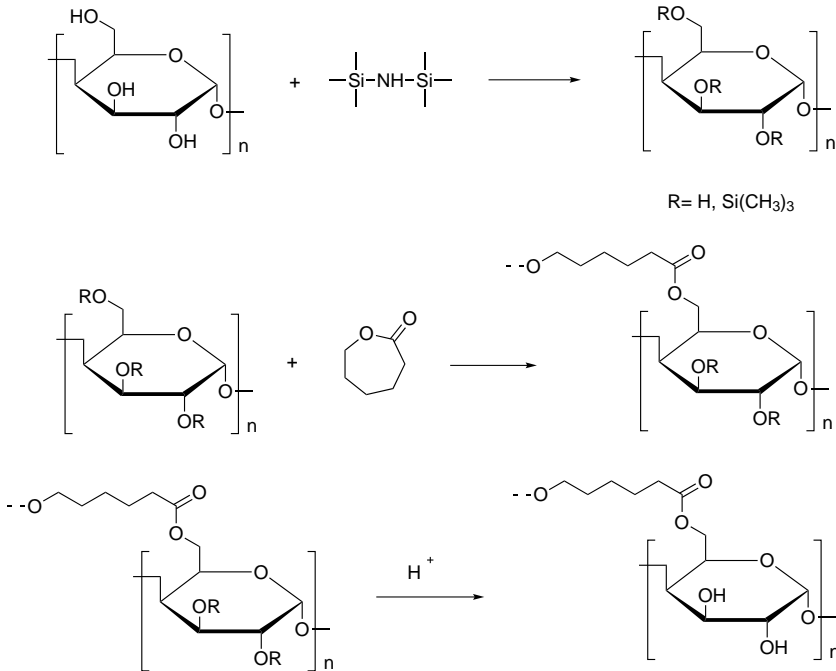


Figure 6.13 General strategy for starch silylation, grafting of PCL, and desilylation.

is generally heterogeneous. This makes the systems not well characterized and thus in principle unsuitable for a better understanding of the compatibilization mechanism. As suggested by Sugih *et al.* [269] (Figure 6.13), silylation of the St represents a viable route (at academic level) for the preparation of well-characterized systems.

Silylation of the starch is a crucial step since the resulting product is soluble in common organic solvent, thus allowing the grafting reaction to proceed in relatively homogeneous conditions. Upscaling of such processes at industrial level is at the moment strongly hindered by the use of organic solvents. The possibility to carry out such “grafting from” processes in alternative solvents such as ionic liquids [270] or even in scCO_2 [271–273] has already been reported and is a popular research topic at the moment.

6.4.3

Blend Processing: Technological Aspects

Improvement of the mechanical and thermal behavior of blends can also be achieved by proper selection of the processing technology. A typical example is the use of a one-step extrusion system for ST-based blends [274]. As in the case of TPS/LDPE blends [132], the general idea is to feed the polymer (LDPE) via a single-screw extruder to a double-screw containing starch and the plasticizers (in this case glycerol). Water is used as processing aid but is removed (volatilization) before St is

mixed with LDPE. The connection between the two extruders contains efficient mixing elements, thus allowing accurate control of the blend morphology. The mechanical properties of the corresponding blends are comparable with the ones of compatibilized blends.

New blending technologies, such as solid-state shear pulverization, have been proposed recently [275]. However, simple modification of existing processing tools still remains preferable in terms of industrial applicability. In this respect, the formation of fibers in the biopolymer matrix (in this case St) during extrusion is an interesting opportunity [276]. Blends produced via this new concept display significantly higher tensile strengths and modulus compared to simple extruded blends.

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