Effect of Mixing Conditions on Mechanical Properties of Polylactide/Montmorillonite Clay Nanocomposites

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ABSTRACT: Biopolymer nanocomposites are of great interest to the packaging industry as they can overcome the inferior properties of biopolymers compared with synthetic polymers. However, studies on property improvement have been inconclusive about optimum filler levels and mixing conditions. This article reports on a systematic study of effect on mechanical properties of varying melt mixing conditions and filler level in PLA organoclay composites. Samples were mixed in a batch mixer at various temperatures, times, and speeds, at three filler levels. Tensile properties were measured and morphology characterized using small angle X-ray scattering (SAXS). An empirical model was used to predict the optimum mixing conditions. Samples produced at those conditions had the highest modulus of all samples, 66% higher than the average. Samples with different filler levels were made at the optimum conditions and tested for modulus and morphology. The maximum modulus, 40% higher than natural PLA, was achieved at 4 wt % filler level, and above that level modulus decreased, similar to findings in some studies but contrary to others. SAXS measurements indicated the samples had a similar intercalated morphology, so the excellent modulus results may be attributed to presence of smaller tactoids and absence of agglomerates rather than exfoliation. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1489–1493, 2010

Key words: biopolymer; nanocomposite; montmorillonite; mixing

INTRODUCTION

Polymer clay nanocomposites have been studied intensively for two decades. Biopolymers are of interest as replacement for synthetic polymers in many applications such as single use packaging. Polylactic acid (PLA) is one of the most widely used biodegradable biopolymers. Disadvantages of biopolymers include inferior rheological, thermal, and mechanical properties. These may be improved by addition of fillers such as organoclays, in particular, montmorillonite (MMT). Hence, recently, biopolymer nanocomposites have become an area of greater interest.

A few studies have reported on changes in biopolymer properties after adding small amounts of organoclay. Two techniques are generally used to produce nanocomposites: *in situ* polymerization and melt blending. Exfoliated structures are produced more readily by *in situ* polymerization. Paul et al.[1] found that *in situ* polymerization of PLA with 3% MMT (modified with quaternary ammonium ion, Cloisite 30B from Southern Clay Products) produced exfoliated morphology. Melt blending is the more common industrial technique and is the process used in most other studies. For example, Ray et al.[2,3] found that by melt blending 4% organoclay (MMT modified with octadecylammonium cation, from Nanocor) with PLA, the storage modulus increased 40% and by adding 7% clay, flexural modulus increased 20%. Hasook et al.[4] found melt blending 5% organoclay (treated with dimethyl distearyl ammonium ions) with PLA increased the tensile modulus by 20%. Di and coworkers[5] found that melt blending 5% organoclay (Cloisite 30B) with polycaprolactone (PCL) increased tensile modulus by 80%.

Good mixing is also needed to achieve good properties: the organoclay is agglomerated when added to the polymer and must be dispersed to achieve the high aspect ratios that produce excellent properties at low filler levels. However, few mixing studies have been done with these composites. Ray et al. produced intercalated PLA/clay nanocomposites using a twin screw extruder using one set of conditions (190°, no rpm given). Di and coworkers[6] produced well-dispersed PCL/clay nanocomposites using a twin screw mixer at 100°, 100 rpm for 12 min[5] and exfoliated PLA/clay nanocomposites at 170°, 100 rpm for 10 min. Neither group[7] reported how the conditions were chosen. Bourbigot et al.[8] reported a mixing study for PLA/clay

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nanocomposites with 3% Closite 30B using a DSM twin screw micro extruder at various speeds and residence times. They produced samples at 25, 50, and 100 rpm at 185° and residence time of 1–15 min under a nitrogen blanket. They reported the optimum conditions were "high shear stress" (100 rpm) for 1 min, then low shear stress (25 rpm) for an additional 5 min. These conditions produced a homogeneous partly exfoliated partly intercalated morphology. A DSM micro extruder has a recirculating channel so that residence time can be controlled. Hasook and coworkers[9] reported a mixing study for intercalated PLA/clay nanocomposites with 5% and 10% organoclay using a TSE co-rotating twin screw extruder at two speeds. They produced samples at 180° and 65 and 150 rpm, and found better properties at the higher speed.[4] This paper reports on effect of changes in temperature, screw speed and mixing time on nanocomposite morphology, and tensile properties, using an experimental design to develop a model to predict the optimum loading of clay required to obtain desired properties for packaging application.

Compatibilisers can be added to improve properties of polymer composites, but have not been used in most studies of PLA nanocomposites to date. Ray et al.[6] reported a study of PLA nanocomposites where up to 3% PCL was added as a compatibiliser. They reported an enhancement of mechanical properties and a change in morphology, attributed to better stacking of silicate layers. Hasook and coworkers reported a similar study of PLA nanocomposites where 5% PCL was added as a compatibiliser. They reported that addition of low molecular weight PCL decreased modulus, increased tensile strength, and did not change degree of dispersion, so concluded PCL was not acting as a compatibiliser. Paul and coworkers[1] demonstrated exfoliated morphology can be produced in *in situ* polymerized PLA/Cloisite 30B nanocomposites without using a compatibiliser,[1] and Di and coworkers[7] found the same in melt mixed PLA/Cloisite 30B nancomposites. Hence, no compatibiliser was used in this study.

Increasing the level of filler is also expected to improve properties, especially tensile modulus. Ray et al. reported that flexural modulus increased as loading was increased from 4 to 7 wt % of filler,[3] and Hasook et al.[4] reported that tensile modulus increased when filler was increased from 5 to 10 wt % in similar melt mixed PLA nanocomposites. However, Ray and coworkers identified 4 wt % filler as an optimum, as other mechanical properties decreased above this level. Nicolais and coworkers[3] reported finding an optimum level of loading of (5 wt %), above which all measured mechanical properties, including modulus, decreased, attributed to enhanced crystallization at the optimum filler level.[7] The different findings in different studies may be due to complex interactions of factors that change modulus at higher filler loadings. The level of filler was varied in this study to determine if an optimum could be found.

In summary, this article reports a study aimed at extending our understanding of the structure-property relationships of nanocomposites produced from a biodegradable polymer and a suitable organoclay by melt mixing. The mechanical properties were measured for samples produced with different filler levels and a variety of mixing conditions.

EXPERIMENTAL

The biopolymer used was PLA Natureworks sheet extrusion grade 2002D, melt flow index 5–7 g/10 min (210°, 2.16 kg). Polymer nanocomposite samples were produced by melt mixing PLA with 2 wt % organoclay montmorillonite (MMT) Southern Clay Products grade Cloisite® 30B. Cloisite® 30B is modified with a quaternary ammonium ion containing methyl tallow bis-2-hydroxyethyl. The PLA and MMT were dried for 24 h at 90° and then hand mixed before being introduced into the barrel of the Haake Rheochord Mixer preheated to 180°. The samples were mixed according to a full factorial experimental design. The advantage of experimental design is that it allows interactions between the parameters to be evaluated. The centre point was 175°, 60 rpm and 11 min mixing time. The "lo" settings were 165°, 40 rpm and 7 min. The "hi" settings were 185°, 80 rpm and 15 min. The conditions for each sample are shown in Table I. MINITAB™ was used to produce an empirical model for modulus in terms of the mixing parameters (MINITAB™ is a software program that can be used to determine the optimum values for control parameters).

After mixing, the melt was compressed into tensile test specimens or plaques in a compression molder at 180° for 5 min at 40 kN pressure. Tensile properties were evaluated using an Instron Universal Tester, with at least five specimens per sample, tested at 5 mm/min. The calculated average standard deviation for modulus was 10%, for tensile strength 5%, and for elongation at break 20%, consistent with other published work. Morphology of samples was evaluated using a Bruker Nanostar small angle X-ray scattering diffractometer (SAXS) with nickel filtered CuKα radiation of wavelength 1.54 Å operated for a range of 2θ angles from 0.5° to 12°.

RESULTS AND DISCUSSION

The results for tensile properties (modulus, tensile strength, and elongation at break) are given in Table

TABLE I
Sample Processing Conditions and Measured Tensile Properties

Mixing parameters (time/speed/temperature) (min/rpm/°C)	Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
7/60/175	4900	58	5.4
11/60/175	2800	59	3.3
15/60/175	3800	59	4.3
11/40/165	2600	60	3.2
11/40/175	3200	58	4.9
11/40/185	2900	57	5.4
11/60/175	2800	59	3.3
11/80/175	3200	59	4.4
15/80/185	2400	53	6.8
Average	3300	58	4.6
Standard deviation (s.d.)	320	2.9	0.9

I. Varying, the mixing parameters had the most effect on modulus. The values varied very significantly, ranging from 2400 to 4900 MPa (average ± ~ 3 s.d.). Elongation at break also varied significantly, from 3.2% to 6.8% (average ± ~ 1.5 s.d). The effect on tensile strength was not significant. Tensile strength varied from 53 to 60 MPa (average ± ~ 1 s.d.). Hence, modulus was used as the variable for modeling mechanical property behavior, to predict the optimum.

The mixing parameters and measured modulus for each point were input to MINITAB^{TM}, which then calculated the best fit quadratic equation of the form:

$$Y = \beta_o + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \quad (1)$$

where β_o is a constant, β_i is the coefficient of ith individual factor, β_{ii} is the coefficient of ith factor squared, β_{ij} is the coefficient of interaction between the ith and jth factors, and x_n ($n = i, j$) is the variable or factor value.

The values for the coefficients for each term of the model are shown in Table II. The coefficients are relatively large for the primary factors (A, B, and C) and smaller for the square of the factors and the interactions. If the coefficient is positive, the modulus increases. The model shows that mixing time increases modulus, whereas temperature and speed have a complex effect (as one coefficient is positive and one negative from the linear and squared terms). The interaction between temperature and mixing time was too small to measure. The model predicted that the mixing conditions (7/80/185 min/rpm/°) would produce the remarkably high modulus of 6900 MPa.

The model was tested for robustness by making samples at the predicted optimum mixing conditions. Samples made at these conditions were then tested for modulus. The measured modulus was

5500 MPa, which is in reasonable agreement with the model, although it is not as high as the model's prediction. It is noteworthy that 5500 MPa was significantly higher than the modulus measured for any of the other samples. It was 12% higher than the "best" sample made at nonoptimized conditions (4900 MPa), 66% higher than the average for all the samples (3300 MPa), and 130% higher than the "worst" sample (2400 MPa). Hence, making samples at optimized conditions significantly improved properties compared with processing the samples at other conditions.

Samples were then produced at the optimum mixing conditions with varying levels of Cloisite® 30B (0, 2, 4, and 6 wt %). Two samples were produced with 4 wt % to assess repeatability. A control sample with no filler was produced, with the same mixing history, to assess property improvement compared with the base polymer.

Table III shows the results for mechanical properties and composite morphology for samples produced at the optimum mixing conditions (7/80/185 min/rpm/°) at various levels of filler (0, 2, 4, and 6 wt %). The two samples produced at 4 wt % filler have similar properties, showing good repeatability

TABLE II
Terms and Coefficients for Model of Mixing Conditions and Modulus

Term		Coefficient
Constant	β_o	2700
Temperature (A, °)	β_1	170
Mixing time (B, min)	β_2	−550
Mixing speed (C, rpm)	β_3	100
Temperature × mixing temperature (A^2)	β_{11}	−450
Mixing time × mixing time (B^2)	β_{22}	1600
Mixing speed × mixing speed (C^2)	β_{33}	470
Temperature × mixing time (A × B)	β_{12}	−300
Mixing time × mixing speed (B × C)	β_{23}	−1800
Temperature × mixing speed (A × C)	β_{13}	~ 0

TABLE III
Measured Properties for Samples Produced at Varying Levels of Filler

Cloisite 30B (wt %)	Modulus (MPa)	Increase in modulus (%)	Tensile strength (MPa)	Elongation at break (%)	d (001) (2θ) (°)
0	4200	0	32	2.3	–
2	5500	31	53	2.6	2.44
4 (a)	5900	40	58	3.2	2.48
4 (b)	5800	38	59	2.8	
6	5200	24	45	2.3	2.44

of nanocomposite manufacture in our laboratory. The results further show that as the filler level increases, the modulus first increases compared with the unfilled PLA, then decreases slightly after 4 wt % filler (Fig. 1). The increase in modulus compared with the unfilled control PLA sample is around 40%, which is a very significant improvement. The increase is double that reported by Ray et al.[3] for flexural modulus and by Hasook et al.[4] for tensile modulus (for similar filler loadings). This demonstrates the efficacy of experimental design in optimizing mixing conditions for polymer nanocomposite manufacture by melt blending.

An empirical model of tensile modulus as a function of filler level was produced using a best fit quadratic equation. This predicted that a filler level of 3.7 wt % would produce the highest modulus value, 6000 MPa, an improvement of 43% compared with PLA. This is in good agreement with the optimum filler level reported by Nicolais and coworkers[7] (5 wt %) in a similar composite. It is also similar to the optimum level reported by Ray et al.[3] (4 wt %) for a basket of properties, although in their study flexural modulus continued to increase as filler loading increased. It is contrary to the findings of Hasook et al.[4] who reported tensile modulus increased when filler was increased in a similar PLA nanocomposite. The different findings in different studies may be due to complex interactions of fac-

tors affecting modulus in nanocomposites. These factors include: agglomeration of the filler at higher loadings, change from exfoliated to intercalated structure above the percolation threshold, degradation due to high heat history at sub optimal conditions, or mixing conditions optimized for low loadings of filler may not be optimal for higher loadings.

The diffraction angle measurements for the nanocomposite samples are shown in Figure 2 and the peak positions are given in Table III. The first 2θ peak was similar for all samples ($\sim 2.4°$), which corresponds to a d (001) peak of 3.6 nm (using Bragg's formula), in good agreement with values reported in the literature for similar systems, of 3 nm and 3.4 nm.[2–4,6] The presence of peaks at these angles indicates that the morphology was intercalated and not exfoliated.

Figure 2 shows that the size of the peak was approximately proportional to the filler level. This suggests that the samples with different filler loadings had similar morphologies. Hence, the improvement in properties for the samples produced at optimum mixing conditions may be attributed to presence of smaller intercalated tactoids, rather than presence of more exfoliated particles or absence of agglomerates. Other samples of different mixing conditions were not considered for SAXS analysis as it is clear from optimal mixing conditions that 7/80/185 gave the best mechanical properties. Thus, it is expected that all other samples will have dominant intercalated morphologies. Similar findings were
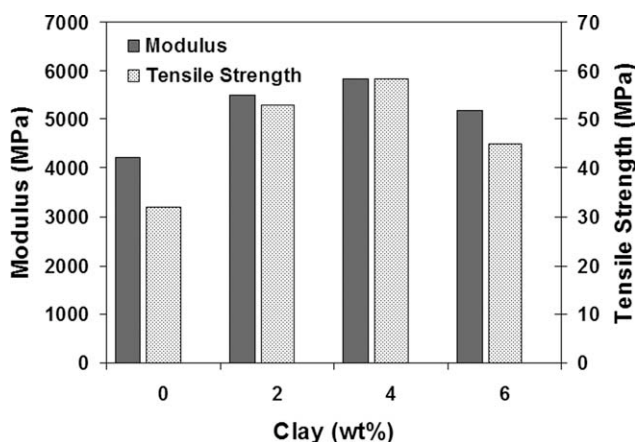

Figure 1 Mechanical properties of PLA and PLA nanocomposites with various clay loadings.
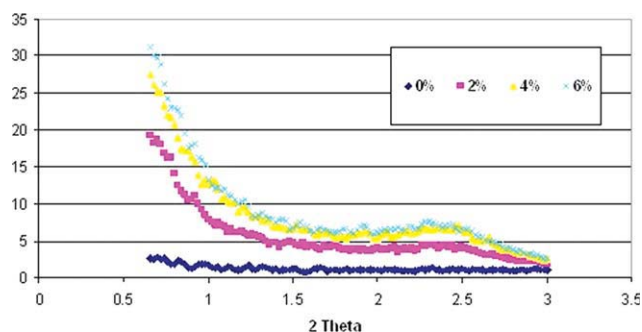

Figure 2 SAX patterns for PLA and PLA nanocomposites with various clay loadings. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

reported by Bhatia et al.[10] as showing TEM images of different PLA/PBS nanocomposites.

The percolation threshold of this system samples will be discussed in a future publication describing the rheology of the samples.

CONCLUSIONS

The best mixing conditions for melt blending of a polymer organoclay nanocomposite can be found by using experimental design and empirical modeling. Samples made at optimal conditions can achieve significant improvements in mechanical properties such as modulus. The tensile modulus is significantly higher than PLA (by 40%) and the "best" sample produced at sub optimal conditions (by 12%). The optimal filler loading for this system is around 4 wt %, consistent with reports of other studies of optimums at 4–5 wt %. The morphology is intercalated for filler loadings from 2 to 6 wt % based on X-ray diffraction. The excellent tensile modulus is attributed to presence of smaller tactoids and absence of agglomerates, rather than exfoliation.

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