

Retarding hydrolytic degradation of polylactic acid: Effect of induced crystallinity and graphene addition

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ABSTRACT: The combination of elevated temperature and humidity leads to rapid degradation of polylactic acid (PLA) because of hydrolysis. Consequently, PLA, which is a bio-derived and biodegradable polymer, is not currently used for durable applications since properties cannot always be maintained over time. In this work, the ability of polymer crystals to reduce the rate of degradation during accelerated aging tests was studied. Also examined was the influence of addition of 2 wt % graphene nanoplatelets to act as moisture transport barriers in the polymer. PLA samples were immersed in aqueous media of different pH or exposed to 100% relative humidity at 50 °C for different lengths of time to study the hydrolytic degradation behavior. In addition to monitoring the loss in mass of the samples, the values of crystallinity, melt viscosity, and mechanical properties, among others, were measured as functions of aging time using techniques such as DSC and rheometry. It was found that both crystallization and graphene addition are able to slow down the rate of degradation at short times, but significant degradation of PLA still occurs at long times. This is because PLA crystallites and graphene nanoplatelets can only reduce, but not eliminate, moisture diffusion into the polymer sample. Between the use of nanoplatelets and crystals, though, the former approach may be the better choice since enhanced crystallization tends to make PLA brittle. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44166.

KEYWORDS: biopolymers and renewable polymers; crystallization; degradation; graphene and fullerenes; mechanical properties; nanotubes

Received 17 December 2015; accepted 7 July 2016

DOI: 10.1002/app.44166

INTRODUCTION

Polylactic acid (PLA) is a linear polyester that is made on a large scale from starch derived from renewable sources such as corn. It is also biodegradable and compostable. Because of these reasons, it is attractive from the viewpoint of sustainability since it can act as a replacement for conventional, petroleum-derived, nondegradable thermoplastics. The polymer is biocompatible, and, for this reason, the first commercial application of PLA was in resorbable sutures and as a bio-absorbable drug delivery matrix. PLA can absorb moisture, and this can cause hydrolysis of ester bonds leading to rapid degradation. In the recent past, large-scale plants have been built to produce this polymer, and a full complement of modifiers and additives has become available. Serious efforts have also been made to create a portfolio of products that can be made using PLA. In particular, its use in disposable food packaging applications has become popular for environmental reasons. PLA is semi-crystalline, and it has good processability. In particular, it can be extruded, foamed, thermoformed, injection molded, and also made into fibers and films. It is also the polymer of choice for 3-D printing or additive manufacturing. Despite this, its use as an engineering

thermoplastic has been limited because of several key reasons: a low glass transition temperature of roughly 60 °C which limits high temperature applications, rapid physical aging leading to poor ductility, and toughness when compared to similar products made from polyethylene terephthalate or polystyrene, and low thermal and hydrolytic stability relative to other similar polymers.^{1,2} More information on PLA and its behavior may be found in the book edited by Auras *et al.*³ For use in durable applications, it is essential that the polymer possess hydrolytic stability.

The degradation of PLA by hydrolysis in media of different pH has been studied extensively [see, for example, Auras *et al.* ref. 3, chapter 21]. It is now well established that pH affects the rate of degradation, and the hydrolysis reaction can be catalyzed by both acid and base; the reaction rate reaches a minimum at a pH of about 4. De Jong *et al.*⁴ conducted a systematic study and found that initially hydrolysis occurs randomly in the polymer. The situation, however changes as degradation proceeds. Based on an examination of the behavior of PLA oligomers, these authors concluded that under acidic conditions the terminal ester bond is preferentially cleaved. Under basic conditions,

however, chain-end scission results in the formation of a lactic acid dimer.

A set of studies examined the degradation behavior of PLA microspheres intended to be used for drug delivery purposes.^{5,6} Since these particles were approximately 1.5 μm in diameter, diffusional resistances were expected to be negligible. Consequently, results would yield the true kinetics of the reaction and would give a proper picture of the stability of the PLA. It was found that as the pH moved away from neutral (highly acidic or basic), the rate of weight loss increased. The pH values in this study ranged from 1.6 to 9.6, and it was determined that PLA specimens displayed the maximum stability in media of pH between 3 and 5. This is in agreement with the work of de Jong *et al.*⁴ Makino *et al.*⁵ also found that the degradation rate of the acid-based polymer was fastest in highly basic media, and the rate showed an Arrhenius type of temperature dependence. It was also determined that acid and base preferentially degraded different segments of the polymer; acidic media attack smaller molecular weight fragments in the bulk, while alkaline solutions are able to attack all segments on the backbone.⁶ These studies were concerned with degradation of PLA at conditions relevant to and applicable for drug delivery and medical applications. For engineering applications, it is necessary to examine degradation under more aggressive hydrolysis conditions. This was done by Mohd-Adnan *et al.*⁷ who carried out PLA hydrolysis in high pressure steam at up to 130 °C and showed that the material degraded into lactic acid oligomers in less than 24 hours. Other studies have considered the effects of PLA crystallinity on the rate of degradation. Kim *et al.*⁸ processed PLA by fiber spinning at various speeds. This can change the nature of crystals and also provide molecular orientation to both the amorphous and crystalline regions of the polymer. It was found that the more crystalline materials retained ductility and strength after hydrolytic degradation, and this was thought to be because of molecular orientation which reduced the capacity of water to diffuse into the bulk. A study done by Zhang *et al.*⁹ investigated the hydrolytic stability of both amorphous and semi-crystalline PLA materials by changing pH and time of exposure. These authors found that the materials undergo a two-stage degradation process involving both surface and bulk erosion steps, with either mass or molecular weight loss. Zhou and Xanthos¹⁰ added nanoclay to amorphous, semi-crystalline and blended PLA samples and exposed the materials to basic media above as well as below the glass transition temperature. The addition of clay to the PLA matrix adds a diffusional resistance, and this increases the time required for the attacking species or ions to fully permeate into the material, enhancing the stability of the composites over short timescales. In addition, they found that reaction rates increased with increasing temperature and that, while increasing crystallinity increased mass transfer resistance, the clays could act as nucleation sites for degradation and tended to enhance the reaction rate. Harris *et al.*¹¹ performed hydrolysis experiments with highly crystalline (~45%) injection molded PLA specimens and found that after 8 weeks of exposure to 50 °C temperature and 90% relative humidity, there was severe degradation in the flexural properties of the PLA samples. Tsuji and coworkers^{12–14}

studied degradation of amorphous and crystalline PLA samples at even higher temperatures and found that PLLA could be easily recycled to lactic acid by hydrolysis in a temperature range of 120–190 °C, and at 190 °C this complete degradation could occur in as little as 30 minutes.

In view of the above discussion, it seems reasonable to find ways to increase the hydrolytic stability of PLA so that it can be used in more durable applications such as automotive components or equipment housing. These approaches could be chemical in nature, such as copolymerization with monomers like ϵ -caprolactone, or these could be physical ones. Given that PLA is now being made in large quantities and given that polymer compounding is an established process for engineering enhanced polymer properties, it was decided to evaluate the effects of crystallinity and nanoadditives on enhancing the hydrolytic stability of PLA. It is well known that heat treatment of semi-crystalline polymers has beneficial effects on mechanical properties and solvent resistance since this tends to enhance crystallinity.¹⁵ Additionally, incorporation of high aspect ratio platelets of nanoclays or graphene can serve to improve chemical resistance by enhancing barrier properties¹⁶; mechanical properties, such as stiffness and strength, may also be improved. Nanoplatelets and crystallites both work as impermeable barriers, and a diffusing molecule has to travel a longer, tortuous path around these obstacles. Consequently, there is an increase in the mass transfer resistance, and the flux of the diffusing species reduces. As a result, the time taken for the polymer to be saturated with moisture increases, and this should help to enhance durability. Separately, polymer molecules within the crystalline regions are better protected and are the last ones to be attacked. Indeed, it has been shown that increasing the crystallinity of PLA decreases moisture diffusion through PLA films.^{17–19} Similarly, nanoclays are widely used as a mass transfer barrier in polymer films.^{19,20} However, for PLA that is likely to be used at an elevated temperature, nanoclay addition may not be appropriate since clay is basic and PLA is prone to hydrolyze under these conditions.²¹ An alternative barrier material is graphene which has been used to make PLA-matrix nanocomposites with improved properties for a variety of applications.^{22–24} Therefore, graphene nanoplatelets were selected as the filler material for this study (see also ref. 16). If these approaches are successful, they may offer a way to extend the use PLA or PLA-based materials to harsher conditions encountered in new applications such as use in automotive components and electronic housing.

EXPERIMENTAL

Materials Used

Ingeo 2002D PLA was purchased from NatureWorks LLC. It is a semicrystalline grade with density of 1240 kg/m³ and melt flow rate of 5–7 g/10 min at 210 °C/2.16 kg conditions. It has a measured glass transition temperature of 55–60 °C and a melting range of 148–155 °C. Graphene nanoplatelets GnP-25 from XG Sciences were used at a loading level of 2 wt %. This graphene is supposed to consist of graphite sheets with nominal width of 25 μm , thickness of 12–15 nm, and specific surface area of 60–80 m²/g.

Blend Preparation

Prior to any processing step, as-received PLA pellets and graphene platelets were dried at 90 °C for 4 hours to minimize moisture content. PLA was then compounded with graphene to form a nanocomposite with the help of a Thermo-Haake Poly-Drive internal mixer using rotor rollers. Fifty gram batches containing 2 wt % graphene (49 g PLA/1 g graphene) were mixed at 240 °C at 80 rpm for 5 minutes.

Specimen Preparation

Both pellets and compression-molded parts were utilized in this research. A PHI-SQ230H compression molding machine was used to make both squares and flexural bars for viscosity and degradation testing. The dried materials were pressed at 225 °C for 10 minutes under 10 tons of compressive force. After cooling, a band saw was used to cut squares from a large sheet into pieces that were approximately $30 \times 30 \times 3 \text{ mm}^3$ in size. Flexural bars were made using templates to give pieces that were nominally $127 \times 12.5 \times 3 \text{ mm}^3$ in size. In order to investigate the effect of crystallinity, selected compression-molded parts and pellets were annealed in a vacuum oven at 80 °C for 48 hours; as the parts had a tendency to warp, they were laid out on an aluminum plate with a small weight on top.

Hydrolytic Degradation

In Liquid Water. PLA is susceptible to degradation in media that are acidic, neutral, or basic even at fairly low temperatures.³ Further, the degradation reactions that are postulated to take place can also regenerate the hydrogen or hydroxyl ion, meaning that the degradation may be self-catalyzing. This is useful if the desired usage is for biodegradable packaging or sutures; however, for more durable applications, one wishes to minimize this occurrence. To study degradation, the compression-molded squares were subjected to attack in acidic, neutral, and basic solvents. The media were acetic acid/sodium acetate buffer of pH = 4.0, distilled water of pH = 7.0, and sodium carbonate/sodium bicarbonate buffer of pH = 10.0, all of which were held at a constant temperature of 50 °C. Degradation took place for up to 6 weeks, and the distilled water was changed weekly to avoid pH change, as was done in a previous study with polyglycolic acid.²⁵ Samples were then vacuum-dried at room temperature, after which weight loss, thermal, and rheological properties were measured.

In Water Vapor. In addition to degrading in media of varying pH, PLA can degrade in the presence of hot water or steam. In the present work, hydrolytic degradation of PLA was studied at 50 °C in the presence of 100% relative humidity (RH). These conditions are typically employed in accelerated aging tests for durable applications.¹¹ PLA pellets were placed in a Pyrex jar with distilled water at the bottom. The jar was sealed and then placed in an oven set at 50 °C, and this created a constant humidity chamber for the pellets. The pellets were withdrawn periodically for analysis. Flexural bars were also placed in this chamber, but for longer durations in order to investigate the effect of aging on mechanical properties. Aged PLA pellets or bars were dried overnight at room temperature under vacuum prior to any subsequent testing.

Mechanical Property Evaluation

The mechanical properties of pristine as well as degraded flexural bars were determined according to ASTM D790 using an Instron 5567 machine with at least four replicates for accuracy. The crosshead speed during the test was 1.387 mm/min.

Thermal Property Evaluation

Crystallinity values of PLA samples were measured using a TA Instruments Q-100 differential scanning calorimeter which was calibrated using standard indium and sapphire samples. Samples weighing 6–9 mg were pressed into sealed aluminum pans, and these were then heated from 10 °C to 250 °C at 10 °C/min under helium flow to investigate any thermal events in this range. Data reported are the average of at least three replicates. The crystallinity of samples, χ_c was calculated using:

$$\chi_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^o(1 - \phi)} \times 100 \quad (1)$$

Here, ΔH_m is the melting enthalpy (J/g), ΔH_c is the cold crystallization enthalpy (J/g), ΔH_m^o is the theoretical value of the melting enthalpy of a 100% crystalline PLA (93 J/g), and ϕ is nanofiller mass fraction.

Flow Property Evaluation

Parallel plate rheometry was used to ascertain the effects of degradation on the flow behavior of PLA parts and pellets. A Rheometrics RMS-800 Mechanical Spectrometer was employed to measure dynamic complex viscosity. The measurements were made at 170 °C using 12% strain with a 1.4 mm gap in order to remain in the linear viscoelastic region. The frequency range was from 0.1 to 100 rad/s, and all measurements reported are averages of at least three replicate experiments. Dynamic viscosity, η^* , was calculated using following expression:

$$\eta^* = \sqrt{\left(\frac{G'}{\omega}\right)^2 + \left(\frac{G''}{\omega}\right)^2} \quad (2)$$

where, G' and G'' are elastic and loss moduli (Pa), respectively, and ω is the dynamic frequency (rad/s).

Gel Permeation Chromatography

To monitor any molecular weight changes in PLA samples because of hydrolytic degradation, Gel Permeation Chromatography (GPC) experiments were performed at Bayer Material Science using a Waters Alliance Gel Permeation Chromatograph. Samples were dissolved in methylene chloride, then diluted 50 : 50 by volume in THF and analyzed in THF at 35 °C with a flow rate of 1.0 mL/min. The molecular weights were determined using a calibration curve relative to polystyrene standards.

RESULTS AND DISCUSSION

Displayed in Figure 1 are percentage crystallinity values of PLA pellets and unfilled compression molded samples before and after annealing at 80 °C for 48 hours. Measurements were also made on both kinds of graphene-filled PLA samples. It can be seen that the unannealed pellets and molded parts have low initial crystallinity. This is because PLA is a very slowly crystallizing polymer.²⁶ Furthermore, the addition of graphene has only a small nucleating effect on crystallization, and, as a result, the graphene-containing pellets and parts have slightly higher initial

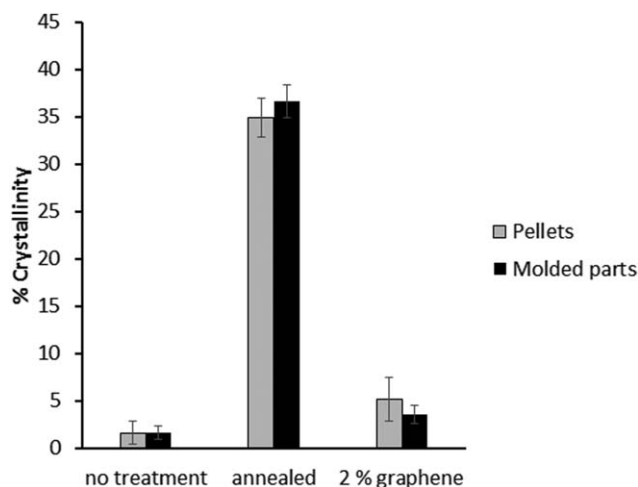


Figure 1. Initial crystallinity values of PLA pellets and specimen.

crystallinities.^{27,28} However, on annealing the unfilled samples, the crystallinity increases to 30–35% for both pellets and molded samples. It should be noted that the graphene-containing samples were not annealed.

Degradation in Liquid Water

Degradation of the molded samples in media of varying pH gives useful information about stability relevant to different possible end-uses. Weight change of the molded parts was monitored as a function of time and pH, and results are shown in Figure 2. This figure shows that for all but one of the samples, even after 6 weeks of immersion, the loss in weight is negligible. Only the unannealed and unfilled sample shows about 15% mass loss at pH = 10 in the last three weeks of immersion. This suggests bulk degradation as the mechanism of attack; here attacking species are able to migrate into the specimen and begin attacking the material from within under highly basic conditions at pH = 10.⁴ For annealed and graphene-containing

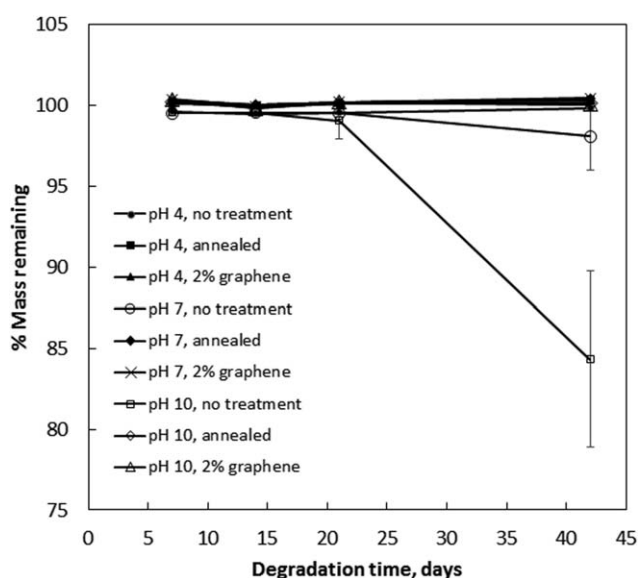


Figure 2. Weight loss of compression-molded parts because of immersion in aqueous solutions of various pH values at a temperature of 50 °C.

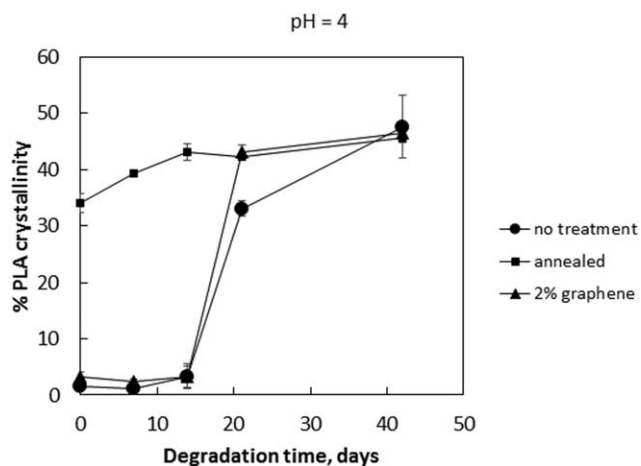


Figure 3. Progression of crystallinity of molded PLA samples resulting from exposure to pH = 4 acetic acid buffer at 50 °C.

samples, there is no significant loss in mass because crystalline regions are impervious to diffusion and crystals as well as graphene platelets dispersed in the PLA matrix act as barriers to mass transfer. Since the molecules of water traverse a longer tortuous path around these largely impermeable barriers, the mass flux decreases. A consequence of this is that the time scale of the sorption process increases, and portions of the PLA sample remain protected from attack by moisture for a longer time period. This provides hydrolytic stability. These data appear to show that either crystallization or the use of nanoplatelets can be effective in increasing the hydrolytic stability of PLA.

Even though there was essentially no mass loss upon immersion of the compression-molded PLA samples in media of different pH values, morphological changes were expected to occur. Measurements were made with a DSC to observe any crystallinity changes as a function of time during the process of degradation. Representative data for changes in crystallinity for all the compression-molded parts as a function of ageing time in the acetic acid buffer of pH = 4 are shown in Figure 3. This figure reveals that, whereas the crystallinity of the annealed samples increases only slightly, both the unannealed and the graphene-containing specimens undergo a large increase in crystallinity with ageing time. Since no mass loss is occurring in these samples at a pH of 4, the increase in crystallinity must be because of rearrangement of imperfect crystals and of PLA molecules in amorphous regions into crystallites. This process is likely facilitated by reduction in polymer molecular weight as the polymer backbone in the amorphous regions of the PLA matrix breaks down because of hydrolysis generating smaller fragments and oligomers. These smaller molecules are more capable of rearranging into crystallites by a process referred to as chemicrystallization,²⁹ thus increasing the net crystallinity of the sample. Since the annealed sample already contains the largest and most perfect crystals, there is little potential for the development of additional crystallinity in this process.

In addition to changes in polymer crystallinity, molecular weight changes were anticipated because of immersion of PLA samples in liquid media. Since the melt viscosity of polymeric

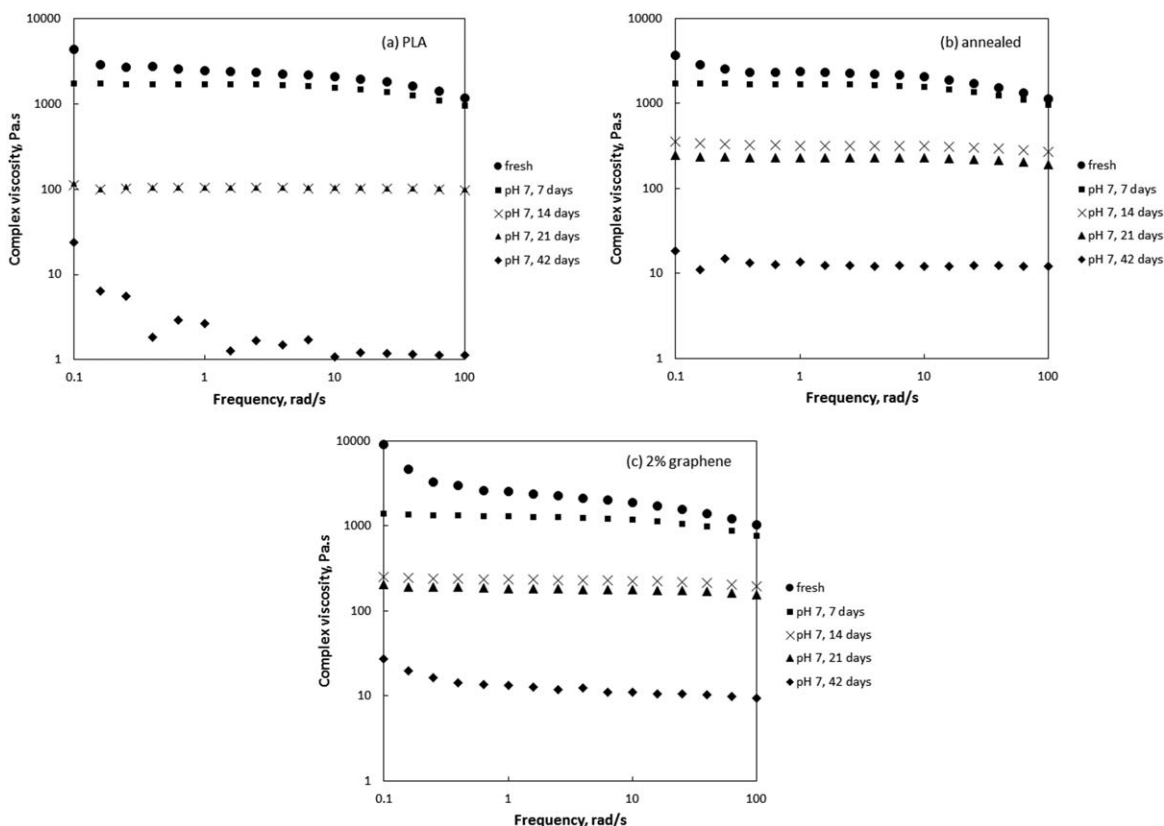


Figure 4. Change in the modulus of complex viscosity after immersion in distilled water at 50 °C over six weeks for: (a) unannealed PLA, (b) annealed PLA, and (c) PLA containing 2wt %graphene. The temperature of measurements is 170 °C.

materials is a strong function of molecular weight,³⁰ the change in linear viscoelastic rheological properties of molded parts subjected to solvent degradation was determined. Figure 4 shows the variation in the complex viscosity of the various samples over the six-week test period in distilled water (pH = 7) at 50 °C; It is evident that there is an appreciable decrease in viscosity in each case, and this corresponds to a significant loss of molecular weight and related physical properties. From Figure 4, it can be seen that an almost two orders of magnitude loss in viscosity has occurred in all the samples by 6 weeks. Similar observations were made for experiments conducted at pH = 4 and 10 as shown in Figure 5 for untreated PLA samples. It may

be noted that the samples exposed to a liquid medium at pH = 4 have slightly higher viscosities values under comparable conditions than at pH = 10. This again shows that PLA is more stable in acidic media as compared to basic media.

The results shown earlier in Figure 4 are examined in a slightly different manner in Figure 6. In this figure, the complex viscosity has been plotted as a function of time of degradation in distilled water at a frequency of 1 rad/s to elucidate the effect of the different treatments. A logarithmic scale is used for the ordinate in Figure 6, and this shows the rapid reduction in properties with time of immersion. It is also evident that the

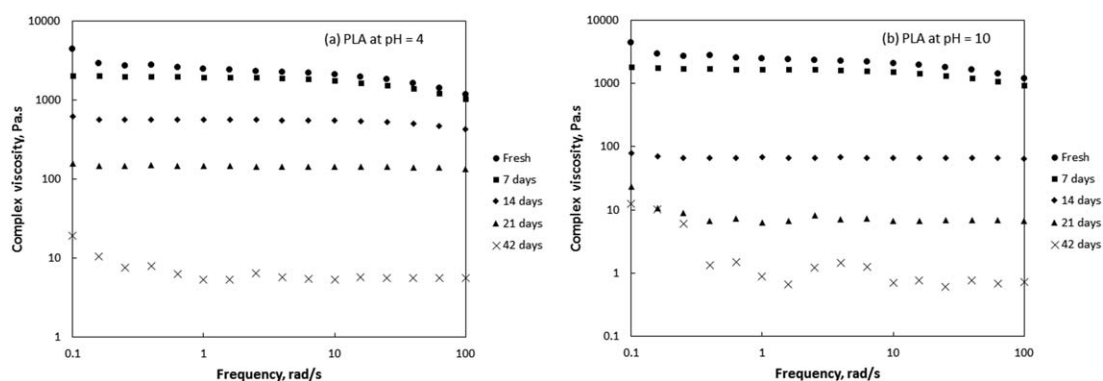


Figure 5. Change in the modulus of complex viscosity of unannealed PLA samples after immersion in distilled water at 50 °C solutions at: (a) pH = 4 and (b) pH = 10. The complex viscosity was measured at 170 °C.

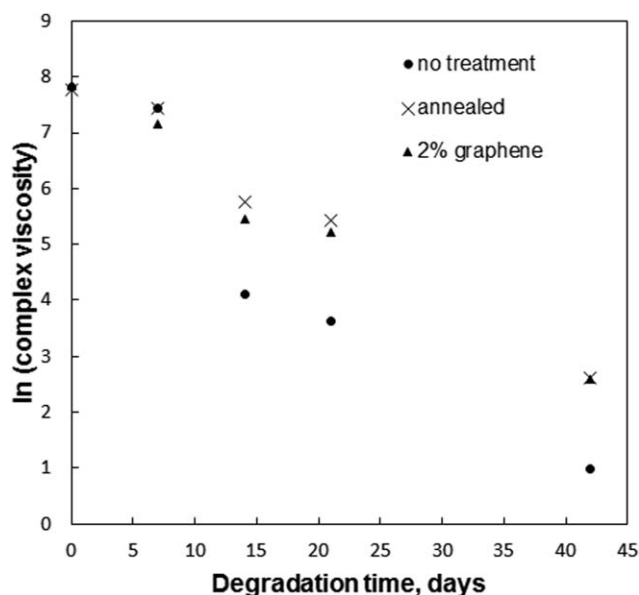


Figure 6. Modulus of complex viscosity at 1 rad/s as a function of aging time in distilled water at 50 °C for: no treatment, annealed and PLA containing 2 wt % graphene. The complex viscosity was measured at 170 °C.

reduction in viscosity is more pronounced in the unannealed sample as compared to the treated samples. It is clear that the presence of crystallinity or the addition of graphene slows the rate of PLA degradation, but a significant amount of degradation still occurs in 6 weeks.

Molecular Weight Change

GPC analysis was performed on a limited number of samples courtesy of Bayer MaterialScience to determine the change in molecular weight of the degraded samples. Results are shown in Table I where number and weight average molecular weights are presented together with the polydispersity index (M_w/M_n). Communications with NatureWorks staff suggested that the initial weight average-molecular weight of PLA is about 210,000 g/mole. GPC measurements suggest that there is a significant drop in molecular weight simply because of mixing graphene with PLA in the internal mixer. A further decrease in molecular weight is observed after just one day of hydrolysis at 50 °C. The GPC results for PLA MW are very limited and their main utility

Table I. GPC Measured Molecular Weights of Various Samples of PLA

Sample	M_n	M_w	M_w/M_n
PLA	—	~210,000 ^a	
PLA/graphene	82,980	155,710	1.88
PLA/graphene, 1 day in water at 50 °C	77,380	150,070	1.94
No treatment PLA, 1 day in water at 50 °C	90,390	166,580	1.84
Annealed PLA, 1 day in water at 50 °C	81,660	151,890	1.86

^a As reported by manufacturer.

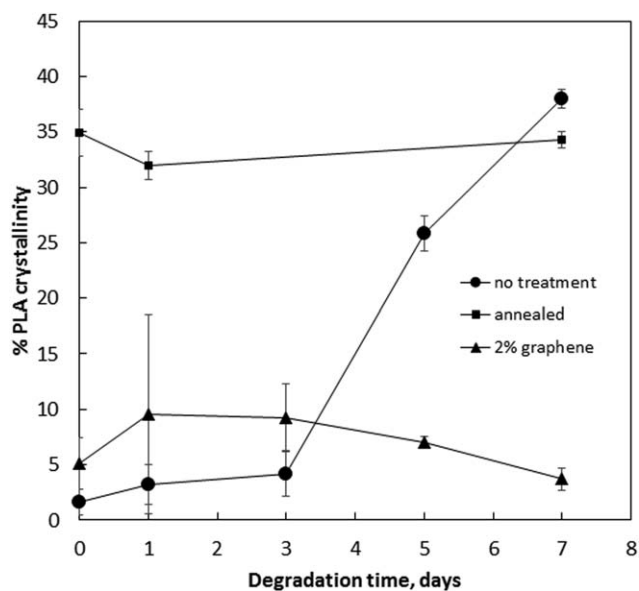


Figure 7. Development of crystallinity with degradation time in PLA pellets because of exposure to saturated water vapor at 50 °C.

is to show that the MW changes rapidly upon processing and aging.

Degradation in Water Vapor

Degradation tests were performed on pellets (~4–5mm) in a humid environment at 100% RH and 50 °C. The pellets have a much larger surface area to volume ratio when compared to the molded parts, and they would, therefore, offer less resistance to mass transfer. This aspect is explored in Figure 7 which shows the observed change in crystallinity with time, measured using a DSC. It is seen that the crystallinity of the annealed sample does not change much, but the unannealed samples show a large increase in crystallinity. These observations are consistent with observations made with immersion tests reported in the previous section. However, the pellets containing graphene show no significant change in crystallinity unlike in the immersion tests. This aspect is explained further in the section below.

As mentioned earlier, mechanical testing was performed on flexural bars that were exposed to the humid atmosphere to determine the effect of hydrolytic ageing on flexural properties. Figures 8–10 show respectively the percent change in flexural modulus, flexural strength, and ductility upon two weeks of ageing. For the untreated as well as for the annealed samples, the flexural modulus increases at first, but then it decreases; for the graphene-containing samples, there is a slight, but progressive, decrease. The increase in modulus is because of an increase in crystallinity as seen in Figure 7, which makes the polymer matrix stiffer. However, on long exposure times, the polymer matrix degrades, negating the effect of crystallinity, and a decrease in modulus is observed. For graphene-containing samples, there is no significant change in crystallinity as was seen in Figure 7, and, therefore, the modulus does not change in any appreciable way in the beginning, and then it decreases slightly because of polymer degradation. Both flexural strength and ductility (or elongation to break) are large strain properties, and

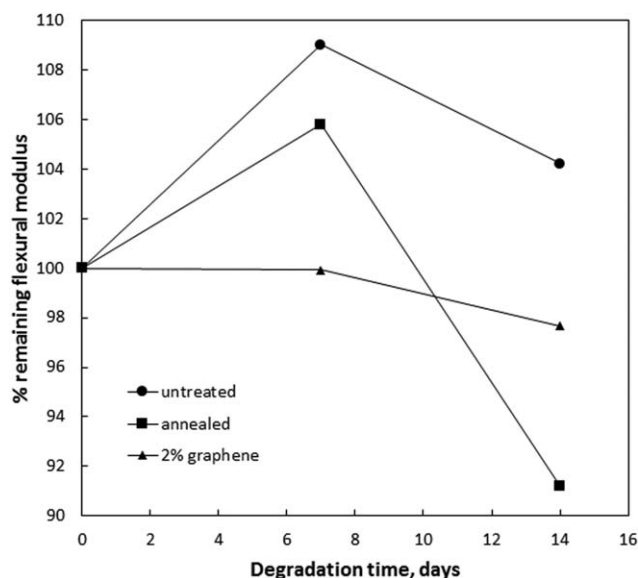


Figure 8. Change in flexural modulus because of exposure to saturated water vapor at 50 °C as a function of time for: no treatment, annealed and PLA containing 2 wt % graphene.

they decrease with increasing crystallinity as the material becomes more brittle. The annealed samples show the largest decline in all three mechanical properties because of development of high crystallinity. In these instances, the untreated samples had the best degradation performance, followed closely by the polymer subjected to graphene treatment; these parts were not high in initial crystallinity, and they were able to degrade without becoming particularly brittle. However, it is possible that with continued aging even these samples would have unacceptably low values of strain to failure. Still, it is clear from these examples that the 2 wt % graphene loading is effective in improving polymer durability.

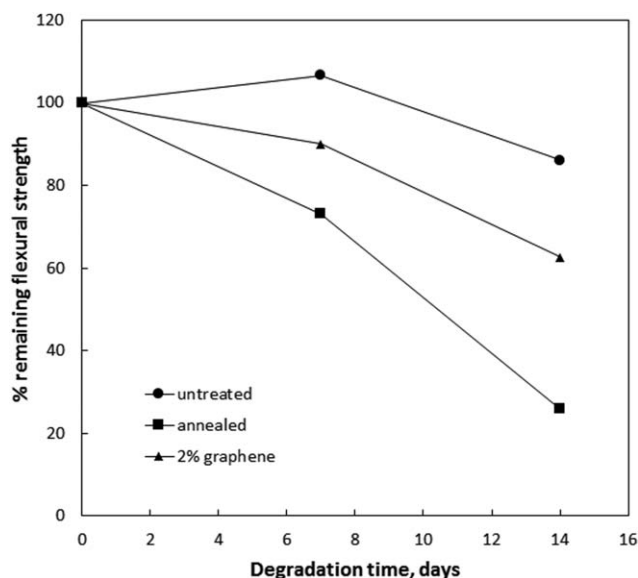


Figure 9. Change in flexural strength of PLA because of exposure to saturated water vapor at 50 °C as a function of time for: no treatment, annealed and PLA containing 2 wt % graphene.

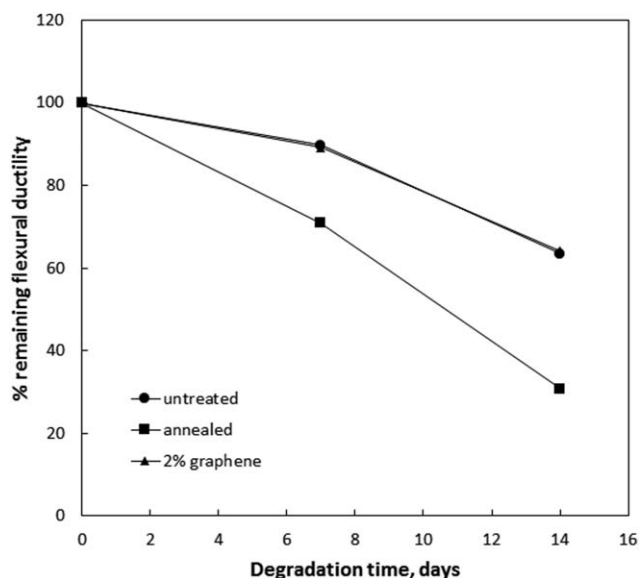


Figure 10. Change in ductility because of exposure to saturated water vapor at 50 °C as a function of time for: no treatment, annealed and PLA containing 2 wt % graphene.

CONCLUSIONS

Accelerated degradation tests described here are meant to simulate long-term ageing behavior of molded PLA samples when they are likely to be used in durable applications. From the results presented in this article, it becomes clear that retarding the diffusion of reactive molecules into the polymer by introducing barriers to diffusion can reduce the rate of degradation for short time periods, but this diffusional resistance will ultimately be overcome. Barriers that one may employ include nanoplatelets and polymer crystals; the presence of crystals not only forces diffusing molecules to follow a tortuous path, but these also protect the polymer molecules contained within the ordered regions. However, a major conclusion of this study is that barriers like graphene nanoplatelets are more effective from the viewpoint of PLA durability and mechanical properties than the use of crystallization. We speculate that this is because the crystallites impart brittleness to the material. As with nanoplatelets, the effect of crystals is not permanent since they too ultimately suffer degradation in the presence of water. We also point out that, in this work, only 2 wt % graphene was used. It may be possible to use higher loadings of graphene nanoplatelets (more than 2 wt %) and further improve the barrier properties and increase the durability. This work, therefore, suggests the potential of using impermeable barriers as an approach to increase the durability of molded PLA parts without a deterioration in mechanical properties.

ACKNOWLEDGMENTS

Adam Finnis thanks the Bayer Foundation for a research fellowship as part of the Bayer Scholars Program at WVU. We also thank D.L. Mullen at Bayer MaterialScience who performed the GPC experiments.

REFERENCES

1. Rasul, R.; Janorkar, A. V.; Hirt, D. E. *Prog. Polym. Sci.* **2008**, *35*, 338.
2. Maharana, T.; Mohanty, B.; Negi, Y. S. *Prog. Polym. Sci.* **2009**, *34*, 99.
3. Tsuji, H. Hydrolytic Degradation. In: Poly(lactic acid): Synthesis, Structures, Properties, Processing, and Applications; Auras, R. A., Lim, L.-T, Selke, S. E. M., Eds.; Wiley: Hoboken, NJ, **2011**; Chapter 21, p 345.
4. de Jong, S. J.; Arias, E. R.; Rijkers, D. T. S.; van Nostrum, C. F.; Kettenes-van den Bosch, J. J.; Hennink, W. E. *Polymer* **2001**, *42*, 2795.
5. Makino, K.; Arakawa, M.; Kondo, T. *Chem. Pharm. Bull.* **1985**, *33*, 1195.
6. Makino, K.; Ohshima, H.; Kondo, T. *J. Microencapsul.* **1986**, *3*, 203.
7. Mohd-Adnan, A. F.; Nishida, H.; Shirai, Y. *Polym. Degrad. Stabil.* **2008**, *93*, 1053.
8. Kim, M. S.; Kim, J. C.; Kim, Y. H. *Polym. Adv Technol.* **2008**, *19*, 748.
9. Zhang, X.; Espiritu, M.; Bilyk, A.; Kurniawan, L. *Polym. Degrad. Stabil.* **2008**, *93*, 1964.
10. Zhou, Q.; Xanthos, M. *Polym. Degrad. Stabil.* **2008**, *93*, 1450.
11. Harris, A. M.; Lee, E. C. *J. Appl. Polym. Sci.* **2010**, *115*, 1380.
12. Tsuji, H. *Biomaterials* **2003**, *24*, 537.
13. Tsuji, H.; Ikarashi, T. K.; Fukuda, N. *Polym. Degrad. Stabil.* **2004**, *84*, 515.
14. Tsuji, H.; Saeki, T.; Tsukegi, T.; Daimon, H.; Fujei, K. *Polym. Degrad. Stabil.* **2008**, *93*, 1956.
15. Renouf-Glauser, A. C.; Rose, J.; Farrar, D. F.; Cameron, R. E. *Biomaterials* **2005**, *26*, 5771.
16. Thompson, M. S.; Agarwal, S.; Gupta, R. K. Diffusion through Polymers Containing Platelike Nanomaterials; In: Graphite, Graphene, and Their Polymer Nanocomposites; Mukhopadhyaya, P., Gupta, R. K., Eds.; CRC Press: Boca Raton, FL, **2012**.
17. Tsuji, H.; Okino, R.; Daimon, H.; Fujii, K. *J. Appl. Polym. Sci.* **2006**, *99*, 2245.
18. Drieskens, M.; Peeters, R.; Mullens, J.; Franco, D.; Lemstra, P. J.; Hristova-Bogaerds, D. G. *J. Polym. Sci. Part B: Polym. Phys.* **2009**, *47*, 2247.
19. Tang, M. C.; Agarwal, S.; Alsewailam, F. D.; Gupta, R. K. *Proc. Soc. Plast. Eng. ANTEC* **2014**, 572. April 28–30, Las Vegas, NV, pp
20. Rhim, J. W.; Hong, S.-I.; Ha, C.-S. *Food Sci. Technol.* **2009**, *42*, 612.
21. Paul, M. A.; Delcourt, C.; Alexandre, M.; Degée, Ph.; Monteverde, F.; Dubois, Ph. *Polym. Degrad. Stabil.* **2005**, *87*, 535.
22. Miculescu, M.; Thakur, V. K.; Miculescu, F.; Voicu, S. I. *Polym. Adv. Technol.* **2016**, DOI: 10.1002/pat.3751.
23. Thakur, M. K.; Thakur, V. K.; Gupta, R. K.; Pappu, A. *ACS Sustain. Chem. Eng.* **2016**, *4*,
24. Young, R. J.; Kinloch, I. A.; Gong, L.; Novoselov, K. S. *Compos. Sci. Technol.* **2012**, *72*, 1459.
25. Ginde, R.; Gupta, R. K. *J. Appl. Polym. Sci.* **1987**, *33*, 2411.
26. Saeidlou, S.; Huneault, M. A.; Li, H.; Park, C. B. *Prog. Polym. Sci.* **2012**, *37*, 1657.
27. Xu, J.; Chen, T.; Yang, C. L.; Li, Z. -M.; Mao, Y. -M.; Zeng, B. -Q.; Hsiao, B. S. *Macromolecules* **2010**, *43*, 5000.
28. Chen, Y.; Yao, X.; Pan, Z.; Gu, Q. *Adv. Mater. Res.* **2011**, *284*, 246.
29. Islam, M. S.; Pickering, K. L.; Foreman, N. J. *Polym. Degrad. Stabil.* **2010**, *95*, 59.
30. Gupta, R. K. Polymer and Composite Rheology, 2nd ed.; Marcel Dekker: New York, **2000**; Chapter 3, p 34.