Mechanical Properties of Polylactide After Repeated Cleanings

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ABSTRACT: The ability of polylactide (PLA) to retain its mechanical properties after repeated cleanings at various pH levels, washing temperatures, and drying conditions has been studied. One of the problems with PLA is its poor resistance to hydrolysis, especially under alkaline conditions. In this study, PLA fabrics were sent through 50 cleaning cycles with different pH levels (8 or 10), washing temperatures (35 or 55°C), and drying conditions (air dry at 21°C/65% relative humidity or tumble dry at 50 or 70°C). The retention percentages of the breaking tenacity, breaking elongation, and modulus of the PLA yarns were measured after every 10 cleaning cycles. A pH of 8 gave greater breaking tenacity, breaking elongation, and modulus retention than pH 10. Washing PLA at 35°C and air drying it at 21°C resulted in greater modulus retention than washing and drying at higher temperatures. Hydrolysis of the polymer was the main cause of the loss in mechanical properties. Equations were developed to predict the retention percentage of the breaking tenacity, breaking elongation, and modulus based on the pH, number of cleaning cycles, and washing and drying temperatures. Recommendations for appropriate conditions for the cleaning of PLA fabrics that result in greater mechanical property retention are given. J Appl Polym Sci 108: 2150–2155, 2008

Key words: biofibers; biopolymers; degradation; mechanical properties; renewable resources

INTRODUCTION

Polylactide or poly(lactic acid) (PLA; see Fig. 1) is the only biodegradable synthetic textile fiber that is manufactured from annually renewable resources. Because petroleum reserves are being depleted rapidly, the production and consumption of textiles from annually renewable resources are important. However, PLA textiles have low popularity among consumers. One reason for their low popularity may be their poor durability due to their poor resistance to hydrolysis.[1–5] However, many people may not know how to properly care for PLA textiles, and this may accelerate the degradation of PLA. Using the proper conditions for cleaning PLA textiles is therefore important for the textiles to retain their properties longer.

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Most studies on PLA textiles concern the ability of PLA to be processed in fiber manufacturing and wet processing.[6–25] There have been few studies on the effects of cleaning conditions on the properties of PLA. A few studies have reported the effects of laundering and dry cleaning on the color, dimensional stability, and strength of fabrics containing PLA.[10,23] To the best of our knowledge, there have been no studies on the effect of cleaning conditions on the properties of PLA after repeated cleanings.

Because the effect of repeated laundering conditions on the mechanical properties of PLA has not been reported previously, the objective of this study was to understand the effect of the pH and water temperature during washing and the effect of drying conditions on the ability of PLA to retain its mechanical properties after repeated laundering. PLA fabric was sent through 50 cleaning cycles with different pHs, washing temperatures, and drying conditions, and the breaking tenacity, breaking elongation, and modulus of the PLA yarn were measured. Statistical analysis was used to identify the cleaning conditions that result in the greatest mechanical property retention and to develop equations to predict the mechanical property retention percentage under a given cleaning condition.

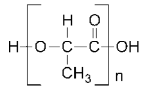

Figure 1 Structure of PLA.

EXPERIMENTAL

Materials

For this study, 100% PLA double-knit interlocked fabric with a weight of 0.159 kg/m^2 (4.68 oz/yd^2) was used. The fabric contained filament and staple fiber yarns. Filament yarns were 90 denier, and staple yarns were 25 cotton count. AATCC 1993 standard reference detergent without optical brightener was used. Acetic acid and sodium hydroxide were reagent-grade chemicals from VWR International (West Chester, PA).

Repeated cleanings of PLA

Repeated cleanings of PLA fabric were performed according to AATCC Test Method 124 (''Appearance of Fabrics After Repeated Home Laundering'') with a type 1 ballast, a normal machine cycle, and normal washing conditions. Modifications to this standard were washing temperatures of 35 $\pm$ 1.5 and 55 $\pm$ 1.5°C and pH values of 8.0 $\pm$ 0.5 and 10.0 $\pm$ 0.5 to study the effects of the washing temperature and pH. The effect of the drying condition was studied for the normal or cotton sturdy drying cycle (tumble drying at 70 $\pm$ 2°C), delicate drying cycle (tumble drying at 50 $\pm$ 2°C), and air drying at 21 $\pm$ 1°C and 65 $\pm$ 2% relative humidity (RH) for 24 h. For each condition, 50 cleaning cycles were performed.

Testing

ASTM D 2256 (''Standard Test Method for Tensile Properties of Yarns by the Single-Strand Method'') was used to evaluate the tensile properties of PLA yarns after repeated cleaning cycles. An Instron 4444 universal testing machine (Canton, MA) was used to evaluate the tensile properties. A gauge length of 50 mm was used, and the average breaking time was 10 $\pm$ 3 s. From each fabric sample, 60 filament yarns were tested to obtain an average. The average breaking tenacity and breaking elongation of the yarns from the control fabric were 142 MPa and 17.7%, respectively. The breaking tenacity retention percentage, breaking elongation retention percentage, and modulus retention percentage for the PLA yarns after 10, 20, 30, 40, and 50 washing and drying cycles were reported.

A Hitachi model S2000N scanning electron microscope (Tokyo, Japan) was used to study the morphological structure of the PLA fibers before and after cleaning. For observing fibers under the scanning electron microscope, fiber samples were held on conductive tape and sputter-coated with gold and palladium.

Statistical analysis

A full factorial analysis of variance was performed to evaluate the statistical significance of the effects of the pH, washing temperature, drying condition, and number of cleaning cycles on the tenacity retention percentage, elongation retention percentage, and modulus retention percentage. An alpha value of 0.05 was used for statistical significance.

To obtain equations to predict the retention percentage of the breaking tenacity, breaking elongation, and modulus based on the pH during washing, washing temperature, drying temperature, and number of washing and drying cycles, linear regressions were performed. The linear regressions were performed on the average tenacity retention percentage or average elongation retention percentage versus the pH and number of cleaning cycles. A linear regression was also performed on the average modulus retention percentage versus the pH, washing temperature, drying temperature, and number of cleaning cycles.

RESULTS AND DISCUSSION

Effect of the pH during washing on PLA's mechanical properties

Using a pH of 8 during the washing of PLA fabric resulted in 27% greater breaking tenacity retention, 21% greater breaking elongation retention, and 18% greater modulus retention of the PLA yarn after repeated cleaning cycles than using a pH of 10, as shown in Figure 2. These differences are statistically

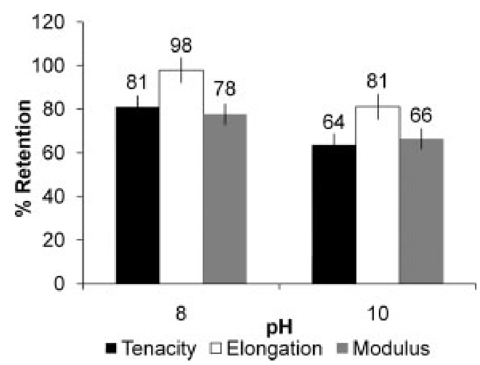

Figure 2 Effect of pH during washing on the retention percentage of the breaking tenacity, breaking elongation, and modulus for PLA yarn after repeated cleanings averaged across all washing temperatures, all drying conditions, and 10, 20, 30, 40, and 50 cleaning cycles.

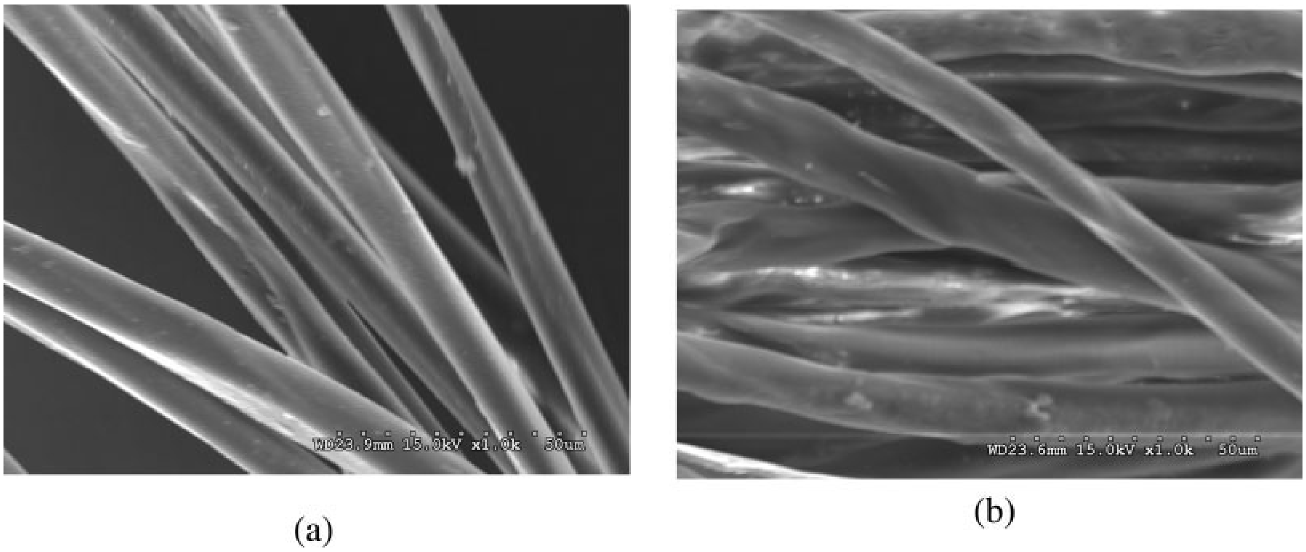

Figure 3 PLA fibers (a) before any cleaning cycles and (b) after 50 cleaning cycles at pH 10 with a washing temperature of 55°C and with tumble drying at 70°C.

significant with respect to the tenacity retention percentage ($p < 0.0001$), elongation retention percentage ($p < 0.0001$), and modulus retention percentage ($p = 0.0009$).

The losses in the breaking tenacity, breaking elongation, and modulus for the PLA yarn after repeated cleanings were possibly caused by hydrolysis of the polymer and/or mechanical damage to the fiber. The PLA fibers experienced some mechanical damage during washing and tumble drying because the agitation in these processes caused the fibers to rub against one another. In the scanning electron microscopy picture in Figure 3, the surface of the laundered PLA fibers shows a smoothly eroded surface, and this suggests that damage to the fibers was probably not mechanical damage because mechanically damaged fibers would have a fuzzy and fibrillated surface. In addition, mechanical damage to the fibers probably did not differ with the pH during washing, and therefore less hydrolysis of the polymer was probably the main cause for pH 8 giving greater tenacity, elongation, and modulus retention than pH 10. This finding agrees with studies that have shown that PLA is hydrolyzed more readily under stronger alkaline conditions.[26,27]

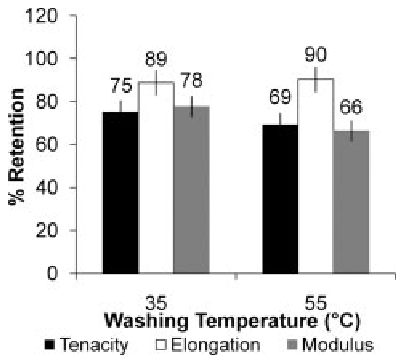

Figure 4 Effect of the water temperature during washing on the retention percentage of the breaking tenacity, breaking elongation, and modulus for PLA yarn averaged across all pH levels, all drying conditions, and 10, 20, 30, 40, and 50 cleaning cycles.

Effect of the washing temperature on PLA's mechanical properties

Using a water temperature of 35°C during the washing of PLA fabric gave 9% greater breaking tenacity retention and 12% greater modulus retention for the PLA yarn than using a water temperature of 55°C, as shown in Figure 4. These differences are statistically significant for modulus retention ($p = 0.0098$). PLA yarn lost less modulus at the lower washing temperature because there was less thermal energy for hydrolysis of the polymer to occur. The effect of the washing temperature is not significant for tenacity retention ($p = 0.1067$) and elongation retention ($p = 0.7047$), and this indicates that within the temperature range studied (35–55°C), the washing temperature does not have much effect on the breaking tenacity and breaking elongation of PLA yarn.

Effect of the drying conditions on PLA's mechanical properties

The tenacity retention percentage and modulus retention percentage for the PLA yarn increased as the temperature used for drying the PLA fabric decreased from 70 to 21°C, as shown in Figure 5. Air drying at 21°C and 65% RH resulted in 12% greater breaking tenacity retention and 23% greater modulus

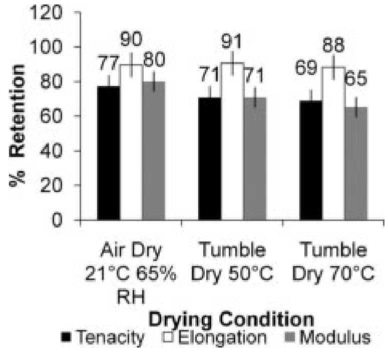

Figure 5 Effect of the conditions during drying on the retention percentage of the breaking tenacity, breaking elongation, and modulus for PLA yarn averaged across all pH levels, all washing temperatures, and 10, 20, 30, 40, and 50 cleaning cycles.

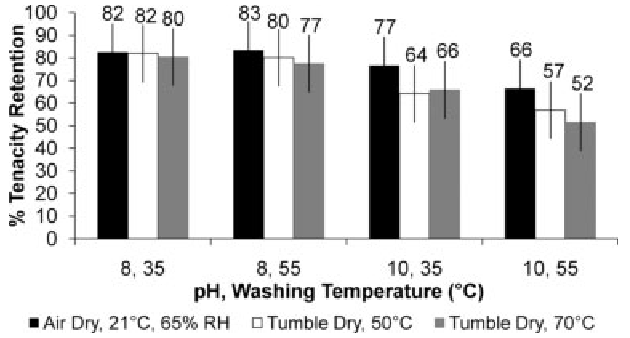

Figure 6 Effect of the interaction between the pH during washing, the water temperature during washing, and the drying conditions on the breaking tenacity retention percentage for PLA yarn averaged across 10, 20, 30, 40, and 50 cleaning cycles.

retention than tumble drying at 70°C. Tumble drying at 50°C gave 3% greater breaking tenacity retention and 9% greater modulus retention than tumble drying at the higher temperature. These differences are statistically significant for modulus retention (p = 0.0016). PLA yarn had greater modulus retention when lower temperatures were used during drying of the PLA fabric because there was less thermal energy in the system for hydrolysis of the polymer. The effect of the drying condition is not statistically significant for breaking tenacity retention (p = 0.1489) and breaking elongation retention (p = 0.8935), and therefore within the temperature range studied (21–70°C), the drying condition does not have a strong effect on the breaking tenacity and breaking elongation of PLA yarn.

Effect of pH/washing temperature/drying condition interactions

The effect of the interaction of the pH, washing temperature, and drying condition on the breaking tenacity retention percentage was not statistically significant (p = 0.9308). However, some combinations of the pH, washing temperature, and drying condition gave significantly greater breaking tenacity retention than other combinations. The pH 8/55°C washing temperature/air dry, pH 8/35°C washing temperature/air dry, and pH 8/35°C washing temperature/tumble dry at 50°C conditions resulted in 58–60% greater breaking tenacity retention than the pH 10/55°C washing temperature/tumble dry at 70°C condition, as shown in Figure 6, and these differences were statistically significant (p = 0.0255, 0.0356, and 0.0422, respectively). The use of a weakly alkaline pH and a lower temperature during the washing or drying of PLA fabric resulted in greater breaking tenacity retention for the PLA yarn than the use of a strongly alkaline pH and higher temperatures during washing and drying because the stronger alkaline conditions accelerated hydrolysis of the polymer and the higher temperature gave more thermal energy for hydrolysis to occur.

The effect of the interaction of the pH during washing, washing temperature, and drying condition on the breaking elongation retention percentage was not statistically significant, as shown in Figure 7 (p = 0.9393).

The effect of the interaction of the pH, washing temperature, and drying treatment on the modulus retention was not statistically significant (p = 0.9530). However, some combinations of the pH, washing temperature, and drying condition gave significantly greater modulus retention than other combinations. As shown in Figure 8, the pH 8/35°C washing temperature/air dry condition gave 50–64% greater modulus retention than the pH 10/55°C washing temperature/tumble dry at 50°C and pH 10/55°C washing temperature/tumble dry at 70°C conditions, and these differences were statistically significant (p = 0.0211 and 0.0021, respectively). The use of a combination of a weakly alkaline pH and lower temperatures during washing and drying of the PLA fabric resulted in

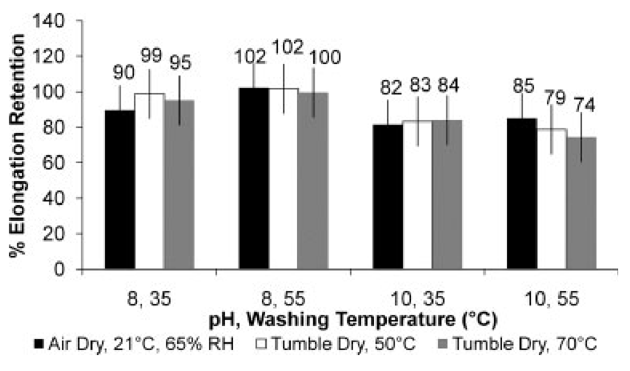

Figure 7 Effect of the interaction between the pH during washing, the water temperature during washing, and the drying conditions on the breaking elongation retention percentage for PLA yarn averaged across 10, 20, 30, 40, and 50 cleaning cycles.

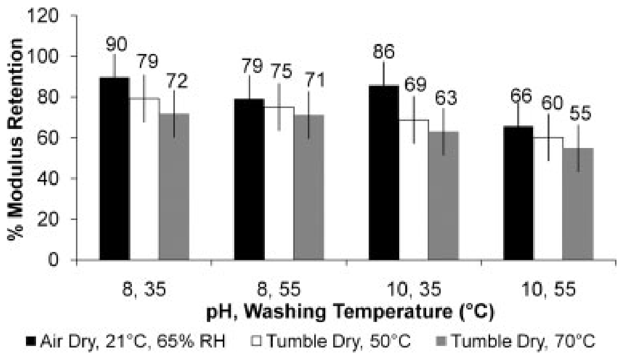

Figure 8 Effect of the interaction between the pH during washing, the water temperature during washing, and the drying conditions on the average modulus retention percentage for PLA yarn averaged across 10, 20, 30, 40, and 50 cleaning cycles.

greater modulus retention for the PLA yarn than the use of a combination of a strongly alkaline pH and higher temperatures during washing and drying because a more strongly alkaline pH accelerated the hydrolysis of PLA and a higher temperature provided greater thermal energy for hydrolysis of the polymer. The pH 10/35°C washing temperature/air dry condition gave 56% greater modulus retention than the pH 10/55°C washing temperature/tumble dry at 70°C condition, and this was a statistically significant difference ($p = 0.0117$). Although a strongly alkaline pH was used for both conditions, the use of lower temperatures during washing and drying resulted in greater modulus retention for the PLA yarn because there was less thermal energy for the polymer to undergo hydrolysis.

Prediction of the mechanical properties

Because the main effects of pH ($p < 0.0001$) and number of cleaning cycles ($p < 0.0001$) are statistically significant for the breaking tenacity retention percentage and elongation retention percentage, a linear regression was performed on the average breaking tenacity retention percentage versus the pH during washing and the number of cleaning cycles. This linear regression gives eq. (1) ($R^2 = 0.747$):

$$\%TR = 171.9 - 8.7\ pH - 0.7\ \#C \quad (1)$$

where %TR is the tenacity retention percentage, pH is the pH during washing, and #C is the number of cleaning cycles. A linear regression of the average elongation retention percentage versus the pH and number of cleaning cycles gives eq. (2) ($R^2 = 0.766$):

$$\%ER = 182.4 - 8.3\ pH - 0.6\ \#C \quad (2)$$

where %ER is the breaking elongation retention percentage.

Because the main effects of the pH ($p = 0.0009$), washing temperature ($p = 0.0098$), drying condition ($p = 0.0016$), and number of cleaning cycles ($p = 0.0010$) on the modulus retention percentage are statistically significant, a linear regression was performed on the average modulus retention percentage versus the pH, washing temperature, drying temperature, and number of cleaning cycles. This linear regression gives eq. (3) ($R^2 = 0.879$):

$$\%MR = 172.4 - 5.7\,pH - 0.5\,\#C - 0.4\,WT - 0.3\,DT \quad (3)$$

where %MR is the modulus retention percentage, WT is the water temperature during washing, and DT is the temperature during drying.

The high R^2 values of eqs. (1)–(3) indicate that there are strong linear relationships between the average mechanical property retention percentage and the corresponding conditions during cleaning. These equations can be used to predict the breaking tenacity retention percentage, breaking elongation retention percentage, and modulus retention percentage for PLA yarn after cleaning of the PLA fabric for a given number of cleaning cycles, at a given pH and temperature during washing, and at a given drying temperature.

CONCLUSIONS

The ability of PLA to retain its mechanical properties after repeated cleaning cycles at various pH levels and temperatures during washing and under various drying conditions has been explained. For the cleaning of PLA fabric, washing the fabric at pH 8 results in greater breaking tenacity, breaking elongation, and modulus retention for the PLA yarn than washing it at pH 10. Washing PLA fabric at a water temperature of 35°C and air drying it at 21°C and 65% RH give greater modulus retention for the PLA yarn than washing the fabric at 55°C and tumble drying it at 70°C. Mechanical damage to the PLA fibers possibly caused some loss in the mechanical properties because agitation during washing and tumble drying caused the fibers to rub against one another. However, hydrolysis of the polymer was probably the main cause of the loss of mechanical properties because PLA is hydrolyzed more readily under strongly alkaline conditions and at higher temperatures.

Linear regressions were performed on the breaking tenacity retention percentage, breaking elongation retention percentage, and modulus retention percentage versus certain cleaning parameters, and linear equations were obtained with high R^2 values. The equations can be used to predict the breaking tenacity retention percentage, breaking elongation retention percentage, and modulus retention percentage for PLA yarn after the PLA fabric has been sent through a given number of cleaning cycles at a given pH during washing, washing temperature, and drying temperature.

On the basis of the findings of this study, we recommend certain conditions for the cleaning of PLA fabrics that will result in greater retention of the mechanical properties for PLA. PLA fabrics should be cleaned with detergents with a low pH (i.e., pH 8), and detergents with a high pH (i.e., pH 10) should be avoided. PLA fabrics should be washed at relatively cold temperatures (i.e., 35°C), and hot washing temperatures should be avoided (i.e., 55°C). PLA fabrics should be air-dried, but if tumble drying is preferred, low temperatures (i.e., 50°C) should be used. High drying temperatures should be avoided (i.e., 70°C).

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