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AN OVERVIEW OF STARCH-BASED PLASTIC BLENDS FROM REACTIVE EXTRUSION

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ABSTRACT: The North American market for biodegradable plastics in 2005 was estimated to be around 60 million pounds (27 kt). Starch-based polymer blends were expected to account for 30 million pounds (14 kt) with significantly lower growth rates than other biodegradable polymers such as polyesters. The main hurdle in the growth of starch-based products is the thermodynamic immiscibility and non-wetting of starch with other polymers which leads to serious deterioration of mechanical properties at >25–30 wt% starch. Higher amounts of starch in the blends entail adding suitable functional groups on starch and other polymers in the blend to make them more compatible. The primary challenge is to develop fast reaction chemistries that can be transformed into viable processes and integrated into existing process lines with economically viable formulations. This article briefly reviews some of the most promising chemistries available for the reactive extrusion of starch-based polymer blends (biodegradable/non-biodegradable).

KEY WORDS: biodegradable, starch, polyesters, immiscibility, reactive extrusion, blends.

INTRODUCTION

POLYMER BLENDS CONTAINING varying amounts of starch have been studied extensively as possible replacements for plastics mainly in the area of packaging. Starch by itself is unsuitable because of various disadvantages. These include:

1. brittleness in the absence of suitable plasticizers,

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2. hydrophilic nature of starch and poor water resistance,
3. deterioration of mechanical properties upon exposure to environmental conditions like humidity, and
4. soft and weak nature of starch in the presence of plasticizers.

Thus, starch needs to be blended with other synthetic polymers to eliminate these disadvantages. However, most of the synthetic polymers are hydrophobic and thermodynamically immiscible with hydrophilic starch, thus simple mixing will result in phase incompatibility and poor mechanical properties. Ideally, starch and the second polymer should be covalently bonded through existing functional groups or by introduction of new functional groups. In this article, simple mixing of starch with other polymers is referred to as composites and reactive mixing is referred to as blends. Simple mixing does not lead to phase separation if the starch present is below certain levels in the composites [1]. Below this critical level, the deterioration in properties has been found to be insignificant. For example in starch-polyester composites, this critical level is approximately 25–30 wt% [1].

Synthetic polymers that have been reactively blended with starch have the following functional groups – carboxyl, anhydride, epoxy, urethane, or oxazoline – that can react with the hydroxyl or carboxyl groups in native and modified starches, respectively. Another method for synthesizing starch-based blends is graft copolymerization. Synthetic monomers are covalently bonded to hydroxyl positions on starch and then polymerized to produce starch graft copolymers. Figure 1 illustrates various methods of reactive blending.

Recent advances have prompted this review on reactive extrusion and compatibilization chemistries for starch-polymer blends. This article will review several reaction mechanisms including reactive extrusion blending of starch with other polymers and also starch graft co-polymerization techniques. We have also reviewed the effects of various reactive processes on the mechanical and functional properties of these blends. Though hundreds of reactive processes have been studied, very few of them promise to significantly increase the market demand for starch in plastic applications. The primary challenges for synthesizing starch-based blends with commercial utility are: (1) overcoming miscibility problems at high starch contents, (2) mechanical property deterioration at high starch content even in reactive blends, and (3) cost, especially for biodegradable starch-polyester blends at low starch contents (<30 wt%).

Figure 1. A scheme for synthesizing reactive starch blends.

Starch-based Plastic Market

The biodegradable polymer market for North America is expected to be 60 million pounds in 2005 – up from 25 million pounds in 2000 [1]. However, the starch-based polymer consumption is expected to only grow from 20 to 30 million pounds during this time. Most of the future growth will be in the area of synthetic biodegradable polyesters [1]. Some of the prominent applications of starch composites and blends that exist in the market today are as follows:

1. Loose-fill packaging: most of the starch-based products in this category consist of different kinds of starches – corn, wheat, hydroxypropylated high amylose corn – with a small amount of additives like polyvinyl alcohol, glycerol, polyethylene glycol (PEG), or silicon dioxide. There is also a product derived from methyl acrylate grafted corn starch. This product is made by Uni-Star Industries Ltd in Illinois and is called ‘STAR-KORE’ [2].
2. Starch–polyester films: starch–polycaprolactone (PCL) film composites and blends are currently used in the market primarily as compost bags. For example, ‘Envar’ is a reactive blend of starch and PCL developed at Michigan State University and is marketed for use in manufacture of compost bags.

Other applications of starch-based plastics include agricultural mulches, hygiene products, and paper coating.

STARCH-POLYMER REACTIVE BLENDS

Addition of Maleic Anhydride (MA) Functional Groups

Maleic anhydride (MA) has been grafted onto many different hydrophobic polymers – biodegradable and non-biodegradable – to produce functional polymers. In the plastic industry MA-grafted polymers were generally used as compatibilizers between ungrafted polymer and other polar polymers like nylon [3–7]. The use of these functional compatibilizers was found to improve strength, modulus, and elongation by helping to form a co-continuous phase in the polymer blend. Thus maleated polymers can act as compatibilizers between the non-functional polymer and the starch. Blends can also be made from maleated polymer and starch without any unmodified polymers.

Maleic Anhydride (MA) Functionalized Non-biodegradable Polymer–Starch Blends

Addition of MA has been done on many non-biodegradable synthetic plastic polymers, many of which were blends with polyamides. These include poly(ethylene-propylene) rubber (EPR) elastomer [8–11], polyethylene (PE) [3,12–14], polypropylene (PP) [15–17], poly(phenylene ether) (PPE) [18], poly(acrylonitrile-butadiene-styrene) (ABS) [19], and polystyrene (PS) [6,20,21]. The main reason for the wide use of MA functionalized polymers is the ease with which the anhydride can be grafted onto many polymers at normal melt processing temperatures without significant homo-polymerization and undesirable scission side reactions. Figure 2(a) illustrates a simplified reaction scheme of MA addition to a polyolefin (PE).

The addition reaction can be done in solution or melt states. The reaction is initiated by the presence of peroxide initiators like benzoyl peroxide (BPO) or dicumyl peroxide (DCP). Commercially available MA-functionalized polymers may be synthesized by adding MA directly onto a whole or growing polymer chain. Figure 2(b) illustrates reaction of MA-grafted PE with starch. This reaction is mostly done in melt state during extrusion. The maleated polymers can react with starch through the presence of free anhydride groups; this reaction of anhydride with starch hydroxyl to form an ester does not produce water during the reaction.

The maleated polymers that have been blended with starch are styrene-MA (SMA) polymer [22,23], ethylene-propylene-MA (EPMA) polymer [22,23], ethylene-vinyl acetate-MA (EVAMA) polymer,

Figure 2. Simplified reaction scheme showing: (a) addition of MA to PE and (b) reaction of maleated PE with starch.

low-density polyethylene MA (LDPEMA), and high-density polyethylene MA (HDPEMA) [24]. Blending was done in a melt extrusion process. The tensile strengths of the SMA/EPMA blends are given in Table 1. Tensile strengths of starch-SMA/EPMA blends were at least twice those of starch-PS/ethylene-propylene(EP) composites demonstrating compatibility of starch and SMA/EPMA polymers [22]. The authors explained the improvement in properties as occurring because of interaction between the anhydride functionality on EPMA/SMA forming esters with starch and they predicted that free anhydride carboxyls on maleated polymer in the blends could form covalent/hydrogen bonds with starch hydroxyls. Water absorption was found to be significant in the blends. Starch-EPMA blends at 80 wt% starch absorbed 18 wt% after immersion in water for 60 days compared to 27 wt% for SMA

Table 1. Mechanical properties of starch–SMA/EPMA blends [22].

Material	Tensile strength (MPa)
Starch/SMA, 60/40	18.4
Starch/polystyrene (nonfunctional), 60/40	9.6
SMA	33
PS	31
Starch/EPMA, 70/30	8.3
Starch/ethylene–Propylene (EP) co-polymer, 70/30	2.8
EPMA	6.2
EP	>9

Table 2. Mechanical properties of starch–LDPE/HDPE/EVA composites and blends with maleation [24].

Material	Tensile strength at break (MPa)		% Elongation at break		Flexural strength at break (MPa)	
	With MA	Without MA	With MA	Without MA	With MA	Without MA
Starch–EVA	7	2.5	13	9.4	–	–
Starch–LDPE	13.7	6.9	4	3	22	13
Starch–HDPE	22	10	5	3.2	42	16.4

blends [22]. Dynamic mechanical analysis (DMA) studies showed two glass transitions (T_g) for starch–EPMA blends and one broad T_g for starch–SMA blends. The broad T_g peak for starch–SMA blends did not indicate miscibility but arose because the two transitions for starch and SMA were close to each other and could not be resolved. Biodegradation studies showed that the starch component was biodegradable but EPMA and SMA were not affected. Bhattacharya et al. [24] also studied blends of starch (70 wt%) with EVAMA, HDPEMA, and EMA. Tensile and flexural strength and ultimate elongation of these blends with maleated plastics increased significantly over that of composites containing unmodified plastics. Table 2 illustrates the effect of polymer maleation on the mechanical properties of the starch-maleated polymer blends.

Maleic Anhydride (MA) Functionalized Biodegradable Polyester–Starch Blends

Maleated polyesters have been synthesized from high molecular weight PCL [25], polybutylene succinate (PBS) [26], polytetramethylene

Figure 3. Simplified reaction scheme showing MA addition to PCL and reaction between maleated PCL and starch [25].

adipate terephthalate (PAT) [26], and polylactic acid (PLA) [26,27]. These were used as compatibilizers in corresponding starch–polyester blends [28,29]. A simplified reaction scheme proposed by Bhattacharya et al. [25] is given in Figure 3 for starch–PCL blends with maleated PCL as compatibilizer. Except for PLA, maleated polyesters were prepared from reactive extrusion in the presence of organic peroxide initiators like BPO, DCP, and dimethyl dibutylperoxy hexane [26]. Maleated PLA was synthesized in a toluene media. Grafted MA quantities ranged

from 0.4 to 1.6% in PCL [25], and 0.2 to 1.2% for PBS, PAT, and PLA polyesters [26]. Bhattacharya et al. [25,26] reported little change in the molecular weight of polyesters before and after the MA addition process. Extrusion parameters like temperature, initiator and monomer concentration, and residence time were optimized to avoid crosslinking and scission side-reactions during extrusion. The same authors [28] evaluated the properties of starch–polyester blends containing small amounts of maleated polyesters (5%). For starch–PCL blends with 5% compatibilizer and 50 wt% starch, a three-fold increase in strength over starch–PCL composites was observed (Table 3) although there was no change in elongation or modulus. Similarly, addition of compatibilizer to starch–PBS blends resulted in a two-fold increase in tensile strength – approaching that of 100% PBS – with no effect on modulus or elongation (Table 3). No significant effect of compatibilizer on tensile strength and elongation of starch–PAT blends was observed. The DMA studies showed a decrease in T_g of starch from 74 to 65°C in compatibilized starch–PBS blends and it was related to better miscibility between starch and PBS in the presence of maleated PBS.

Narayan et al. [27] studied the maleation of PLA by reactive extrusion and evaluated the effects of initiator concentration and temperature on % maleation. Up to 0.6% maleation was achieved with 2 wt% MA concentration in the presence of peroxide initiators at 180–200°C. They also evaluated interfacial adhesion by scanning electron microscopy (SEM) in blends containing 70 wt% maleated-PLA and 30 wt% starch [29]. Though mechanical properties were not evaluated, starch particles did not show surface dewetting in these blends, thus indicating good adhesion between starch and maleated PLA.

In addition to MA, other anhydrides have also been used to prepare anhydride modified polyesters. Avella et al. [30] reported grafting of pyromellitic anhydride on PCL and its use as a compatibilizer in starch–PCL blends. However, they used a low molecular weight ($M_w = 20,000$) PCL for anhydride addition and high molecular weight

Table 3. Tensile properties of starch–polyester blends [28].

Material	Tensile strength at break (MPa)		% Elongation at break	
	With MA	Without MA	With MA	Without MA
Starch–PBS	33	15	10–20	10–20
100% PBS	37	37	–	300
Starch–PCL	21	8	10–20	10–20
100% PCL	25	25	–	650

($M_w = 80,000$) polymer as the unmodified polyester in the blend. The anhydride addition process was done in molten state in the presence of small amounts of tetrahydrofuran. Infra-red analysis of modified PCL showed appearance of a new band at 3200 cm^{-1} indicating the stretching of PCL carbonyl groups due to chemical bonding with anhydride functionality. The anhydride modification of PCL shifted the T_g from -66 to -55°C . This was correlated with reduced segmental chain mobility due to the presence of pyromellitic groups attached to the PCL backbone. The SEM pictures of fractured samples of starch-PCL (70:30 wt ratio) with compatibilizer showed better interfacial adhesion than in samples without compatibilizer. The addition of starch decreased resilience compared to the 100% PCL, but addition of compatibilizers was found to reduce the decrease of resilience in blends containing 30–50% starch. The authors found no differences in biodegradation rate of blends and composites with and without compatibilizers. However, starch in the blend increased the rate of degradation.

Introduction of Oxazoline (OXA) Functional Groups

Oxazoline (OXA) compounds grafted on polymers can form amidoester and amidoether linkages with other polymers containing carboxyl or phenolic groups, respectively. For example, modified starches containing carboxyl groups can form amidoester linkage with OXA-grafted polymers. The general reaction scheme of OXA-grafted polymer with carboxyl and phenolic polymers is shown in Figure 4.

Figure 4. Reactions of OXA-grafted polymers with carboxyl and phenolic groups to form amidoester and amidoether linkages respectively. A and B are chains of polymers A and B respectively.

Oxazoline (OXA) Functionalized Non-biodegradable Polymer–Starch Blends

The OXA-functionalized polymers have been used to compatibilize the following blends:

1. OXA-grafted poly(styrene-acrylonitrile) (SAN) for compatibilizing polyamide 6 (PA6)-SAN blends [31].
2. OXA-grafted PS for compatibilizing PS-oxidized PE, PS-natural rubber (NBR) [31], and high impact polystyrene (HIPS)-NBR blends [32].
3. OXA-grafted ABS for compatibilizing poly (styrene-co-acrylic acid) (SAA)-ABS blends [33].

Very few studies have been reported yet on OXA-grafted non-biodegradable polymer blends with starch or modified starch.

Oxazoline (OXA) Functionalized Biodegradable Polyester–Starch Blends

Bhattacharya et al. [34] grafted oxazoline functional groups on PCL through a free radical chain mechanism. The grafting process was done in an extruder and grafts of 0.9–2.2% were achieved. Ricinoloxazoline, which is a 2-oxazoline, was used as the grafting monomer. The structure of ricinoloxazoline is given in Figure 5. The double bonds on carbon atoms indicated by a and b were found to react with the polyester chain similar to MA grafting on PCL shown in Figure 3. When used as an initiator, DCP was found to produce minimum homopolymerization, high grafting efficiency, and minimum decrease in

Figure 5. Structure of ricinoloxazoline used for OXA-grafting of PCL. a and b carbons function as chain extenders during grafting reaction.

PCL molecular weight. Though no blending studies with starch were carried out, the authors predicted reactions with starch and modified starch containing carboxyl groups and wheat gluten because of the presence of carboxyl and hydroxyl groups.

Introduction of Carboxyl Groups

Carboxyl Functionalized Non-biodegradable Polymer–Starch Blends

Jane et al. [35] blended PE and native corn starch (NCS) in the presence of oxidized polyethylene (OPE) using extrusion. They observed that carboxyl and keto functional groups on OPE interacted strongly with starch hydroxyls. Best properties were achieved in blends containing starch and OPE in the ratios between 1 : 1 and 3.3 : 1, with PE being the rest of the blend. Improvements in properties were achieved due to compatibilizing effect of OPE on starch–PE polymer matrix (examples in Table 4).

Starch-Urethane and their Blends with Polyesters

Mei et al. [36] synthesized urethane-based starch derivatives and blended them with polyhydroxy butyrate (PHB). They reported improved processability of PHB with starch urethane addition due to improved compatibility between starch urethanes and PHB. Three types of starch-urethanes were produced by reacting isocyanates with starch and PEG, polypropylene glycol (PPG) or polyadipic acid ester. The modified starches were then blended with PHB. Infrared analysis confirmed formation of the characteristic –N–H group in starch urethanes and also showed unreacted isocyanate groups ($-\text{N}=\text{C}=\text{O}$). When blended with PHB, the unreacted isocyanate groups were no longer seen on the infra-red scan, resulting in an increase in intensity

Table 4. Tensile properties of starch/PE/OPE blends illustrating compatibilizing effect of OPE on Starch–PE blends [35].

Formulation	Ultimate tensile strength		Ultimate elongation (%)
	psi	MPa	
PE/7%NCS	2193	15.1	543
PE/15%NCS	1611	11.1	242
PE/7%NCS/7%OPE	2407	16.6	523
PE/15%NCS/15%OPE	2330	16.1	581

of -N-H- groups. Tensile strengths of starch-urethane-PHB blends only showed a slight increase over native starch-PHB composites, while modulus and elongation did not show any improvements. However, the mechanical properties of starch urethane-PHB blends (10–30 wt% starch urethanes) were significantly lower than that of 100% PHB, with strength reaching only one-third of 100% PHB and no significant increase in elongation.

Monomer Grafting and Polymerization on Starch

ϵ -Caprolactone Grafting and Polymerization on Starch

Narayan et al. [37–40] synthesized starch-PCL blends by polymerizing ϵ -caprolactone monomer in the presence of starch. The authors used three different pathways for carrying out the polymerization reaction:

1. Polymerization in the presence of a Lewis acid catalyst, stannous octoate – this reaction was carried out in melt state between 100–150°C. High monomer conversions (>98%) were achieved. However there were certain disadvantages with this method – low grafting efficiency, formation of cyclic and linear oligomers, and long reaction times (3 h).
2. Polymerization in the presence of aluminum or titanium alkoxides – in batch preparation methods [37], a low conversion of 30% was achieved in the presence of starch and aluminum alkoxides. However, the use of titanium alkoxides led to 98.5% conversion. High conversions were achieved during the reactive extrusion process [38–40] with PCL molecular weights (M_w) ranging from 25,000 to 400,000 at residence times of 1–3 min. Relevant patents [38–40] mentioned a temperature of 180°C during the extrusion process and discussed effects of screw configuration, residence time, and acid value of the monomer on molecular weight. The patent indicated that the starch-PCL blends were synthesized in three extrusion steps (i) homopolymerization of ϵ -caprolactone to PCL in the presence of aluminum alkoxides, (ii) extrusion of starch-plasticizer pellets, and (iii) extrusion blending of materials from (i) and (ii). The mechanical properties of films produced by this method are given in Table 5. These films are currently marketed under the name of 'Envar.'
3. Polymerization in the presence of triethyl aluminum – the reaction was found to be the fastest in batch preparation methods using this catalyst. High monomer conversions (>99.9%) and grafting

Table 5. Tensile properties of starch-g-PCL films [38–40].

Material	Starch (wt%)	Maximum strength (MPa)	Ultimate elongation (%)
Starch-g-PCL (Envar)	30	16	257
100% PCL	0	25	360

efficiencies (up to 95%) were achieved in batch methods. The authors proposed the formation of starch–aluminum alkoxides *in situ* by the reaction of triethyl aluminum with starch, which then acted as an initiator species for lactone polymerization.

The reaction mechanisms proposed by the authors are illustrated in Figure 6. Figure 6(a)–(c) shows the Lewis catalyst, alkoxide and triethyl initiated polymerization reactions respectively.

Other Grafting Reactions

There have been several studies on grafting of various monomers on starch – styrene [41,42], methyl acrylates [42], vinyl acetates [43], ethylene oxide [44,45], ethylene-acrylic acid [46], and acrylamide [47]. However, these blends were limited by the fact that the mechanical properties of these blends were significantly lower than those of the 100% synthetic polymer. Also, the starch component in these blends was biodegradable whereas the synthetic/non-biodegradable component was not.

CURRENT STUDIES BY OUR GROUP

Our research group has recently developed a reactive extrusion process in which high amounts of starch (approx. 40 wt%) can be blended with a biodegradable polyester (PCL) in the presence of nanoclay resulting in tough nanocomposite blends with elongational properties approaching that of 100% PCL [1,48]. Starch, PCL, plasticizer, modified montmorillonite (MMT) organoclay, and Fenton's reagent (H_2O_2 and ferrous sulfate) were extruded in a conical co-rotating twin-screw extruder at 120°C and injection molded at 150°C. The primary reactions taking place during extrusion are illustrated in Figure 7. Native starch was partially oxidized by the peroxide, and ester groups in PCL can crosslink with the carbonyl

Figure 6. Grafting and polymerization of caprolactone on starch and their initiation by: (a) Lewis acid catalyst; (b) aluminum alkoxide; and (c) triethyl aluminum [37].

and/or carboxyl groups in oxidized starch through a peroxide initiated free radical process. This crosslinked starch-PCL fraction acted as a compatibilizer between unmodified starch and PCL. A single extrusion step with a low residence time (~ 74 s) was found to accomplish the above set of reactions. Elongation of these reactively extruded starch-PCL nanocomposite blends with 3 and 6 wt% organoclay approached that of 100% PCL (Table 6). However, strength and modulus remained the same as that of starch-PCL composites prepared from simple physical mixing. X-ray diffraction results showed mainly intercalated flocculated behavior of clay at 1,3,6, and 9 wt% organoclay. The SEM showed that there was improved starch-PCL interfacial adhesion in reactively extruded blends compared to starch-PCL composites. Dynamic mechanical analysis showed changes in primary α -transition temperatures for both the starch and PCL fractions, reflecting cross-linking changes in the nanocomposite blends at different organoclay content. Also, starch-PAT blends prepared by the above reactive extrusion process showed a trend of elongational properties approaching that of 100% PAT. The reactive extrusion concept can be extended

I. Reactive species from H_2O_2

- a) $\text{HO} - \text{OH} + \text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + \text{HO}^- + \text{OH} \cdot$ (hydroxyl radical)
 b) $\text{HO} - \text{OH} \longrightarrow \text{OOH}^-$ (perhydroxyl anion)

II. Starch Oxidation

III. Crosslinking pathway

Figure 7. Simplified reaction scheme showing oxidation and crosslinking between starch and PCL using Fenton's reagent [1,48].

Table 6. Tensile properties of starch-PCL blends and composites from reactive extrusion.

Material	Maximum strength (MPa)	Ultimate elongation (%)
100% PCL ^a	31	1240
STPCL (no reactive extrusion) ^b	13	300
STPCLPERI-3 ^c	14	1200
STPCLPERI-6 ^d	16	1010

a: 100% PCL, extruded at 120°C and molded at 150°C;

b: native wheat starch : PCL : glycerol wt ratio 1 : 1 : 0.5, 0% clay, extruded at 120°C and molded at 150°C;

c: native wheat starch : PCL : glycerol wt ratio 1 : 1 : 0.5, ferrous sulfate catalyst at 0.07 g/g starch, H_2O_2 (30% solution in water) = 0.07 mL/g starch, 3% clay, extruded at 120°C and molded at 150°C;

d: native wheat starch : PCL : glycerol wt ratio 1 : 1 : 0.5, ferrous sulfate catalyst at 0.07 g/g starch, H_2O_2 (30% solution in water) = 0.07 mL/g starch, 6% clay, extruded at 120°C and molded at 150°C

to other starch-PCL like polymer blends with polyhydroxy polymers like polyvinyl alcohol and starch on one side and PBS, polyhydroxy butyrate-valerate, and PLA on the other to create cheap, novel, and compatible biodegradable polymer blends with increased toughness.

CONCLUSIONS

Many reactive chemistries are available to compatibilize starch and synthetic polymers. Current research activities have focused on starch-polyester biodegradable blends. Even though starch-based plastics have captured a major portion of biodegradable plastic market, it is not the fastest growing one. Significant and faster growth is expected for products synthesized from 100% biodegradable polyesters like polylactic acid (PLA). This is because significant hurdles exist in using high amounts of starch (>25–30 wt%) even in reactive blends without compromising material properties. Thus the application of starch-based blends is now limited to niche applications. Future research activities need to focus on reactive starch blends containing significant amounts of starch or modified starch that allow them to be used in a larger number of applications.

REFERENCES

1. Kalambur, S. and Rizvi, S.S.H. (2005). Biodegradable and Functionally Superior Starch-Polyester Nanocomposites from Reactive Extrusion, *J. Appl. Polym. Sci.*, **96**(4): 1072–1082.
2. Tatarka, P.D. and Cunningham, R.L. (1998). Properties of Loose-Fill Foams, *J. Appl. Polym. Sci.*, **67**(7): 1157–1176.
3. Chuang, H.K. and Han, C.D. (1985). Blends of Nylon 6. I. Rheology-structure Relationships, *J. Appl. Polym. Sci.*, **30**(6): 2431–2455.
4. Chuang, H.K. and Han, C.D. (1985). Blends of Nylon 6. II. Property-morphology Relationships, *J. Appl. Polym. Sci.*, **30**(6): 2457–2474.
5. Fontan, E., Chen, C.C., Min, K. and White, J.L. (1988). An Investigation of Instability of Phase Morphology of Blends of Nylons with Polyethylenes and Polystyrenes and Effects of Compatibilizing Agents, *Polym. Eng. Sci.*, **28**(2): 69–80.
6. Kim, B.K. and Park, S.J. (1991). Reactive Melt Blending of Nylon with Poly(styrene-co-maleic anhydride), *J. Appl. Polym. Sci.*, **43**(2): 357–363.
7. Choudhury, N.R. and Bhowmick, A.K. (1989). Compatibilization of Natural Rubber-polyolefin Thermoplastic Elastomeric Blends by Phase Modification, *J. Appl. Polym. Sci.*, **38**(6): 1091–1109.
8. Borggreve, R.J.M., Gaymans, R.J. and Schuijjer, J. (1989). Impact Behavior of Nylon-rubber Blends, *Polymer*, **30**(1): 71–77.

9. Greco, R., Malinconico, M., Martuscelli, E., Ragosta, G. and Scarinzi, G. (1987). Role of Degree of Grafting of Functionalized Ethylene-propylene Rubber on the Properties of Rubber-modified Polyamide-6, *Polymer*, **28**(7): 1185–1189.
10. Cimmino, S., Coppola, F., D'Orazio, L., Greco, R., Maglio, G., Malinconico, M., Mancarella, C., Martuscelli, E. and Ragosta, G. (1986). Ternary Nylon-6/Rubber/Modified Rubber Blends: Effect of the Mixing Procedure on Morphology, Mechanical and Impact Properties, *Polymer*, **27**(12): 1874–1884.
11. Cimmino, S., D'Orazio, L., Greco, R., Maglio, G., Malinconico, M., Mancarella, C., Martuscelli, E., Palumbo, R. and Ragosta, G. (1984). Morphology-properties Relationships in Binary Polyamide 6/Rubber Blends: Influence of the Addition of a Functionalized Rubber, *Polym. Eng. Sci.*, **24**(1): 48–56.
12. Hobbs, S.Y., Bopp, R.C. and Watkins, V.H. (1983). Toughened Nylon Resins, *Polym. Eng. Sci.*, **23**(7): 380–389.
13. Kim, B.K., Park, S.Y. and Park, S.J. (1991). Morphological, Thermal and Rheological Properties of Blends Polyethylene/Nylon-6, Polyethylene/Nylon-6/(maleic anhydride-g-polyethylene) and (maleic anhydride-g-polyethylene)/Nylon-6, *European Polymer J.*, **27**(4): 349–354.
14. Liu, N.C., Baker, W.E. and Russell, K.E. (1990). Functionalization of Polyethylenes and their use in Reactive Blending, *J. Appl. Polym. Sci.*, **41**(9): 2285–2300.
15. Ide, F. and Hasegawa, A. (1974). Studies on Polymer Blend of Nylon 6 and Polypropylene or Nylon 6 and Polystyrene using the Reaction of Polymer, *J. Appl. Polym. Sci.*, **18**(4): 963–974.
16. Park, S.J., Kim, B.K. and Jeong, H.M. (1990). Morphological, Thermal and Rheological Properties of Blends Polypropylene/Nylon-6, Polypropylene/Nylon-6/(maleic anhydride-g-polypropylene) and (maleic anhydride-g-polypropylene)/Nylon-6, *European Polymer J.*, **26**(2): 131–136.
17. Dagli, S.S., Xanthos, M. and Biesenberger, J.A. (1991). *Proceedings of the Annual Technical Conference of SPE*, p. 969.
18. Campbell, J.R., Hobbs, S.Y., Shea, T.J. and Watkins, V.H. (1990). Polyphenylene Oxide/Polyamide Blends via Reactive Extrusion, *Polym. Eng. Sci.*, **30**(17): 1056–1062.
19. Carrot, C., Guillet, J. and May, J.F. (1991). Blends of Polyamide-6 with ABS, Effect of a Compatibilizer on Adhesion and Interfacial Tension, *Plast. Rubber Compos. Process. Appl.*, **16**: 61–66.
20. Angola, J., Fujita, Y., Sakai, T. and Inoue, T. (1988). Compatibilizer-aided Toughening in Polymer Blends Consisting of Brittle Polymer Particles

- Dispersed in a Ductile Polymer Matrix, *J. Polym. Sci., Part B: Polym. Phys.*, **26**(4): 807–816.
21. Triacca, V.J., Ziaee, S., Barlow, J.W., Keskkula, H. and Paul, D.R. (1991). Reactive Compatibilization of Blends of Nylon-6 and ABS Materials, *Polymer*, **32**(8): 1401–1413.
 22. Vaidya, U.R. and Bhattacharya, M. (1994). Properties of Blends of Starch and Synthetic Polymers Containing Anhydride Groups, *J. Appl. Polym. Sci.*, **52**(5): 617–628.
 23. Bhattacharya, M., Vaidya, U.R., Zhang, D. and Narayan, R. (1995). Properties of Blends of Starch and Synthetic Polymers Containing Anhydride Groups. II. Effect of Amylopectin to Amylose Ratio in Starch, *J. Appl. Polym. Sci.*, **57**(5): 539–554.
 24. Mani, R. and Bhattacharya, M. (1998). Properties of Injection Moulded Starch/Synthetic Polymer Blends – III. Effect of Amylopectin to Amylose Ratio in Starch, *European Polymer J.*, **34**(10): 1467–1475.
 25. Bhattacharya, M., John, J., Tang, J. and Yang, Z. (1997). Synthesis and Characterization of Anhydride-functional Polycaprolactone, *J. Polym. Sci., Part A: Polym. Chem.*, **35**(6): 1139–1147.
 26. Bhattacharya, M., Mani, R. and Tang, J. (1999). Functionalization of Polyesters with Maleic Anhydride by Reactive Extrusion, *J. Polym. Sci., Part A: Polym. Chem.*, **37**(11): 1693–1702.
 27. Narayan, R., Carlson, D., Nie, L. and Dubois, P. (1999). Maleation of Polylactide (PLA) by Reactive Extrusion, *J. Appl. Polym. Sci.*, **72**(4): 477–485.
 28. Mani, R. and Bhattacharya, M. (2001). Properties of Injection Moulded Blends of Starch and Modified Biodegradable Polyesters, *European Polymer J.*, **37**(3): 515–526.
 29. Dubois, P. and Narayan, R. (2003). Biodegradable Compositions by Reactive Processing of Aliphatic Polyester/Polysaccharide Blends, *Macromolecular Symp.*, **198**(1): 233–243.
 30. Avella, M., Errico, M.E., Rimedio, R. and Sadocco, P. (2002). Preparation of Biodegradable Polyesters/High-amylose Starch Composites by Reactive Blending and their Characterization, *J. Appl. Polym. Sci.*, **83**(7): 1432–1442.
 31. Liu, N.C. and Baker, W.E. (1991). *POLYBLENDS-91*, Montreal, Canada, October 1991.
 32. Fowler, M.W. and Baker, W.E. (1988). Rubber Toughening of Polystyrene through Reactive Blending, *Polym. Eng. Sci.*, **28**(21): 1427–1433.
 33. Chen, B.S.Y. and Henton, D.E. (1989). Functionalized Elastomers Blended with Polar Copolymers of Styrene and Acrylic Acid Methacrylic Acid or Maleic Anhydride, US Patent# 4,886,856.

34. Bhattacharya, M., John, J. and Tang, J. (1998). Grafting of Oxazoline Functional Group to Polycaprolactone, *J. Appl. Polym. Sci.*, **67**(11): 1947–1955.
35. Jane, J.L., Schwabacher, A.W., Ramrattan, S.N. and Moore, J.A. (1992). Biodegradable Starch Plastics Incorporating Modified Polyethylene, US Patent# 5,115,000.
36. Innocentini-Mei, L.H., Bartoli, J.R. and Baltieri, R.C. (2003). Mechanical and Thermal Properties of Poly(3-hydroxybutyrate) Blends with Starch and Starch Derivatives, *Macromolecular Symp.*, **197**(1): 77–87.
37. Narayan, R., Krishnan, M. and Dubois, P. (1999). Aliphatic Polyester-grafted Starch-like Polysaccharides by Ring-opening Polymerization, *Polymer*, **40**(11): 3091–3100.
38. Narayan, R., Krishnan, M., Snook, J.B., Gupta, A. and DuBois, P. (1999). Bulk Reactive Extrusion Polymerization Process Producing Aliphatic Ester Polymer Compositions, US Patent# 5,969,089.
39. Narayan, R., Krishnan, M., Snook, J.B., Gupta, A. and DuBois, P. (1999). Bulk Reactive Extrusion Polymerization Process Producing Aliphatic Ester Polymer Compositions, US Patent# 5,906,783.
40. Narayan, R., Krishnan, M., Snook, J.B., Gupta, A. and DuBois, P. (1999). Bulk Reactive Extrusion Polymerization Process Producing Aliphatic Ester Polymer Compositions, US Patent# 5,801,224.
41. De Graff, R.A. and Janssen, L.P.B.M. (2000). The Production of new Partially Biodegradable Starch Plastic by Reactive Extrusion, *Polym. Eng. Sci.*, **40**(9): 2086–2094.
42. Bagley, E.B., Fanta, G.F., Burr, R.C., Doane, W.M. and Russell, C.R. (1977). Graft Copolymers of Polysaccharides with Thermoplastic Polymers. A New Type of Filled Plastic, *Polym. Eng. Sci.*, **17**(5): 311–316.
43. Fanta, G.F., Trimnell, D. and Salch, J.H. (1993). Graft Polymerization of Methyl Acrylate-vinyl Acetate Mixtures onto Starch, *J. Appl. Polym. Sci.*, **49**(9): 1679–1682.
44. Tahan, M. and Zilkha, A. (1969). Anionic Graft Polymerization of Ethylene Oxide on Starch. I, *J. Polym. Sci., Part A1*, **7**: 1815–1824.
45. Tahan, M. and Zilkha, A. (1969). Anionic Graft Polymerization of Ethylene Oxide on Starch. II, *J. Polym. Sci., Part A1*, **7**: 1825–1837.
46. Otey, F.H., Westhoff, R.P. and Doane, W.M. (1980). Starch-based Blown Films, *Ind. Eng. Chem. Prod. Res. Dev.*, **19**: 592–595.
47. Pledger, Jr., H., Young, T.S., Wu, G.S., Butler, G.B. and Hoegen-Esch, T.E. (1985). Synthesis and Characterization of Water-soluble Starch-Acrylamide Graft Copolymers, *J. of Macromol. Sci.- Chem.*, **A22**(4): 415–436.
48. Kalambur, S. and Rizvi, S.S.H. (2004). Starch-based Nanocomposites by Reactive Extrusion Processing, *Polym. Int.*, **53**(10): 1413–1416.

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