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Phosphite stabilization effects on two-step melt-spun fibers of polylactide

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Abstract

The effects of molecular weight stabilization on mechanical properties of polylactide (PLA) fibers are investigated. The textile-grade PLA contains a 98:02 ratio of L:D stereocenters and fibers are produced by the two step method, involving a primary quench and cold drawing. Molecular weight loss, which is approximately 30% for unstabilized PLA, can be eliminated by the addition of small amounts of tris(nonylphenyl) phosphite prior to processing. The thermal and mechanical properties of fibers produced with two different concentrations of TNPP are compared to those of unstabilized PLA. Faster crystallization rates are obtainable with addition of the stabilizer, but final crystallinities are unaffected. Mechanical properties of the TNPP-enriched fibers are greatly improved over their unstabilized counterparts. Tensile strengths can be improved by 10–30% at a given draw ratio, while modulus may be improved by 10–25%. Excessive amounts of TNPP or insufficient mixing result in inhomogeneities that are deleterious to mechanical properties. Based on the available information, chain extension is believed to be the most likely mechanism for the molecular weight stabilization. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Polylactide; Poly(lactic acid); Stabilization; Fibers; Melt spinning; Molecular weight

1. Introduction

Although polylactide (PLA) has been traditionally used in biomedical applications, its pending competitiveness in the commodities market has raised the interest of a number of plastics manufacturers. The main applications currently targeted are fibers and packaging. Large-scale commercialization of PLA is underway: Cargill-Dow is now producing polymer in its first 300-million-lb-per-year PLA production plant in Blair, Nebraska. PLA is degradable, but the rate of degradation may be controlled through a variety of methods thus enabling a number of uses. Advantages of PLA include (1) availability from renewable resources, (2) reduction in carbon dioxide emissions generated during manufacturing compared to conventional commodity plastics, and (3) significant property advantages over other materials [1,2].

An important feature of PLA is that its monomer possesses chirality. The lactide monomer may contain identical stereocenters (L:L or D:D) or enantiomeric stereocenters (L:D). Copolymers of varying L:D composition can be synthesized from mixtures of the monomers. Fully amorphous materials can be made by including relatively high D content (greater than 20%), while highly crystalline materials are obtained when D content is low (less than 2%) [3].

Because PLA rapidly degrades at elevated temperatures, molecular weight loss during processing is an important issue. Previous fiber-spinning studies have resulted in losses between 28 and 43% [4,5]. Yuan et al. [6] encountered losses of up to 69% and Schmack et al. [7] experienced a 31% molecular weight reduction. Similarly, melt spinning by Fambri et al. [8] and Penning et al. [9] resulted in losses of over 60%. Generally, thermal degradation is more severe for melt spinning than for solution spinning [10]. Higher initial molecular weights also tend to degrade to greater extents. One of the main degradation mechanisms at high temperatures is hydrolysis. Although minimizing moisture content can help reduce losses, molecular weight preservation through the addition of a stabilizer agent during extrusion may be warranted.

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This study investigates the use of Tris(nonylphenyl) phosphite (TNPP) as a model stabilizer during the formation of PLA fibers via the two-step fiber spinning process (TSP). NMR is used to elucidate the mechanism of TNPP stabilization. Fibers processed in the presence of TNPP are compared to ones formed without stabilizer addition and it is clearly shown that fiber properties can be improved by the addition of TNPP.

2. Materials and methods

The polylactide used in this study was 6200D standard staple-fiber-grade, with an L:D ratio of approximately 98:02, provided by Cargill Dow (Minnetonka, MN). Initial number- and weight-averaged molecular weights were $M_n = 47{,}600$ and $M_w = 98{,}500$, respectively, as measured by light scattering. Tris(nonylphenyl) phosphite (TNPP) was obtained from Aldrich and used as received.

NMR spectra were recorded on a Chemagnetics Infinity 400 NMR spectrometer operating at 161.8 MHz for ^{31}P. Chemical shifts are relative to external 85% H_3PO_4, which was assigned a chemical shift of 0 ppm. The solvent was $CDCl_3$ and all the spectra were recorded at 25 °C. Two different samples were investigated: initial and final. Initial describes PLA compounded with TNPP at 180 °C for approximately 5 min. Final refers to disk shaped samples held at 200 °C for 30 min under flowing hot air to accentuate chemical effects of residence time during processing. Spectra for both initial and final samples were recorded in blocks of about 3 h. The final sample ^{31}P NMR spectra were independent of time and thus this spectrum corresponds to the addition of 20 blocks (about 60 h). In contrast, the initial sample ^{31}P NMR spectra exhibited significant changes as function of time and thus the spectrum for this sample correspond to only one block of data.

Prior to processing, the pellets were dried by spreading a 1-inch thick layer in the bottom of a stainless steel pan and placing it in a convection oven at 82 °C overnight (approximately 14 h). Expected water concentrations after drying were approximately 100 ppm [11]. After removal from the oven, the pellets were soaked with pure TNPP and the polymer pellet slurry was stirred to distribute the stabilizer. Two different concentrations were acheived: 0.11 and 0.80 wt.%. In the later case, in order to facilitate diffusion of TNPP into the pellets, the slurry was placed in an ultrasound bath at 70 °C for 60 min. Mass measurements of the initial pellets and the final TNPP soaked pellets were used to determine concentrations. After preparation and weighing, the mixture was placed into the extruder hopper, covered with plastic wrap to prevent water uptake and stabilizer evaporation, and immediately processed.

A two-step melt spinning process, detailed in a previous study [5], was used to prepare fibers. PLA is melt-extruded and quenched (Step 1) then heated to between the glass transition temperature and the melting temperature while being drawn (Step 2). The apparatus consisted of a Killion KL-125 single screw extruder mated to a pilot scale Killion monofilament line. In this study, the draw ratio (DR) refers to the cold-draw ratio, defined as the ratio of the velocity at the take-up winder to the velocity at the first godet. The nip roller and take-up winder speeds were adjusted to keep tension on the fiber. The first godet was operated at 60 feet per minute, and the speed of the second godet (and the winder) was varied to provide different draw ratios.

Light scattering, with THF as a solvent, was used to determine molecular weight of the starting PLA resin as well as the spun fibers. The molecular weight loss during processing was defined as

$$MWLoss = \frac{M_{wr} - M_{wf}}{M_{wr}} \times 100\%, \quad (1)$$

where M_{wr} and M_{wf} are the weight-average molecular weights of the resin and fiber, respectively.

Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC 7 running Pyris software. The DSC was calibrated with an indium standard prior to each set of analyses. Samples were prepared by cutting fibers into pieces of 2–4 mm in length and drying in a vacuum oven at 40 °C overnight, then placing approximately 10 mg into each aluminum pan. To minimize recrystallization in the DSC, the samples were ramped to 125 °C at the maximum heating rate (about 1000 °C/min) and subsequently scanned up to 200 °C at 15 °C/min.

Mechanical properties were measured using an Instron tensile tester fitted with fiber fixtures. Using a 2-kg load cell, specimens of 2-inch length were tested at a crosshead speed of 1.2 in/min. Prior to tensile testing, fiber diameters were measured with an optical microscope and LECO image analysis software after calibration. Results were reported as averages of ten tests for each sample.

3. Results and discussion

Triphenylphosphite (TPP) has been demonstrated to promote chain extension during the processing of polyethylene terephthalate (PET) [12]. The mechanism of chain extension occurs predominately by the rapid reaction of hydroxyl chain ends of the PET with the TPP, followed by esterification of carboxylic acid chain ends of PET with the phosphited chain end. This study investigates the use of an alternative triarylphosphite,

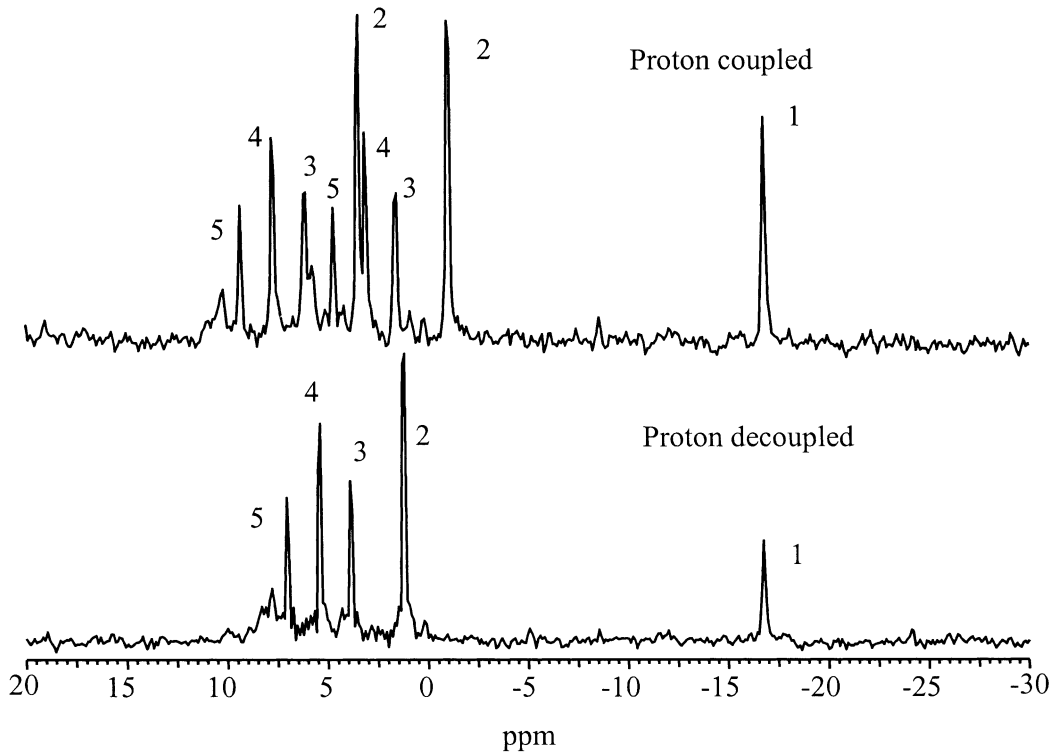


Fig. 1. Proton coupled and proton decoupled 161.9 MHz ^{31}P NMR spectra for the final sample of PLA with 4 wt.% TNPP.

tris(nonylphenyl) phosphite (TNPP), as an additive during processing of the completely aliphatic polyester, PLA. Previously reported rheology measurements show that the storage modulus of PLA at constant temperature can increase with time when TNPP is present, indicating that chain extension may occur [13,14]. Ultimately, the storage modulus decreases again at long enough times as the TNPP is consumed. The objectives of the present study are to investigate the effects of stabilization by TNPP, presumably due to chain extension reactions, on the mechanical properties of melt spun PLA fibers.

It should be noted that the degradation of PLA chains occurs via hydrolytic and non-hydrolytic mechanisms. Based on experimental evidence, Witzke reports that for non-hydrolytic degradation at 180 °C modeled using a zeroth-order rate law that the degradation rate is equal to 0.29 (mmol/kg h). For hydrolytic degradation modeled as first order in water and ester linkages, the corresponding degradation rate is 14.59 (mmol/kg h). Witzke reaches the conclusion that hydrolysis is the dominant degradation mechanism up to 215 °C after which non-hydrolytic degradation becomes equally important [11]. Nonetheless, in the present study it is prudent to keep in mind that at 180 °C there is a small contribution to PLA degradation by free radical and other non-hydrolytic mechanisms and that the phosphite may also help to suppress these degradation mechanisms.

An NMR analysis was performed in order to determine the phophorus species involved during processing. Figs. 1–3 show 161.9 MHz ^{31}P NMR spectra of PLA that has been compounded with 4 wt.% Tris(nonylphenyl) phosphite (TNPP). Fig. 1 shows both proton coupled and proton decoupled ^{31}P NMR spectra for the final (that is, heated at 200 °C for 30 min) sample. The proton decoupled spectrum shows five major resonance lines. When proton coupling is introduced, the spectrum becomes more complicated, indicating the presence of a number of phosphorus sites with ^{1}H–^{31}P couplings.

Both the proton coupled and proton decoupled spectra show a resonance line with a chemical shift of −16.7 ppm. Proton decoupling has no effect on its appearance, indicating negligibly small ^{1}H–^{31}P *J*-coupling for this phosphorus site. The lack of fine structure in the proton coupled spectrum indicates that protons are at least four bonds away. The chemical shift value of −16.7 ppm and the absence of fine structure indicate that this resonance is due to an organic phosphate phosphorus site; accordingly, peak 1 is assigned to the general structure (referred to as structure A) shown in Fig. 4. In this structure, each R can be a different organic group. No care was taken to prevent O_2 gas from entering the system during treatment; therefore, the formation of an organic phosphate may be the result of the reaction of TNPP with O_2.

Peaks 2–5 of Fig. 1 are all split into doublets when proton coupling is introduced, indicating that for these compounds, each phosphorus is coupled to one hydrogen. The values of the isotropic chemical shifts and ^{1}H–^{31}P J-couplings are summarized in Table 1.

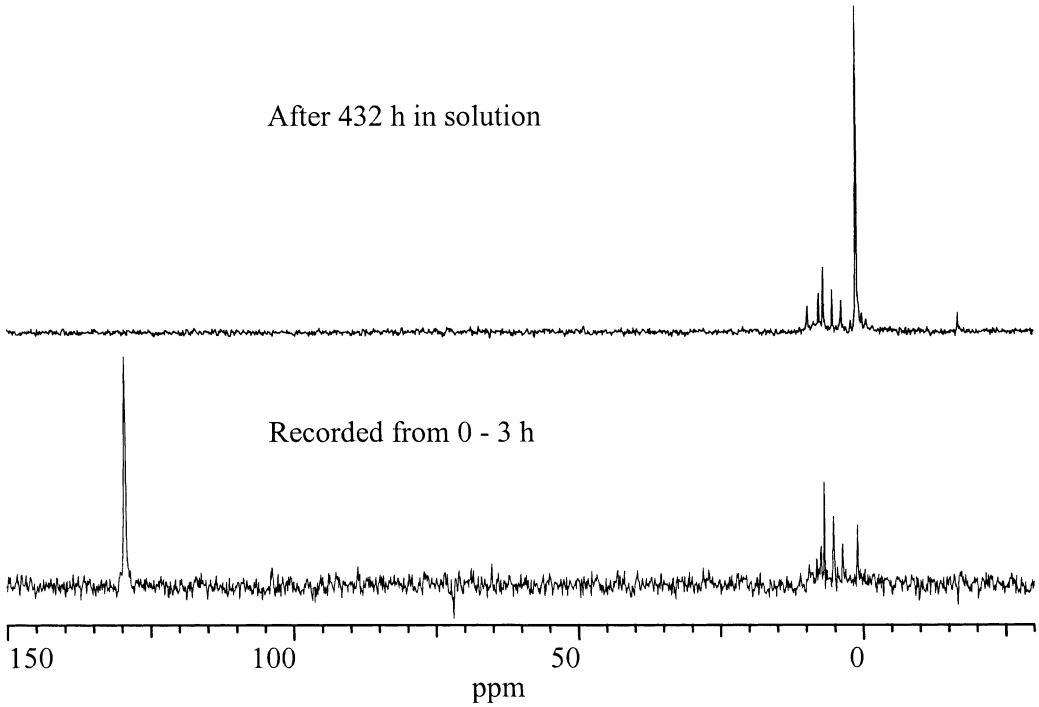


Fig. 2. 161.9 MHz ^{31}P NMR spectra for the initial sample at two different residence times in chloroform-d. The TNPP resonance line intensity decreases over time while the bis(nonylphenyl) phosphite line intensity increases.

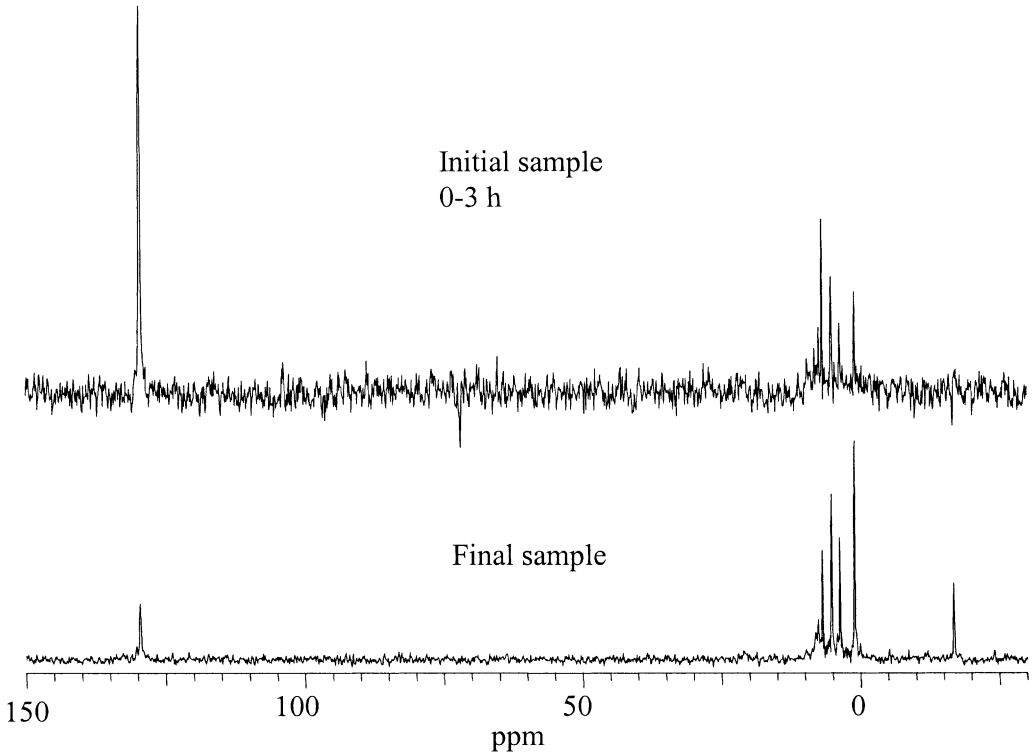


Fig. 3. Comparison of initial and final samples with 161.9 MHz ^{31}P NMR spectra. Thermal treatment, simulating residence time in an extruder, clearly results in consumption of TNPP.

The J-coupling of peaks 2–5 are all in the range of 725–750 Hz [13]. This range is expected for a phosphorus atom directly bonded to hydrogen. Based on comparison of the ^{31}P NMR spectrum obtained for the commercially available model compound diphenyl phosphite ($\delta = 0.89$ ppm, $^{1}J_{CH} = 730.6$ Hz), peak 2 is assigned to the structure (referred to as structure B) shown in Fig. 5, which is bis(nonylphenyl) phosphite.

The PLA used in this study was produced by a stannous octoate catalyzed ring opening polymerization of lactide monomer. PLA is expected to have hydroxyl and carboxylic end groups. These same end groups are also produced from any hydrolysis of the PLA. The hydroxyl groups are expected to react rapidly with the TNPP in a similar fashion to that demonstrated by PET stabilized with TPP [12]. The phosphited chain ends can then react with any carboxylic acid terminated PLA to result in chain extension through transesterification. This series of reactions is shown in Schemes 1 and 2. Scheme 2 provides one possible route towards the observed bis(nonylphenyl) phosphite. It should be noted that in Scheme 2, phosphorous may or may not be incorporated into the backbone of the polymer chain during chain extension.

The hydroxyl end group of PLA may also react with structure A (the phosphate resulting from the reaction of oxygen and TNPP) to produce structure D as shown in Scheme 3. The carboxylic acid end group reacting with structure D will provide structure E according to

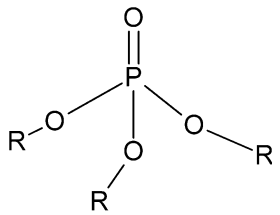


Fig. 4. General structure of organic phosphate present in the TNPP doped materials.

Table 1
Isotropic chemical shift and J-coupling values

Peak	Chemical shift (ppm)	J-coupling (Hz)
2	1.16	723.7
3	3.74	730.5
4	5.35	743.9
5	6.90	745.7

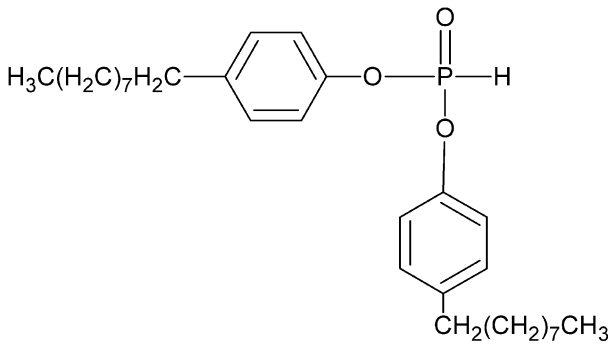
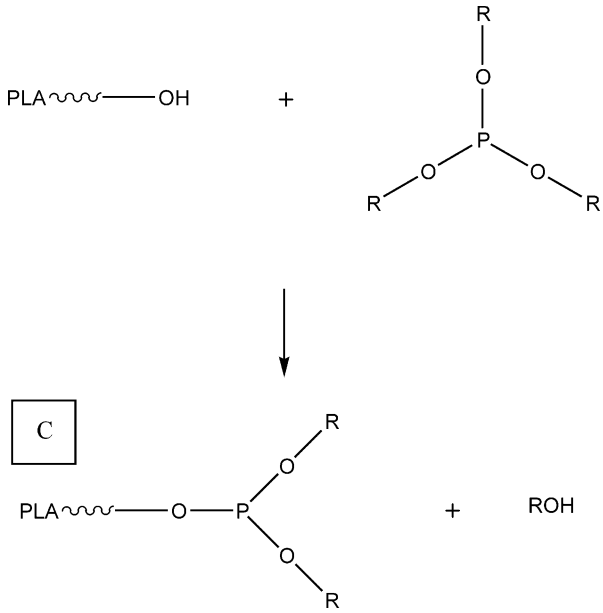
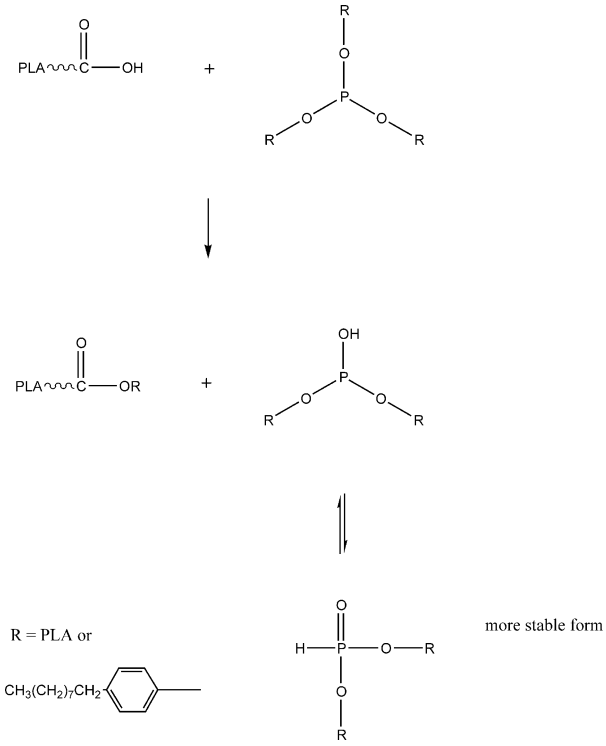


Fig. 5. Structure of bis(nonylphenyl) phosphite present in the TNPP doped materials.

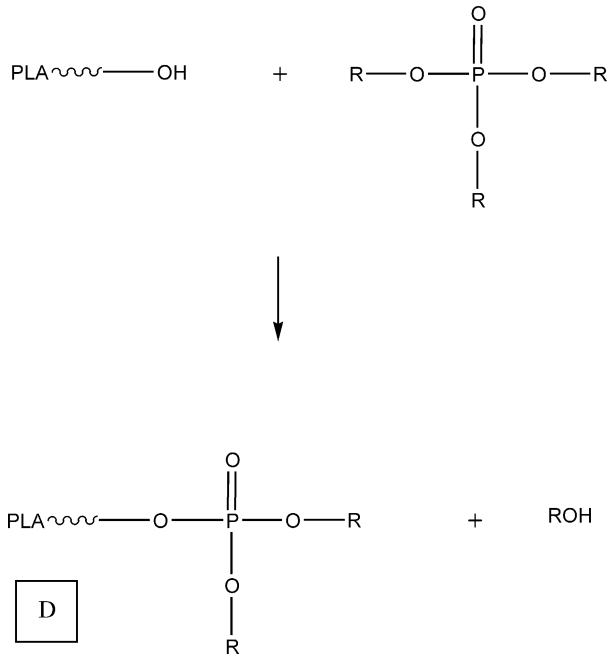


Scheme 1.

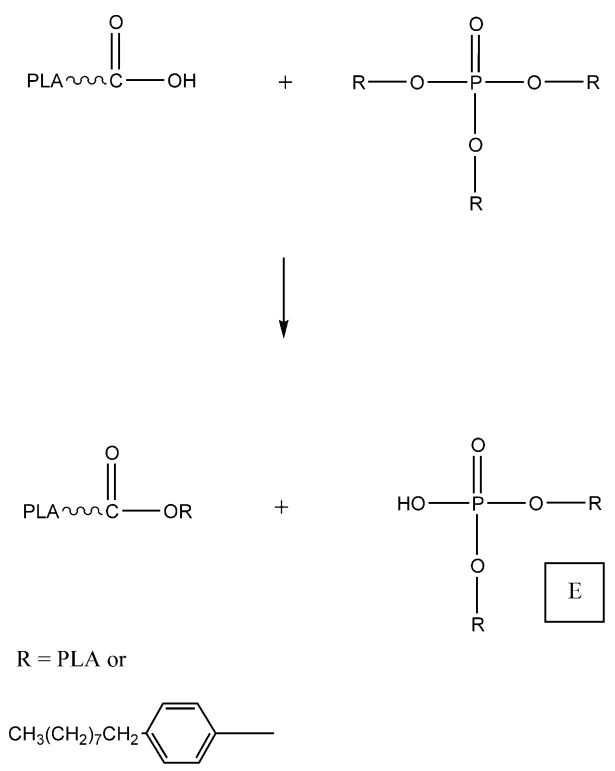


Scheme 2.

Scheme 4. However, there is no NMR evidence suggesting the existence of structure E in this system. This implies that this species is either generated only in trace quantities or that it is rapidly converted to another species.



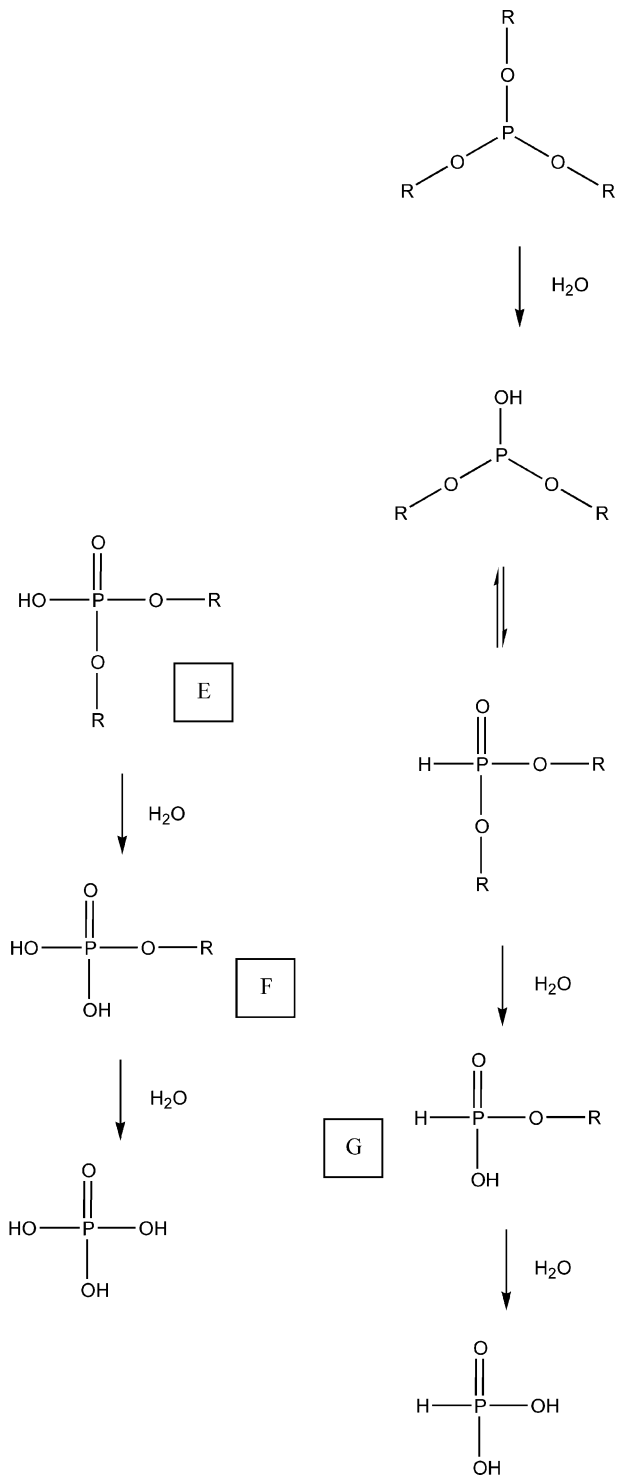
Scheme 3.



Scheme 4.

In addition to the chain-extending transesterification reactions, water may react with a number of phosphorus compounds, ultimately yielding phosphorous and phosphoric acids. These reactions are exhibited in Scheme 5 and give rise to structures labeled F and G.

For reference, dimethyl, diethyl and dibutyl phosphites have chemical shifts of 11, 8 and 8 ppm respec-



Scheme 5.

Table 2
Molecular weight change during processing for stabilized and unstabilized PLA

Material	M_{wr}	M_{wf}	Change (%)
0.11 wt.% TNPP	98 500	101 000	2
0.80 wt.% TNPP	98 500	97 400	−1
Unstabilized	98 500	71 300	−28

tively, and $^1J_{CH} = 673–707$ Hz. A 30% aqueous solution of phosphorous acid exhibits a chemical shift of 5 ppm and $^1J_{CH} = 690$ Hz. Phosphoric acid and structures E, F, and G probably have chemical shifts and *J*-couplings close to those listed in Table 1. Hence, it is not possible to assign structures to peaks 3–5 in Fig. 1 based on comparison with literature results alone.

Fig. 2 shows two ^{31}P NMR spectra of the initial sample. Each spectrum took about 3 h to acquire. The lower spectrum was recorded in the first 3 h after dissolution of the polymer in chloroform-d and the upper spectrum was obtained about 430 h later. The intensity of the TNPP peak, with a chemical shift of 129 ppm, decreases over time while that of the bis(nonylphenyl) phosphite, with chemical shift of 1.16 ppm, increases. The phosphate peak (compounds with general structure A and chemical shift of –16.7) also increases. These results indicate that the increased mobility of the TNPP and other reactants upon dissolution into chloroform-d increases encounters of reactive sites and hence formation of bis(nonylphenyl) phosphite.

Fig. 3 compares ^{31}P NMR spectra of the initial and final samples. Exactly as for the dissolution of the initial sample, the spectrum of the final material shows that the resonance lines at 1.16 and –16.7 ppm grow in intensity at the expense of the TNPP resonance line. Thus, thermal treatment increases the mobility of the TNPP and PLA sufficiently for reaction to occur, thereby increasing the concentration of bis(nonylphenyl) phosphite and phosphates due to transesterification.

Attention is now turned to the application of TNPP in fiber processing. Three types of PLA samples are employed. In the first, the PLA contains 0.11 wt.% TNPP. The concentration in the second is 0.80 wt.%, and the third data set represents the 0 wt.% (unstabilized) control. Experiments reveal that concentrations higher than 0.80 wt.% cause the extrudate to be highly inhomogeneous, presumably due to phase separation. Eight different draw ratios (1–8) are studied for each material. For a detailed review of the properties of unstabilized fibers, the reader is referred to a previous study [5].

The important aspects of molecular weight loss are summarized in Table 2. The loss for the unstabilized PLA is 28%, while enrichment with 0.80-wt.% TNPP reduces the loss to 1.1% while the molecular weight for the 0.11-wt.% batch increased by 2.5%. Given the experimental uncertainty in molecular weight measurement of a few thousand grams per mole established by repeated runs, it can be concluded that the TNPP is effective at concentrations above 0.10-wt.%. These findings are consistent with the premise that TNPP serves as a chain extender. It is evident that addition of TNPP in low concentrations drastically reduces thermal degradation of PLA during processing.

DSC shows no remarkable differences in the melting behavior of the unstabilized versus stabilized fibers. The melting temperature, T_m, is taken as the temperature at the maximum of the melting endotherm. Melting peaks for unstabilized samples are in the range of 160–163 °C while those of the stabilized fall in the range of 161–164 °C. In some unstabilized scans, a distinct second peak appears a few degrees lower than the main peak. In others, a clear shoulder can be seen on the low-temperature side of the melting peak. Similar observations have been made by Fambri et al. [8] and Spruiell et al. [15]. Although no two-peak melting endotherms are found for the stabilized fibers, a shoulder is visible on almost all samples. The presence of broad melting endotherms, endotherms with shoulders, and double-peak structures are usually interpreted as indicating different populations of lamellae thicknesses.

Fig. 6 is a plot of percent crystallinity vs. draw ratio for each batch. Percent crystallinity is determined by dividing the area under the melting endotherm by a value of 93.6 J/g for 100% crystalline PLA [16]. Essentially, no difference between the samples exists for draw ratios of 2–8. The only exception arises when DR = 1. Here, the 0.11-wt.% TNPP fibers are over 40% crystalline, but the unstabilized fibers are almost completely amorphous. It is possible that the TNPP may serve as a nucleating agent.

Stress–strain behavior for the three sets of fibers is nearly indistinguishable except for magnitude. The only difference lies in those fibers drawn to DR = 5. Typical stress–strain curves for these fibers are shown in Fig. 7. It is clear that immediately after the yield point for the unstabilized fiber, there is a significant plateau in the data, making the plot markedly non-monotonic. The curves for the stabilized fibers do not demonstrate the plateau. Accordingly, the unstabilized PLA probably necks more during the deformation. For all samples, modulus is determined by the slope at low deformations while tensile strength and strain-at-break are taken at the point of fracture, which is also the point of highest stress.

A plot of modulus vs. draw ratio is presented in Fig. 8. The effects of the TNPP stabilization are most apparent at intermediate draw ratios where the stabilized fibers have significantly higher values than the unstabilized ones. The modulus gain is presumably due to the higher molecular weight of the stabilized fibers. One aspect of the higher molecular weight is greater viscosity, which corresponds to greater stress in the spinline for the same

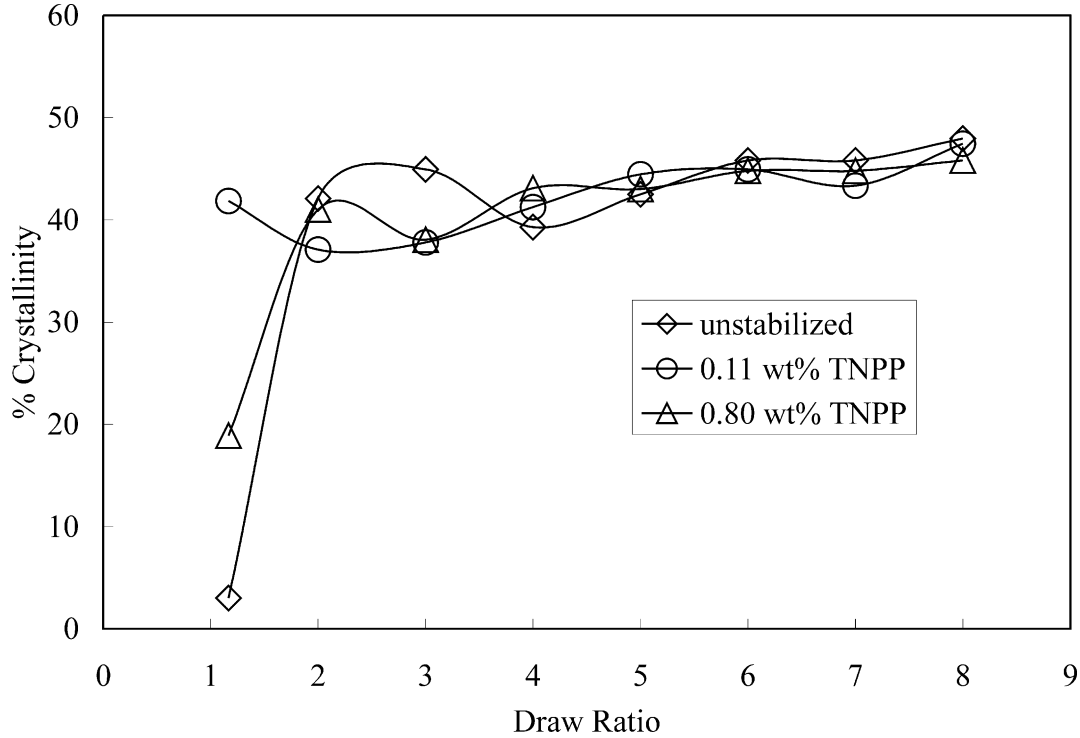


Fig. 6. Percent crystallinity vs. draw ratio for 0.11-wt.% TNPP, 0.80-wt.% TNPP, and unstabilized fibers. Note that the only real difference between the three batches occurs at DR = 1, where it is clear that addition of stabilizer results in faster crystallization kinetics.

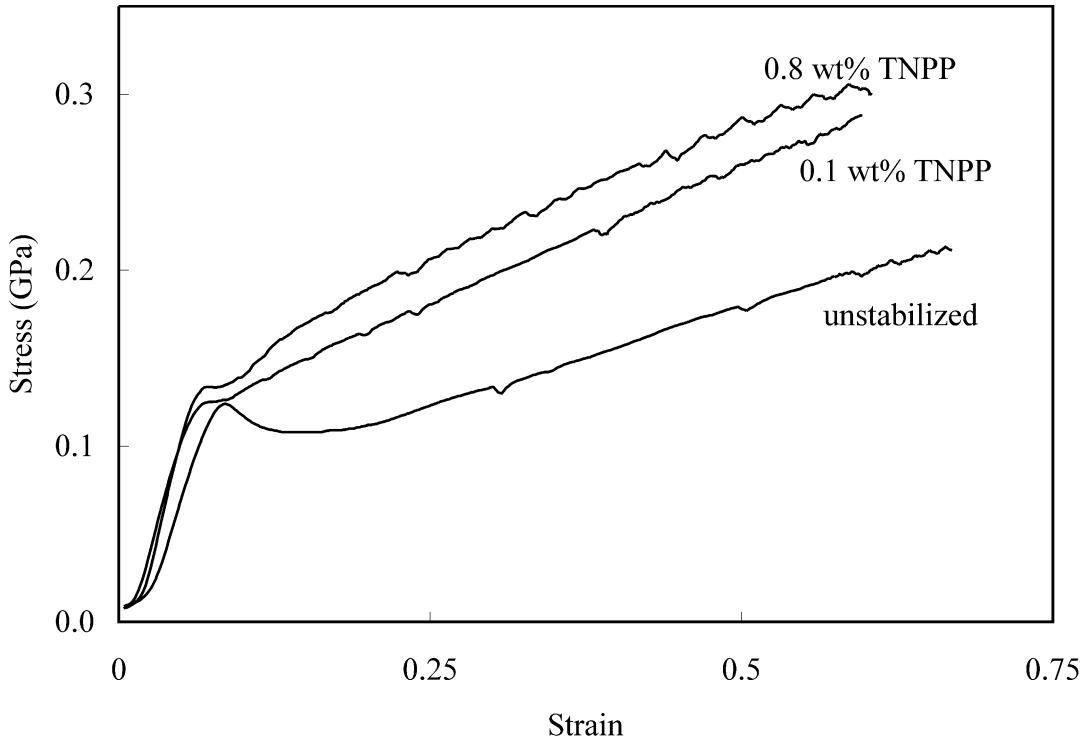


Fig. 7. Typical stress–strain curves at a draw ratio of 5. The behavior of the three batches is noticeably different at the yield point.

deformation field. The result of greater stress should be increased molecular orientation. At draw ratios of 6 and above, however, the large gap narrows and the increase associated with the TNPP shrinks. One positive aspect of stabilization at high draw ratios is the preservation of the modulus—for 0.80 wt.% TNPP, the modulus plateaus at 3.2 GPa. The unstabilized modulus drops off, falling to 2.9 GPa at DR = 8. The difference between 0.11 and 0.80-wt.% TNPP is insignificant over the majority of draw ratios.

The dependence of strength on draw ratio, depicted in Fig. 9, exhibits more of a separation between the samples.

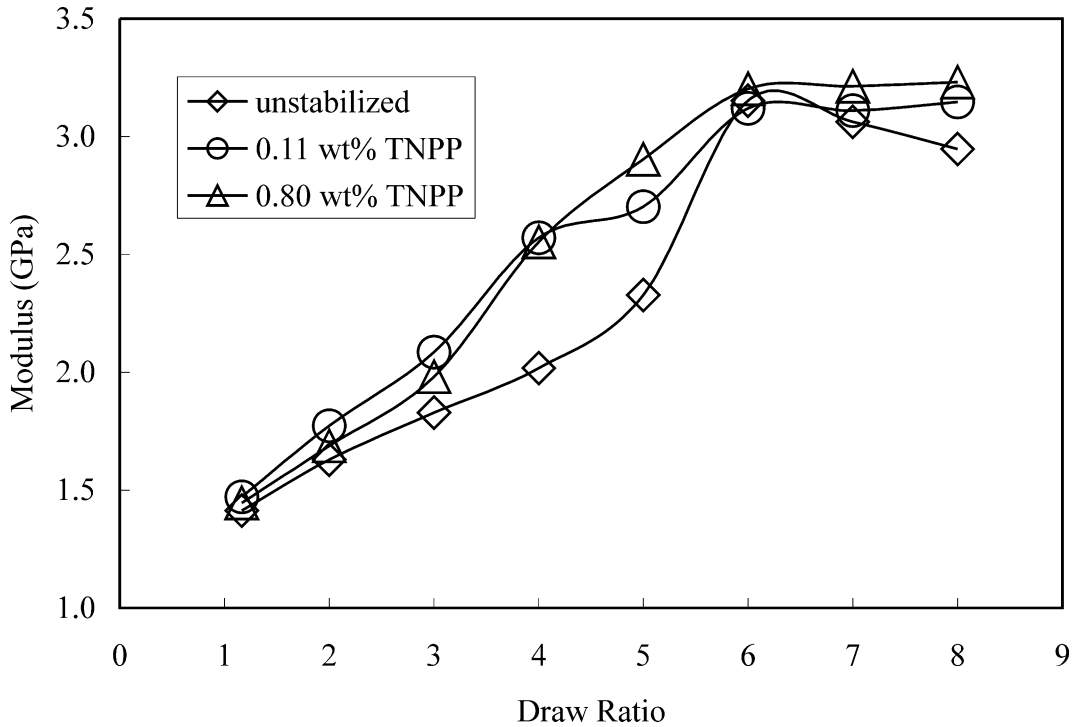


Fig. 8. Modulus vs. draw ratio for the three fiber batches. Modulus at high draw ratios is preserved with addition of TNPP.

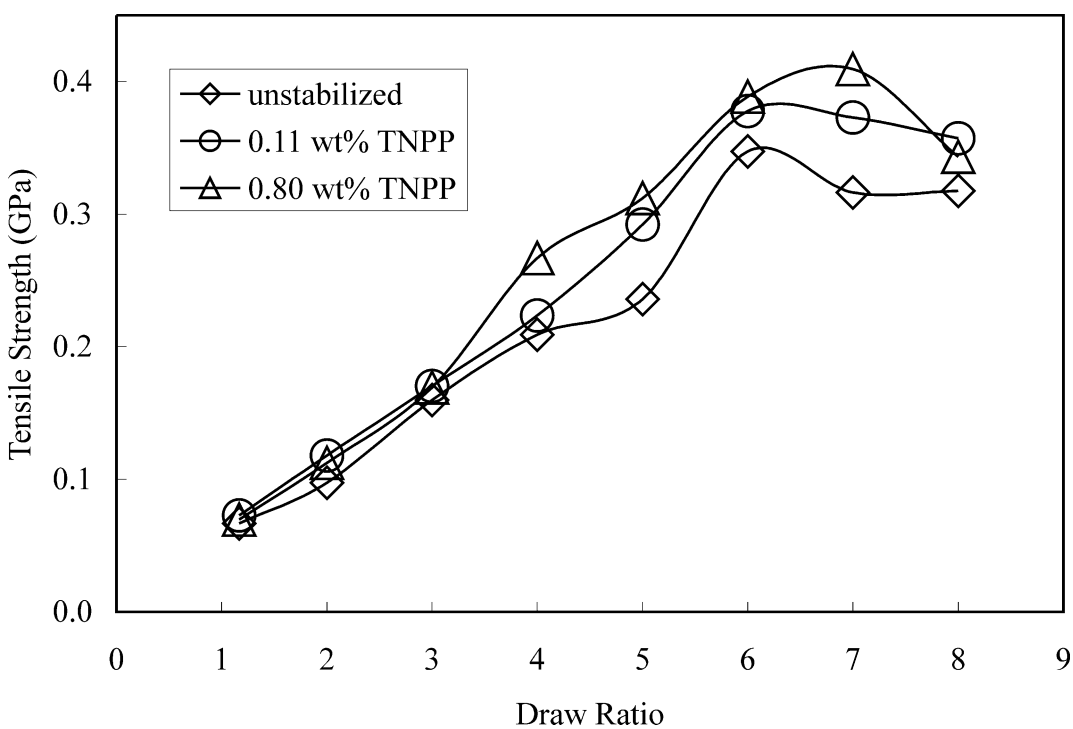


Fig. 9. Tensile strength vs. draw ratio. Addition of stabilizer greatly improves strength for draw ratios above 3.

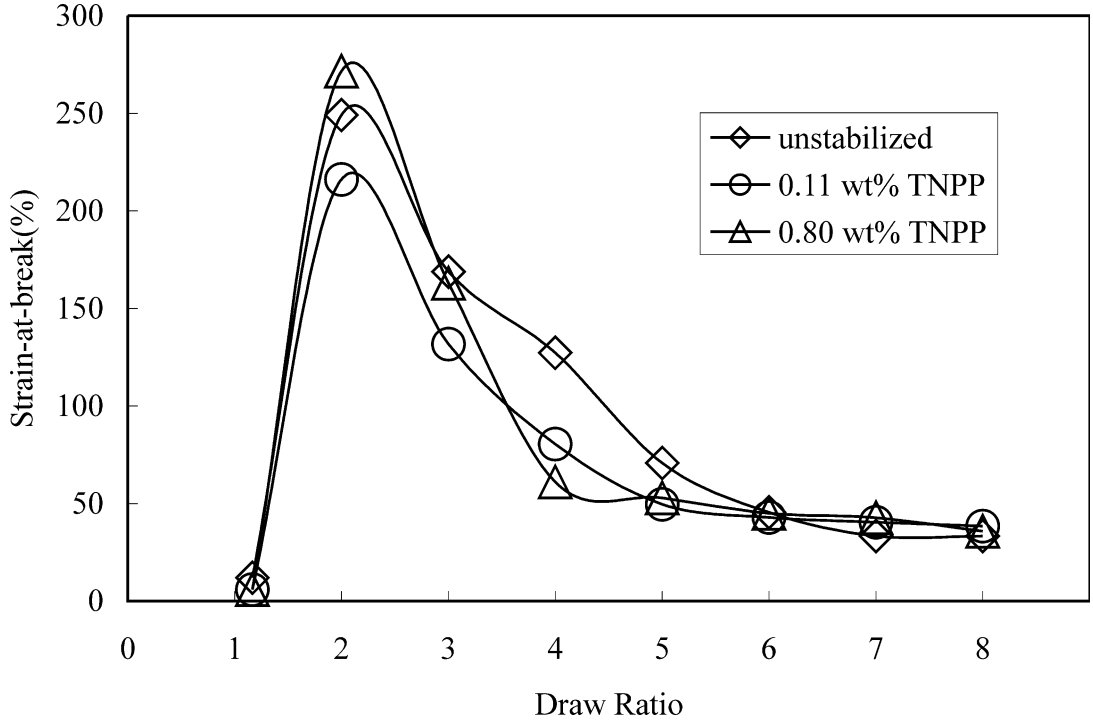


Fig. 10. Strain-at-break vs. draw ratio. No major differences between the stabilized and unstabilized fibers are evident.

As with modulus, low-draw ratio differences are small. Once DR = 4 is reached, however, a greater strength in the stabilized fibers is clearly demonstrated. Although the 0.80-wt.% TNPP curve dominates draw ratios of 4 through 7 (reaching a strength of 0.41 GPa at DR = 7, which is 30% higher than its unstabilized counterpart), it drops below the 0.11-wt.% curve at DR = 8. This decrease in strength is attributed to minute inhomogeneities in the fiber associated with surface crazing.

Fig. 10 is a plot of strain-at-break vs. draw ratio. The differences between the three batches are small in most cases, and values plateau at about 40% at high draw ratios for all fibers. The lowest draw ratio, DR = 1, has a small elongation to break of a few percent. This result is similar to other unoriented PLAs; for example, tensile test bars compression molded from pellets [14]. It appears that there is an optimal level of molecular-scale orientation, allowing maximum elongation, found at DR = 2 for both stabilized and unstabilized PLA fibers. Stabilization thus seems to have only modest effects on fiber extensibility.

4. Conclusions

The molecular weight of extrusion-processed PLA may be stabilized by adding a relatively small amount (less than 1 wt.%) of tris(nonylphenyl) phosphite prior to extrusion. Based on previously reported studies on the stabilization of PET, previously reported rheology experiments, and NMR observations, the mechanism of stabilization is most likely chain extension. However, detailed mechanistic understanding remains elusive. Perhaps one of the most important unresolved issues is whether phosphorous is incorporated into the backbone of TNPP stabilized PLA. This topic remains open to future work.

Mechanical properties and molecular weight retention are improved by the addition of TNPP. Crystallinity is approximately equal for both stabilized and unstabilized fibers. However, fibers produced from TNPP modified PLA using a two-step melt spinning process possess mechanical properties superior to unstabilized fibers. For example, moduli for fibers produced with 0.80-wt.% TNPP remain at 3.2 GPa for all high draw ratios, as opposed to the unstabilized fibers, where moduli drop off above DR = 6. Tensile strengths are greatly increased by the addition of TNPP at intermediate and high draw ratios. The strength of 0.32 GPa at DR = 7 for unstabilized PLA fibers can be increased to 0.41 GPa with the addition of 0.80-wt.% TNPP. At other draw ratios, increases of 10–25% are obtainable. Mechanical properties are improved to a lesser extent by the addition of 0.11–wt.% TNPP. Fiber extensibility is relatively unaffected by stabilization, as demonstrated by small changes in the strain-at-break.

Acknowledgements

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