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New intercalated layer silicate nanocomposites based on synthesized starch-*g*-PCL prepared via solution intercalation and in situ polymerization methods: As a comparative study

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ABSTRACT

Starch-*g*-polycaprolacton (Starch-*g*-PCL) nanocomposites have been prepared with graft polymerization through in situ ring-opening polymerization of ε-caprolacton in the presence of starch and $Sn(Oct)_2$ (Tin(II) 2-ethyl hexanoate) as an initiator/catalyst. A surface-modified montmorillonite by dimethyl (hydrogenated tallow alkyl) ammonium cation, was used. In fact, the related nanocomposites prepared via two methods in solution and in situ with introducing different amount of loading clay. The effect of swelling time on *d*-spacing of silicate layers was investigated and the obtained nanocomposites were analyzed using X-ray diffraction technique. The morphology of the synthesized nanocomposites examined using Scanning Electron Microscopy (SEM) and also the thermal degradation behavior of the prepared nanocomposites accomplished with using TGA.

1. Introduction

In order to develop an environmentally friendly material, many efforts have been made to solve problems generated by plastic wastes, particularly by one-time-use disposable commodity materials. Most of the research attention was focused on the replacement of Petro-based commodity plastics in a cost-effective manner by biodegradable material with competitive mechanical properties. Biopolymers have been considered as most promising materials for this purpose. Among natural polymers, starch has been considered as one of the most promising candidates for the future, primarily because of an attractive combination of availability, price and performance. Starch consists of the linear α-glucan amylose and highly branched amylopectin. Starches in their native forms, are organized into semi crystalline granules (Hizukuri, Takeda, Yasuda, & Suzuki, 1981; Thompson, 2000; Hoover, 2001; Gérard, Planchot, Colonna, & Bertoft, 2000). Several studies have been carried out on starch-based films obtained by melt processing or casting film of a solution or gel with addition of a plasticizer (García, Martino, & Zaritzky, 2000; Kalambur & Rizvi, 2006). The addition of water or other plasticizers such as sorbitol (Gaudin, Lourdin, Forssell, & Colonna, 2000) and glycerol, considerably improves mechanical properties. Even though, starch films have poor mechanical properties when compared to those of synthetic polymers. This is due to their hydrophilic nature and thus their sensitivity to moisture content, a factor that is difficult to control. In order to improve mechanical properties and water resistance, starch has been modified (Morikawa & Nishinari, 2000; Curvelo, de Carvalho, & Agnelli, 2001; Mani, Tang, & Bhattacharya, 1998; Rutot, Degee, Nayaran, & Dubois, 2000; Matzinos, Tserki, Kontoyiannis, & Panayiotou, 2002; Mani & Bhattacharya, 2001; Dufresne, 2006) by blending with synthetic or natural polymers and modified with aliphatic polyesters, such as PCL, poly (hydroxyl butyrate), poly lactic acid and poly (glycolic acid) (Namazi & Dadkhah 2008; Wang & Gross, 1998). Among them poly (ε-caprolacton) is a particularly promising polymer. It is a plastic with high flexibility and also is biodegradable. Recently a new class of hybrid materials of polymers and layered silicates has emerged (Dietsche & Mulhaupt, 1999; Lim & Park, 2001). This class of materials have improved the material properties due to the high aspect ratio and easy phase-to-phase energy transfer, even at very low filler concentration, if the filler is uniformly and completely dispersed in the host matrix (LeBaron et al.,1999; Lee, Hur, Yang, Lim, & Kim, 2006; McGlashan & Halley, 2003; Ray & Okamoto, 2003). The introduction of inorganic fillers that commonly used nanoclays includes montmorillonite, a 2:1 phylosilicate. Nanoclays have a stacked platelet structure with each platelet having a thickness of approximately 1 nm and lateral dimensions on the order of micrometers.

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Unmodified nanoclays have a hydrophilic interlayer between each platelet that can be rendered more hydrophobic through a cation exchange process involving alkylammoniums. Starch has been filled with layered silicates and an improvement in mechanical and barrier properties was observed (Park et al., 2002; Pandey & Singh, 2005; Kalambur & Rizvi, 2004; Avella et al., 2005; Pandey et al., 2005). In the present work we investigated the preparation of starch-*g*-PCL nanocomposites with Closite 15A (montmorillonite surface-modified by dimethyl hydrogenated tallow alkyl ammonium cation) and in fact related nanocomposites were prepared through two methods in solution intercalation and in situ polymerization with different amount of loading clay. The dispersion of clay into starch-*g*-PCL matrix examined using XRD and morphology of some samples investigated through SEM.

2. Experimental

2.1. Materials

Potato starch was obtained from Merck. (Germany) Organo clay (Closite 15A) was from Southern Clay Product (USA), having CEC of 125 meq/100 g clay. Stannous 2-ethylhexanoate $Sn(Oct)_2$ and ε-caprolacton were purchased from Fluka.

2.2. Preparation of starch-g-PCL

In a typical experiment, 3 g of ε-caprolacton was added to 3 g of starch in a 100 ml round-bottomed flask equipped with a stirrer and a rubber septum and previously purged with nitrogen (Dubois, Krishnan, & Narayan, 1999). A determined amount of $Sn(Oct)_2$ was then introduced via a conditioned syringe at the desired temperature (see Table 1). Polymerization was stopped by fast cooling to room temperature and monomer conversion determined by selective precipitation of the polymeric fraction and starch in heptane. The homopolymers was extracted in toluene after 24 h at room temperature and the characteristic peaks at 1730 and 3400 cm^{-1} FT-IR spectrum was confirmed the graft formation of ε-caprolactone.

2.3. Preparation of starch-g-PCL nanocomposites with solution intercalation method

The different amount of C15A dispersed and swelled in 10 ml toluene for 3 h. Then 3 g starch-g-polycaprolacton was added for 2 h at 100–110 °C with continuous stirring and the products was then poured on dishes and solvent evaporated at 50–60 °C. The prepared samples are shown in Table 2.

2.4. Preparation of starch-g-PCL nanocomposites through in situ polymerization method

The 5 wt% C15A swelled and dispersed in 3 g ε-caprolacton for 18 h under nitrogen atmosphere, then 3 g starch was added for 3 h with continuous stirring and a determined amount of $Sn(Oct)_2$ was then introduced via a conditioned syringe at the desired temperature. Polymerization stopped by fast cooling at room temperature. Methods of sample preparations are shown in Table 3.

Table 1
Synthesis of Starch/PCL (50/50 wt%)

Sn content (wt%)	T(°C)	Reaction time (h)	Conversion monomer
0.4	100	20	99.5
0.2	150	5	98

Table 2
Preparation nanocomposites with solution intercalation method

Samples	Loading clay (wt%)	Starch-*g*-PCL (g)	Reaction time (h)
C15A	100	0	0
NC_1	2.5	1	5
NC_2	2.5	1	20
NC_3	5	1	5
NC_4	5	1	20
NC_5	7.5	1	5
NC_6	7.5	1	20
NC_7	10	1	5
NC_8	10	1	20

Table 3
Preparation of starch-*g*-PCL nanocomposites by in situ polymerization method (starch/clay: 50/50)

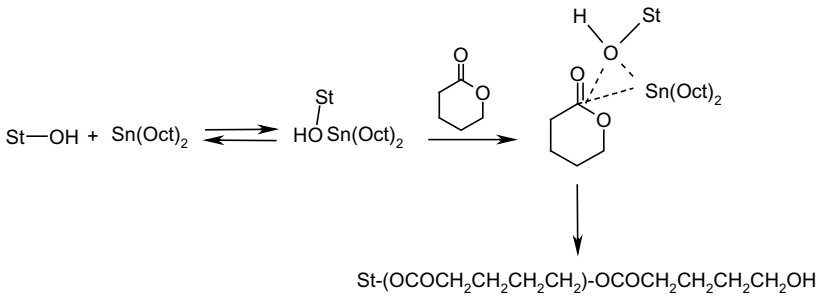
Samples	Loading clay (wt%)	Swelling time (h)	T(°C)	Reaction time (h)
NC9	5	1.5	150	5
NC10	5	18	150	5
NC11	5	18	100	20
NC12	5	48	100	20

3. Results and discussion

3.1. X-ray diffractions

The samples were prepared through the ring-opening polymerization as shown in Scheme 1 and FT-IR data analysis was confirmed the formation of grafting (Chen et al., 2005). The pattern of X-ray diffraction of the samples was obtained by Siemens diffractometer with Cu-kα radiation at 35 kV in the scan range of 2θ from 2° to 30°. The *d*-spacing was calculated by Bragg's equation where λ was 0.154 nm. This dispersion extent of silicate layers has typically been elucidated by XRD, which allow a direct evidence of polymer chain confinement into the silicate gallery. The presence of narrow peaks for all samples except pattern of pure starch is an evidence of the ordinary in clay layers and confirming the finite diffusion of copolymer chains with a repeat distance of few nanometers. It is generally thought that the polymer enters the organo clay galleries and forces apart the platelets (intercalation). As more polymers enter the gallery, the platelets become disordered, thus causing broader peak and a wider distribution of such peak. Starch has hydrophilic property in comparison to organo clay which is hydrophobic. The resulted copolymer from grafting polycaprolacton on starch showed a hydrophobic property and its compatibility increased with organo clay due to reaction time of 20 h which caused a better yield in comparison to 5 h reaction time. The samples NC2, NC4, NC6 and NC8 are related to the reaction time of 20 h and samples NC1, NC3, NC5 and NC7 for 5 h reaction time. The results of X-ray diffraction analyzes which are shown in Table 4 indicating that the first series of copolymer samples have been better diffused into gallery of organo clay (C15A) with interlayer spacing of $d = 3.15$ nm in comparison with second series of copolymer samples.

The obtained *d*-spacing of XRD patterns showed that the entrance of copolymer into gallery of organo clay and formation the intercalated structure for the prepared nanocomposites. The highest increased *d*-spacing related to NC4 with its loading amount of clay 5 wt% and 20 h reaction time. In all of the prepared samples by in situ method the C15A loading was 5 wt%. In sample NC9 *d*-spacing decreased due to 2 h swelling time of monomer in organo clay and addition of starch in 30 min time. The reason of this result could be related to the little diffusion of monomer into layers



Scheme 1. The reaction route of graft polymerization on starch granules.

Table 4
Results of X-ray diffraction

Samples	Loading clay wt%	2θ	*d*-Spacing (Å)
C15A	100	2.81	31.5
NC1	2.5	2.66	33.22
NC2	2.5	2.26	39.16
NC3	5	2.60	34.03
NC4	5	2.25	39.31
NC5	7.5	2.66	33.30
NC6	7.5	2.43	36.42
NC7	10	2.69	32.82
NC8	10	2.26	39.03
NC9	5	2.98	29.66
NC10	5	2.50	35.35
NC11	5	2.38	37.16
NC12	5	2.49	35.47

which allows the polymerization of PCL to take place out of the internal area of layers and pushing the polymer chains into layers and therefore, *d*-spacing decrease. As shown in Fig. 1 for the sample NC10 the swelling time was increased from 2 h to 18 h and X-ray results showed one peak in $2\theta = 2.5$. The sample NC11 with $2\theta = 2.38$ by swelling time of 18 h that was prepared in 20 h reaction time at 100 °C. In NC12 sample swelling time also was increased to 48 h and *d*-spacing = 3.47 nm was observed. Therefore, according to the X-ray data *d*-spacing was increased with changing reaction time, temperature and swelling time.

3.2. Scanning electron microscopy

For the prepared nanocomposites morphology and their changes was investigated by using SEM. Image of granules of

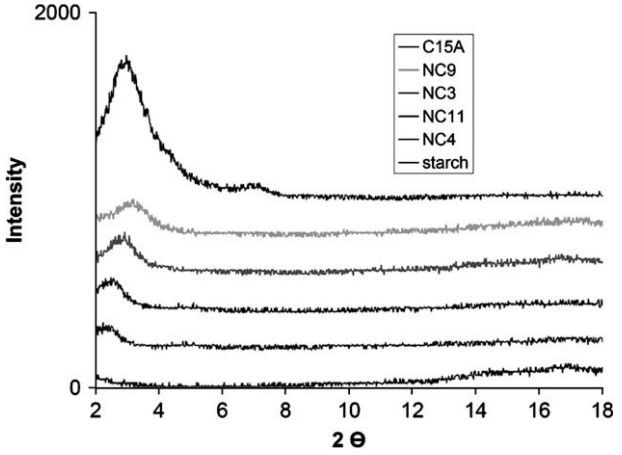


Fig. 1. Comparison of XRD patterns for different samples.

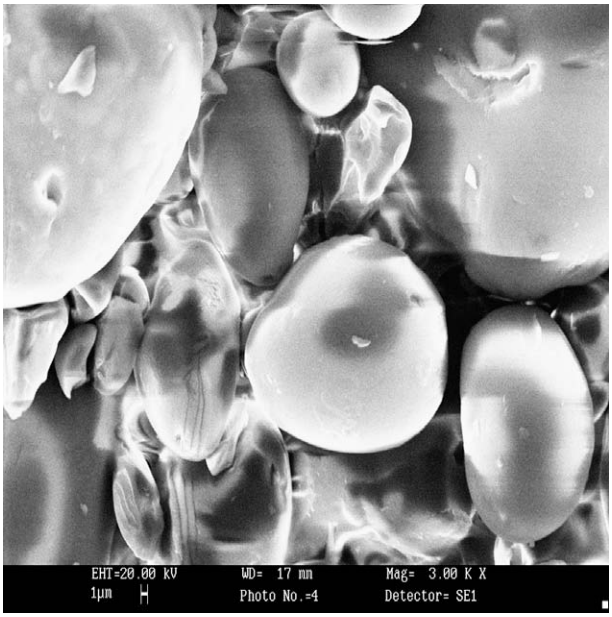


Fig. 2. Granules of pure potato starch.

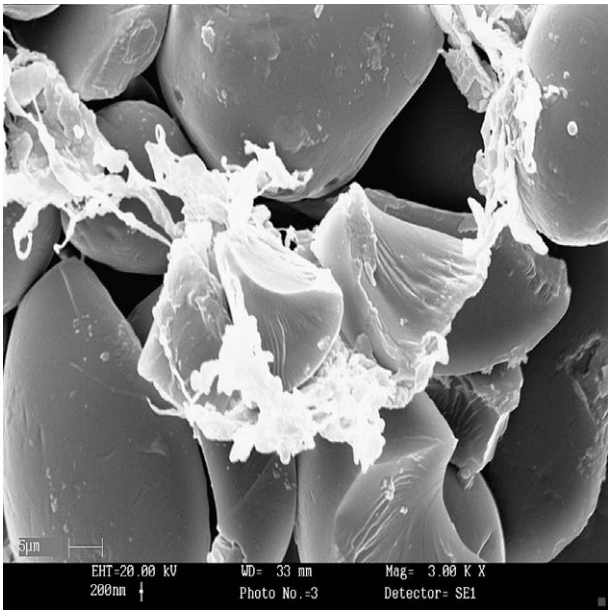


Fig. 3. Starch-*g*-PCL/5 h reaction time.

starch are shown in Fig. 2. Dimensions of granules are between 10 to several hundreds. SEM images related to starch-*g*-PCL with 5 and 20 h reaction times are shown in Figs. 3 and 4, respectively.

As shown in these images the reaction yield increased with using PCL for graft reaction on starch when the reaction time increased (Mani et al., 1998). In nanocomposite samples the shape of granules completely changed. The images of NC10 and NC4 are shown in Figs. 5 and 6, respectively.*3.3. Thermal gravimetry analyzes*

Thermal degradation behavior of prepared nanocomposite samples was studied through thermo gravimetric analysis TGA under an N_2 flow at a heating rate of 20 °C/min and Fig. 7 shows

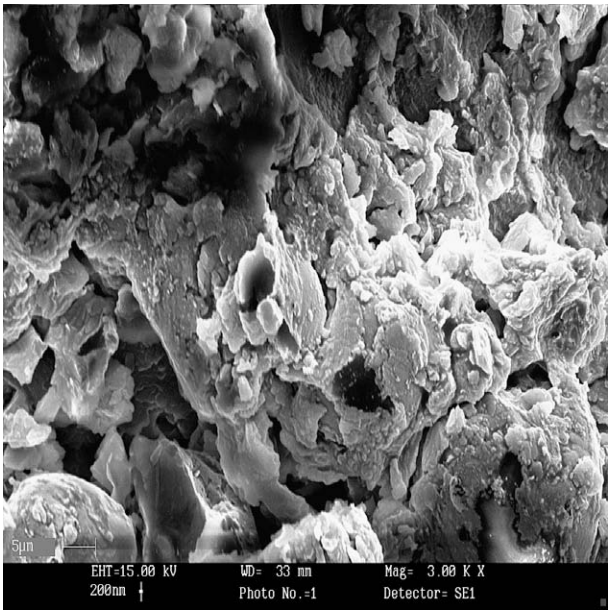


Fig. 4. Starch-*g*-PCL / 20 h reaction time.

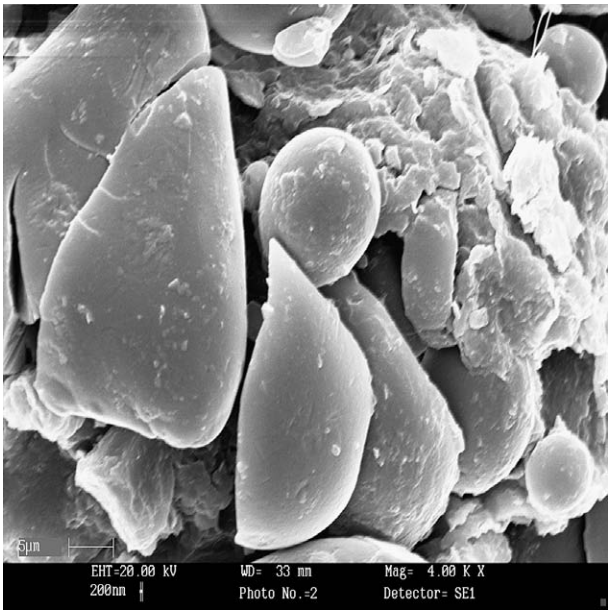


Fig. 5. Starch-*g*-PCL/clay (NC10).

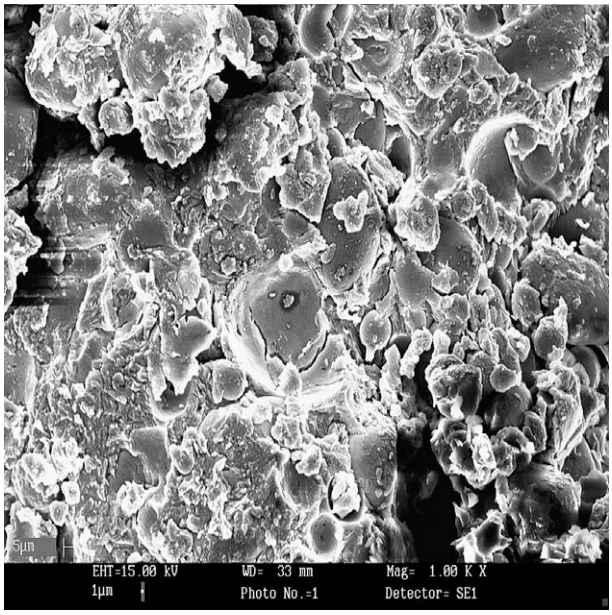


Fig. 6. Starch-*g*-PCL/clay (NC4).

TGA values and the data of related TGA is shown in Table 5 for the samples. The curves show that the decomposition of the samples takes place at different temperature. For starch alone the weight lost starts at 260 °C however, with rising grafting PCL chains on starch it happens at 360 °C. Also the thermal decomposition curves related to CN4 and CN11 nanocomposite samples shift towards the higher temperature in comparison to starch. The thermo gram shows that degradation of CN11and CN4 samples have been started in order at 282 °C and 323 °C. This shift to higher temperature might be explained by a lower permeability/diffusivity of oxygen and volatile degradation product through the sample as the result of barrier properties. At about 600 °C, all the curves merge together and became flat which indicates the presence of inorganic residue (i.e., AL_2O_3, MgO and SiO_2) (Yu, Lin, Yeh, & Lin, 2003). Therefore, as seen the decomposition product is mainly due to the polymer matrix and not from the clay particles.

4. Conclusions

Results of XRD analyses showed the best diffusion and intercalation of copolymer into galleries of organo clay that occurs through solution intercalation in comparison with in situ method. Because organo clay is compatible with copolymer starch-*g*-PCL while, it is not compatible with pure starch. Images of SEM showed a good yield for graft polymerization at 20 h reaction time and morphology of the granules had been changed. TGA investigations showed that with grafting caprolacton on starch thermal stability of both grafted starch and also their nanocomposites improved in comparison with thermal stability of pure starch.

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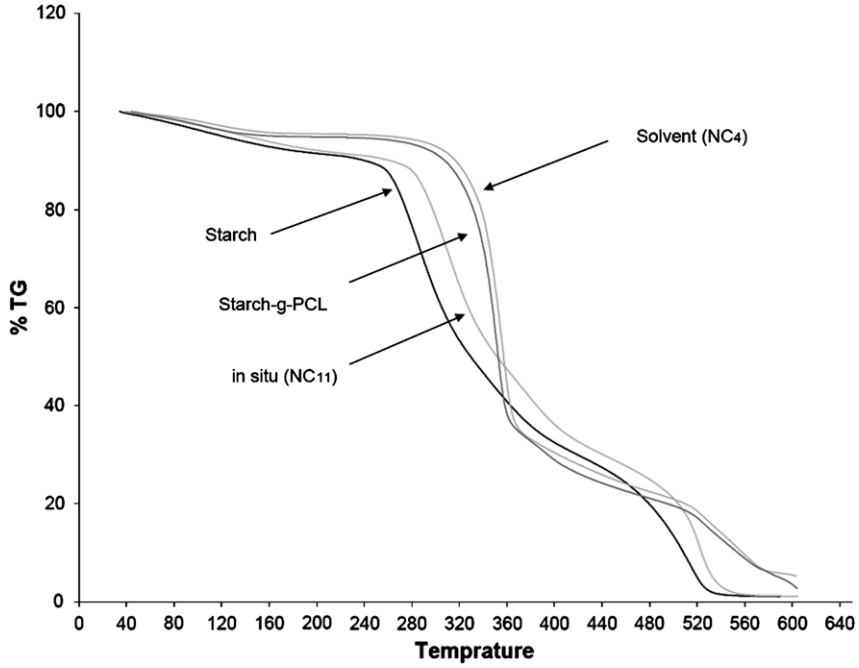

Fig. 7. Thermograms of starch, NC11, starch-*g*-PCL (20 h), NC4.

Table 5
Collected data from TGA

Sample	Loading clay (%)	T (°C) of loss 10 wt%	T (°C) of loss 50 wt%
Starch	0	258	326
Starch-*g*-CL	0	307	352
NC4 (solvent)	5	316	354
NC11(in situ)	5	262	352

References

Avella, M., Vlieger, J. J. D., Errico, M. E., Fischer, S., Vacca, P., & Volpe, M. G. (2005). Biodegradable starch/clay nanocomposite films for food packaging applications. *Food Chemistry, 93*, 467–474.

Chen, L., Ni, Yu., Bian, Xi., Qiu, Xu., Zhuang, Xi., Chen, Xu., et al. (2005). A novel approach to grafting polymerization of caprolactone on to starch granules. *Carbohydrate Polymers, 60*, 103–109.

Curvelo, A. A. S., de Carvalho, A. J. F., & Agnelli, J. A. M. (2001). Thermoplastic starch–cellulosic fibers composites: preliminary results. *Carbohydrate Polymers, 45*, 183–188.

Dietsche, F., & Mulhaupt, R. (1999). Thermal properties and flammability of acrylic nanocomposites based upon organophilic layered silicates. *Polymer Bulletin, 43*, 395–402.

Dubois, Ph., Krishnan, M., & Narayan, R. (1999). Aliphatic polyester-grafted starch-like polysaccharides by ring-opening polymerization. *Polymer, 40*, 3091–3100.

Dufresne, A. (2006). Comparing the mechanical properties of high performances polymer nanocomposites from biological sources. *Journal of Nanoscience and Nanotechnology, 6*, 322–330.

García, M. A., Martino, M. N., & Zaritzky, N. E. (2000). Microstructural characterization of plasticized starch-based films. *Starch–Starke, 52*, 118–124.

Gaudin, S., Lourdin, D., Forssell, P. M., & Colonna, P. (2000). Antiplasticisation and oxygen permeability of starch–sorbitol films. *Carbohydrate Polymers, 43*, 33–37.

Gérard, C., Planchot, V., Colonna, P., & Bertoft, E. (2000). Relationship between branching density and crystalline structure of A- and B-type maize mutant starches. *Carbohydrate Research, 326*, 130–144.

Hizukuri, S., Takeda, Y., Yasuda, M., & Suzuki, A. (1981). Multi-branched nature of amylose and the action of debranching enzymes. *Carbohydrate Research, 94*, 205–215.

Hoover, R. (2001). Composition, molecular structure, and physicochemical properties of tuber and root starches: a review. *Carbohydrate Polymers, 45*, 253–267.

Kalambur, S. B., & Rizvi, S. Sh. (2004). Starch-based nanocomposites by reactive extrusion processing. *Polymer International, 53*, 1413–1416.

Kalambur, S. B., & Rizvi, S. Sh. (2006). An overview of starch-based plastic blends from reactive extrusion. *Journal of Plastic Film and Sheeting, 22*, 39–58.

LeBaron, P. C., Wang, Z., & Pinnavaia, T. J. (1999). Polymer-layered silicate nanocomposites: an overview. *Applied Clay Science, 15*, 11–29.

Lee, S. S., Hur, M. H., Yang, H., Lim, S., & Kim, J. (2006). Effect of interfacial attraction on intercalation in polymer/clay nanocomposites. *Journal of Applied Polymer Science, 101*, 2749–2753.

Lim, Y. T., & Park, O. (2001). Phase morphology and rheological behavior of polymer/layered silicate nanocomposites. *Rheologica Acta, 40*, 220–229.

Mani, R., & Bhattacharya, M. (2001). Properties of injection moulded blends of starch and modified biodegradable polyesters. *European Polymer Journal, 37*(3), 515–526.

Mani, R., Tang, J., & Bhattacharya, M. (1998). Synthesis and characterization of starch-graft-polycaprolacton as compatibilizer for starch/polycaprolacton blends. *Macromolecular Rapid Communications, 19*, 283–286.

Matzinos, P., Tserki, V., Kontoyiannis, A., & Panayiotou, C. (2002). Processing and characterization of starch/polycaprolacton products. *Polymer Degradation and Stability, 77*, 17–24.

McGlashan, S. A., & Halley, P. G. (2003). Preparation and characterization of biodegradable starch-based nanocomposite materials. *Polymer International, 52*, 1767–1773.

Morikawa, K., & Nishinari, K. (2000). Rheological and DSC studies of gelatinization of chemically modified starch heated at various temperatures. *Carbohydrate Polymers, 43*, 241–247.

Namazi, H., & Dadkhah, A. (2008). Surface modification of starch nanocrystals through ring opening polymerization of ε-caprolactone and investigation of their microstructures. *Journal of Applied Polymer Science, 40*(4), 2405–2412.

Pandey, J. K., & Singh, R. P. (2005). Green nanocomposites from renewable resources: Effect of plasticizer on the structure and material properties of clay-filled starch. *Starch–Starke, 57*, 8–15.

Pandey, J. K., Kumar, A. P., Misra, M., Mohanty, A. K., Drzal, L. T., & Singh, R. P. (2005). Recent advances in biodegradable nanocomposites. *Nanoscience and Nanotechnology, 30*, 497–525.

Park, H. M., Li, X., Jin, Ch., Park, Ch., Cho, W., & Ha, Ch. (2002). Preparation and properties of biodegradable thermoplastic starch/clay hybrids. *Macromolecular Materials and Engineering*, 553–558.

Ray, S. S., & Okamoto, M. (2003). Polymer/layered silicate nanocomposites: a review from preparation to processing. *Progress in Polymer Science, 28*, 1539–1641.

Rutot, D., Degee, Ph., Nayaran, R., & Dubois, Ph. (2000). Aliphatic polyester-grafted starch composites by in situ ring opening polymerization. *Composite Interfaces, 7*, 215–225.

Thompson, D. B. (2000). On the non-random nature of amylopectin branching. *Carbohydrate Polymers, 43*, 223–239.

Wang, L. M., & Gross, R. A. (1998). Reactive compatibilization of biodegradable blends of poly(lactic acid) and poly(ε-caprolacton). *Polymer Degradation and Stability, 59*, 161–168.

Yu, Y. H., Lin, Ch. Y., Yeh, J. M., & Lin, W. (2003). Preparation and properties of poly(vinyl alcohol)–clay nanocomposite materials. *Polymer, 44*, 3553–3560.