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Molecular modeling study of the resistance of PLA to hydrolysis based on the blending of PLLA and PDLA

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Abstract

Molecular modeling has been used to explain how the blending of poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) affects the resistance of poly(lactide) (PLA) to hydrolysis. Amorphous PLLA/PDLA blends were created using molecular modeling, and the minimum potential energy of the blends before and after hydrolysis were obtained. The 50/50 blend has the greatest resistance to hydrolysis, which agrees with past experiments and is due to its having stronger hydrogen-bonding and dipole–dipole interactions than pure PLLA or PDLA. This is based on the 50/50 blend having more of these interactions and shorter average lengths for the hydrogen-bonds and dipole–dipole interactions compared to pure PLLA and PDLA. Hydrogen-bonding possibly has a greater effect than the dipole–dipole interactions on the resistance to hydrolysis. The change in potential energy for hydrolysis decreases linearly with increasing % PLLA or % PDLA from 0 to 50%.

Keywords: Hydrolysis; Degradation; Polylactic acid

1. Introduction

Poly(lactide) or poly(lactic acid) (PLA) is a type of polyester known for its biodegradability, which is why much research has been conducted on controlling the hydrolysis of PLA for medical uses. PLA has been used as a matrix for the controlled-release of drugs and as scaffolds on which living tissue can regenerate itself [1,2]. PLA is also used in materials that require good stability during their useful life and good biodegradability afterwards. For example, PLA is a suitable packaging material [3]. PLA is also used in textiles such as apparel, indoor and outdoor furnishings, and hygiene products [4–9].

The percentage of poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) in polymer blends affect the crystal structure, melting point, and glass-transition of PLA [10–27]. A 50/50 PLLA/PDLA blend can have a different crystal structure from that of pure PLLA or PDLA [10–17]. The 50/50 blend can form a stereocomplex, which is a complex between PLLA and PDLA [10–14]. The stereocomplex structure of the 50/50 PLLA/PDLA blend has a glass-transition temperature of 65–72 °C [18–20] and a melting point of 220–230 °C, which are both higher than those of pure PLLA and PDLA [18–26]. The glass transition temperature of pure PLLA and pure PDLA is 50–65 °C [18–20,27], and their melting point is 170–195 °C [11,18,20,21,25–27].

The percentage of PLLA and PDLA in blends affects the mechanical properties of PLA. Fibers containing a 50/50 PLLA/PDLA blend have been found to have relatively high Young's modulus (2.5–4.5 GPa) and tenacity (100–400 MPa), which increase with increasing take-up velocity from 1 to 5 km/min during melt spinning due to increased formation of stereocomplex crystallites and increased crystallinity from 8 to 36% [28]. At a given molecular weight within 1×10^5–1×10^6 g/mol, a 50/50 blended film has been found to have greater tensile strength, Young's modulus, and elongation-at-break than a PLLA or PDLA film [29]. PLA fiber has shown 40% strength loss at pH 4 and 110 °C during dyeing, and it has exhibited complete strength loss at 130 °C. Greater than 55% strength loss has been reported for PLA fiber at 110 °C and pH 7–8, and pH 4–6 at the same temperature has resulted in 35–40% strength loss for the fiber [5]. Improved resistance of PLA to hydrolysis is therefore, desirable.

The percentage of PLLA and PDLA in blends is known to affect the enzymatic hydrolysis of PLA. For hydrolysis of PLA

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films at 20 °C and pH 8.5, a well-stereocomplexed 50/50 PLLA/PDLA blend has shown a much lower rate of hydrolysis than a semi-crystalline PLLA film, and PDLA film has given a much lower rate of hydrolysis compared to the PLLA film because the enzyme proteinase K has preference for PLLA. However, parameters other than the optical isomer content were varied in this case because PLLA had an 11% higher initial molecular weight than PDLA, and the percent crystallinity and orientation of the films were not reported [30]. Differences in these parameters would affect the rate of hydrolysis.

Hydrolysis of PLA at 37 °C and pH 7.4 without the use of enzymes is affected by the percentage of PLLA and PDLA in polymer blends. PDLA film has been observed to have an 11% higher hydrolysis rate constant and a greater extent of hydrolysis compared to a PLLA film [18]. PDLA also has shown 23% weight loss after 24 months of hydrolysis while PLLA has only shown 10% weight loss [19]. However, well-crystallized PLLA and PDLA have given very similar hydrolysis behavior with both showing a 95–96% drop in average molecular weight after 24 months of hydrolysis [31]. A 50/50 PLLA/PDLA blend with pure PLLA and PDLA crystallites and no stereocomplex crystallites has given only a 15–24% lower hydrolysis rate constant compared to pure PLLA and PDLA [18]. In addition, these types of 50/50 blends have shown 14% weight loss after 24 months of hydrolysis, which is very close to the 10% loss for pure PLLA and 23% loss for pure PDLA [19]. However, a well-stereocomplexed 50/50 blend has shown much better resistance to hydrolysis compared to well-crystallized pure PLLA and PDLA with a 53% reduction in the average molecular weight after 24 months of hydrolysis compared to a 95–96% reduction for the pure homopolymers [31]. The contradictions in these studies are due to variability in parameters of the films other than the PLLA and PDLA content such as crystallinity, crystal structure, initial molecular weight, tenacity, Young's modulus, and elongation at break.

For studies that vary the percentages of PLLA and PDLA in blends and study their effect on hydrolysis of PLA, it is difficult to hold the percent crystallinity, molecular weight, and other factors constant experimentally. The purpose of our current study is to explain how the percentages of PLLA and PDLA in blends affect the resistance of amorphous PLA to hydrolysis. We have used molecular modeling to hold these other variables constant.

2. Experimental

2.1. Molecular modeling simulations

The molecular modeling software MS Modeling 3.0, available from Accelrys was used to study the resistance of PLA blends to hydrolysis. With the Amorphous Cell module of MS Modeling 3.0, unit cells of amorphous PLA were created that consisted of various blends of PLLA and PDLA. Each unit cell was built to contain 10 PLA molecules with a DP of 50 since it was the largest system that our computer could process. The unit cell parameters were set at $a=b=c=36.17$ Å and $\alpha=\beta=\gamma=90$, which is a density of 1.27 g/cm^3. This density is based on the amorphous density of PLA from the literature [32]. Hydrolysis of amorphous PLA was modeled because the amorphous regions of a fiber are hydrolyzed first and to a greater extent than the crystal. In addition to 100% PLLA and 100% PDLA, the following PLLA/PDLA blends were created: 80/20, 60/40, 50/50, 40/60, and 20/80. For example, the 80/20 blend contained eight PLLA and two PDLA molecules.

For hydrolysis of each PLA blend, we modeled one situation in which one PLLA chain in the blend was cleaved and another situation in which one PDLA chain was cleaved. In each situation, the ester linkage between the 25th and 26th lactide units of the PLA chain was cleaved so that the hydrolyzed PLA blend contained nine molecules with a DP of 50 and 2 with a DP of 25. The two cleaved segments were then separated by translation and rotation of one segment such that the distance between the two end hydroxyl groups was greater than 10 Å since 10 Å was set as the non-bonded cutoff. The non-bonded cutoff is the distance between any pair of atoms beyond which molecular modeling neglects their van der Waals interactions. The non-bonded cutoff was set at 10 Å since this is within half of the unit cell length of 36.17 Å and since 10 Å is conventionally used in molecular modeling of macromolecules [33,34]. The molecular modeling software accounted for the electrostatic interactions by using the cell multipole method, which calculated the electrostatic interactions between groups of atoms that are grouped based on their location in the unit cell. According to this method, each atom was regrouped when its position in the cell moved by more than 1 Å during a simulation.

To minimize the energy of the unhydrolyzed and hydrolyzed PLA blends, molecular dynamics simulations and energy minimizations were run using the Amorphous Cell and Discover modules of MS Modeling 3.0. The polymer consistent force field (pcff) was the set of parameters used by these modules to calculate the potential energy of the PLA blends. The pcff was chosen since it is accurate for modeling polymers, and partial charges were assigned to each atom according to this forcefield [35–37]. Beginning with each unhydrolyzed PLA structure, an energy minimization was first performed using the conjugate gradient method with convergence criteria of 0.1 kcal/mol per Å. A molecular dynamics (MD) simulation was then performed on this structure using a constant volume/constant temperature ensemble at 383 K. This temperature was selected because this is the temperature at which 40% strength loss has been observed for PLA fiber [5]. The MD simulation was performed for 500,000 steps with a time step of 10^{-15} s and with an equilibration time of 500×10^{-12} s. The final snapshot of the MD simulation was selected for the next energy minimization because at this point in the MD simulation, the potential energy oscillated within ± 150 kcal/mol. An energy minimization was then performed on this structure using the conjugate gradient method and convergence criteria of 0.1 kcal/mol per Å. After the energy minimization of each unhydrolyzed PLA blend, one chain was cleaved as described above to create the hydrolyzed PLA blends. After separating the cleaved segments, an energy minimization, MD simulation, and energy minimization were performed using the same simulation conditions specified for the unhydrolyzed PLA blend. For each blend, MD simulations/energy minimizations were performed five times for the unhydrolyzed and hydrolyzed PLA blends. This many simulations were required to ensure that the conformations of the PLA structures were energy minimized to the extent that the differences between the energies of the hydrolyzed and unhydrolyzed structures did not change by more than 5% after repeated simulations.

2.2. Analysis of molecular modeling data

To evaluate the resistance to hydrolysis of the PLA blends, the change in potential energy for hydrolysis was calculated for the various PLA blends according to Eq. (1).

$$\Delta U = U_{\mathrm{hyd}} - U_{\mathrm{unhyd}} - U_{\mathrm{w}} \tag{1}$$

In Eq. (1), ΔU is the change in potential energy for the hydrolysis of the PLA blend. U_{unhyd} is the potential energy of the PLA blend before hydrolysis, U_{hyd} is its potential energy after hydrolysis, and U_{w} is the potential energy of one water molecule. The potential energy values were obtained from the energy minimizations using molecular modeling.

To evaluate the contribution of the intermolecular interactions to the ΔU of the 50/50 blend and pure PLLA and PDLA, the change in van der Waals interaction energy after hydrolysis ($\Delta U_{\mathrm{van\ der\ Waals}}$) and the change in electrostatic interaction energy after hydrolysis ($\Delta U_{\mathrm{electrostatic}}$) were calculated using the Discover module of MS Modeling 3.0. For hydrogen-bonding in the 50/50 blend and in pure PLLA and PDLA, the Visualizer module of MS Modeling 3.0 was used to obtain the number of hydrogen-bonds of lengths within 3.00, 2.90, 2.80, 2.70, 2.60, 2.50, 2.40, 2.30, 2.20, 2.10, 2.00, 1.90, and 1.80 Å in each of these structures before hydrolysis. There were no hydrogen-bonds of lengths within 1.70 Å. For the 50/50 blend, PLLA, and PDLA before hydrolysis, the average length of the 1952 shortest and 14 shortest hydrogen-bonds were calculated. The average hydrogen-bond length was calculated assuming all hydrogen-bonds within each interval of 0.10 Å had the largest possible length. For example, all the hydrogen-bonds of lengths within 2.50–2.60 Å were assumed to have a length of 2.60 Å. For the dipole–dipole interactions in the 50/50 blend and in pure PLLA and PDLA, the number of dipole–dipole interactions of lengths within 3.00, 2.90, 2.80, and 2.70 Å were obtained. There were no dipole–dipole interactions of lengths within 2.60 Å. The average dipole–dipole interaction length was calculated in a similar way as with the average hydrogen-bond length.

2.3. Evaluation of hydrolysis experimental data

To find if the molecular modeling calculations agree with experimental data from previous studies on the hydrolysis of PLA blends, data for the hydrolysis of PLLA, PDLA, and 50/50 PLLA/PDLA films were obtained. In the previous study, pure PLLA and PDLA were well-crystallized, and the blend was well-stereocomplexed. They underwent hydrolysis in a phosphate-buffered solution at pH 7.4 and 37 °C, and their number average molecular weights (M_n) at certain times of hydrolysis (t) were obtained as indicated in Table 1 [31]. The equilibrium constants for hydrolysis of the PLA films were calculated according to Eq. (2).

Table 1
Molecular weight ($M_n \times 10^{-4}$, g/mol) of PLLA, PDLA, and 50/50 PLLA/PDLA at certain hydrolysis times (t, months)

t, Months	$M_n \times 10^{-4}$ (g/mol)		
	PLLA	PDLA	50/50 PLLA/PDLA
0	9.00	9.50	9.50
4	7.50	7.50	8.50
8	5.50	4.50	8.00
12	2.00	1.50	7.50
16	1.75	0.80	6.00
24	0.45	0.40	4.50
30	0.35	0.30	2.50

Data were obtained from Tsuji [31].

$$K = \frac{[\mathrm{-CHCH_3OH}][\mathrm{HOOC-}]}{[\mathrm{-CHCH_3COO-}][\mathrm{H_2O}]} \tag{2}$$

In Eq. (2), K is the equilibrium constant, [–CHCH$_3$COO–] is the DP of PLA when hydrolysis is at equilibrium, and [H$_2$O] is the number of water molecules at equilibrium. The [–CHCH$_3$OH] and [–HOOC] equal the initial DP of PLA minus the DP at equilibrium. It was assumed that all of the PLA chains had the same DP at a given time during hydrolysis. A fiber-to-liquor ratio of 1:1 was assumed.

3. Results and discussion

3.1. ΔU for hydrolysis

Molecular modeling has been used to explain the effect of blending PLLA and PDLA on the resistance of PLA to hydrolysis. The 50/50 PLLA/PDLA blend is found to have the least negative ΔU of the PLA blends included in this study and therefore, the greatest resistance to hydrolysis while pure PLLA and PDLA have the most negative ΔU as shown in Fig. 1. The difference in the ΔU values between the 50/50 blend and pure PLLA and PDLA is about 37–38 kcal/mol, which indicates that pure PLLA and PDLA are hydrolyzed to a much greater extent compared to the 50/50 blend. This trend agrees with a previous study that found that the extent of hydrolysis at 37 °C and pH 7.4 is less for a 50/50 blend that is well-stereocomplexed compared to well-crystallized pure PLLA or PDLA [31]. Applying Eq. (2) to the data of Tsuji, the K for PLLA (7.82) and PDLA (9.80) are greater than that of a 50/50 PLLA/PDLA blend (0.632).

The ΔU is found to decrease linearly with increasing % PLLA or % PDLA within the range 0–50% as shown in Fig. 1 with an R^2 of 0.998 and 0.995. Blending PLLA and PDLA in

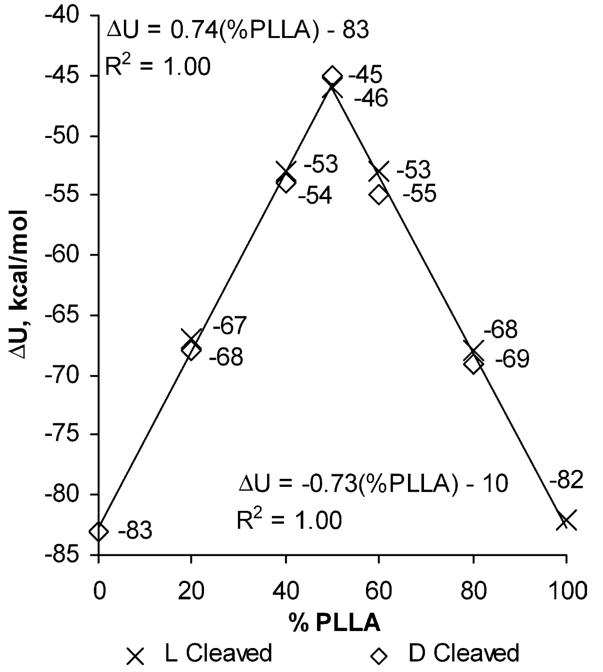

Fig. 1. Change in potential energy for hydrolysis (ΔU) of various blends of PLLA and PDLA graphed by % PLLA in the blend and by whether a PLLA (L-cleaved) or PDLA (D-cleaved) was cleaved.

more equal amounts therefore, improves their resistance to hydrolysis.

3.2. Stability before and after hydrolysis

As shown in Fig. 2, the potential energies (U) before hydrolysis for the PLA blends are relatively high, which indicate that the polymer is very unstable. These potential energies are high compared to values of 376–490 kcal/mol for nylon 6,6 with a DP of 20 calculated using molecular modeling [38]. The U before hydrolysis decreases as the % PLLA or % PDLA in the blend increases from 0 to 50%. Although the difference in the potential energy between the 50/50 blend and PLLA and PDLA is only 0.43 and 0.44%, respectively, it results in a large difference in the resistance to hydrolysis as discussed above. The greater stability of the 50/50 blend compared to that of pure PLLA and PDLA indicates the 50/50 blend has stronger intermolecular interactions. This agrees with findings that a 50/50 blend has higher tensile strength and Young's modulus at a given molecular weight compared to pure PLLA and PDLA [29].

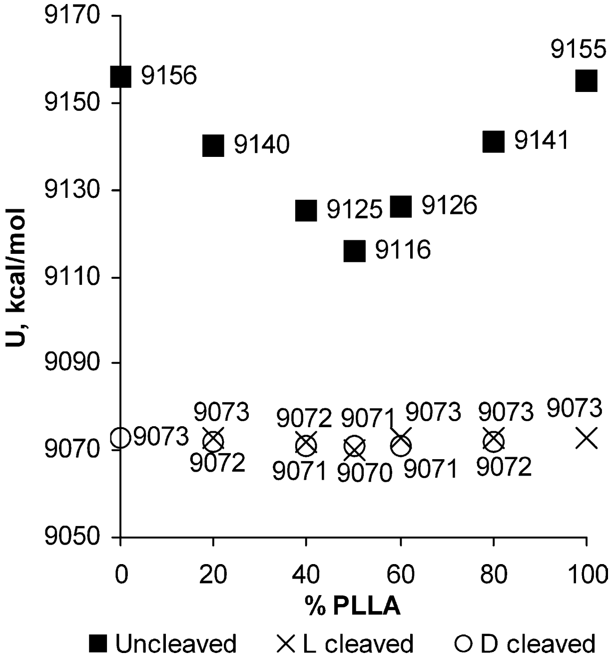

Fig. 2. Potential energies (U) of various blends of PLLA and PDLA before hydrolysis (uncleaved), after hydrolysis of one PLLA (L-cleaved), and after hydrolysis of one PDLA (D-cleaved) graphed by % PLLA in the blend.

The statistical significance of the U values before and after hydrolysis is demonstrated by the fact that for each case where the % PLLA of one blend equals the % PDLA of another blend, their potential energies are equal to within 0.01%, and by the fact that for each blend, the potential energies after hydrolysis for cleavage of a PLLA or PDLA are equal within 0.01%. In each of these cases, the ΔU values are also equal within 1.2–3.8%. A further proof of the statistical significance is that calculation of the U value for cleavage of one PLLA in the 50%/50% blend was replicated, and the U is 9067 kcal/mol, which differs by only 0.03% from the original. Additional support for statistical significance of the calculations is that the linear regressions of the ΔU values versus the % PLLA have R^2 values of 0.998 and 0.995.

3.3. Effect of intermolecular interactions on the resistance to hydrolysis

The 50/50 blend gives better resistance to hydrolysis because it allows for stronger hydrogen-bonding and dipole–dipole interactions compared to pure PLLA and PDLA. This is because the 50/50 blend and the pure homopolymers differ more with respect to the change in electrostatic interaction energy ($\Delta U_{\text{electrostatic}}$) than with respect to the change in van der Waals interaction energy ($\Delta U_{\text{van der Waals}}$). We recognize that dipole–dipole interactions are a type of van der Waals interaction, but in molecular modeling, the $U_{\text{electrostatic}}$ accounts for the potential energy of the hydrogen-bonding and dipole–dipole interactions but not that of the dispersion forces or dipole-induced dipole interactions. The stronger hydrogen-bonding and dipole–dipole interactions for the 50/50 blend are also based on its having more hydrogen-bonds and dipole–dipole interactions compared to pure PLLA and PDLA and having shorter average lengths for its hydrogen-bonds and dipole–dipole interactions.

The differences between the 50/50 blend and the pure homopolymers with respect to the $\Delta U_{\text{electrostatic}}$ are 42–44 kcal/mol, and their differences with respect to the $\Delta U_{\text{van der Waals}}$ are only 3–4 kcal/mol as shown in Table 2. In addition, the 50/50 blend has a less negative $\Delta U_{\text{electrostatic}}$ (-38 and -37 kcal/mol) compared to pure PLLA (-80 kcal/mol) and PDLA (-81 kcal/mol). The intermolecular interactions accounted for by the $U_{\text{electrostatic}}$ therefore, give the 50/50 blend

Table 2
The change in electrostatic interaction energy after hydrolysis ($\Delta U_{\text{electrostatic}}$) and the change in van der Waals interaction energy after hydrolysis ($\Delta U_{\text{van der Waals}}$) for PLLA, PDLA, and the 50/50 blend

	PLLA	PDLA	50/50, L-cleaved	50/50, D-cleaved
$\Delta U_{\text{electrostatic}}$ (kcal/mol)	−80	−81	−38	−37
$\Delta U_{\text{van der Waals}}$ (kcal/mol)	−24	−24	−20	−21

50/50, L-cleaved is the 50/50 blend with a PLLA cleaved, and 50/50, D-cleaved is that with a PDLA cleaved.

greater resistance to hydrolysis compared to the pure homopolymers, and the 50/50 blend and the pure homopolymers are more similar with respect to the intermolecular interactions accounted for by the $U_{\text{van der Waals}}$.

The 50/50 blend before hydrolysis has about 2% more hydrogen-bonds of lengths within 3.00 Å and about 21% more hydrogen-bonds of lengths within 2.00 Å compared to pure PLLA and PDLA as shown in Table 3. In addition to having more hydrogen-bonds than the pure homopolymers, the hydrogen-bonds in the 50/50 blend are shorter in average length for the 1952 shortest hydrogen-bonds (2.71 Å) and for the 14 shortest hydrogen-bonds (1.86 Å) compared to those in the pure homopolymers before hydrolysis (2.72 Å for the 1952 shortest hydrogen-bonds and 1.87 Å for the 14 shortest hydrogen-bonds). The 50/50 blend has about 7–8% more dipole–dipole interactions of lengths within 3.00 Å compared to pure PLLA and PDLA, and the average length of the 200 shortest dipole–dipole interactions is shorter in the 50/50 blend (2.93 Å) than in the pure homopolymers (2.94 Å). The greater number of hydrogen-bonds and dipole–dipole interactions in the 50/50 blend and its shorter average lengths for those hydrogen-bonds and dipole–dipole interactions demonstrate that it has stronger hydrogen-bonding and stronger dipole–dipole interactions compared to pure PLLA and PDLA. The hydrogen-bonding possibly has a greater effect than the dipole–dipole interactions on giving the 50/50 blend greater resistance to hydrolysis because the 50/50 blend has more hydrogen-bonds than dipole–dipole interactions of lengths within 3.00 Å by a factor of about 9, and the average length of the shortest 1952 hydrogen-bonds (2.71 Å) in the 50/50 blend is lower than the average length of the 200 shortest dipole–dipole interactions in that blend (2.93 Å) as shown in Table 3.

Table 3
The number of hydrogen-bonds of lengths within 3.00 Å (number of H-bonds ≤3.00 Å) and within 2.00 Å (number of H-bonds ≤2.00 Å), the average hydrogen-bond length of the shortest 1952 hydrogen-bonds (Avg H-bond length of 1952 shortest H-bonds), the average length of the 14 shortest hydrogen-bonds (Avg H-bond length of 14 shortest H-bonds), the number of dipole–dipole interactions of lengths within 3.00 Å (number of dipole–dipole interactions ≤3.00 Å), and the average length of the 200 shortest dipole–dipole interactions (Avg dipole–dipole length of 200 shortest dipole–dipole) for PLLA, PDLA, and the 50/50 blend before hydrolysis

	PLLA	PDLA	50/50
Number of H-bonds ≤3.00 Å	1953	1952	1992
Avg H-bond length of 1952 shortest H-bonds (Å)	2.72	2.72	2.71
Number of H-bonds ≤2.00 Å	14	14	17
Avg H-bond length of 14 shortest H-bonds (Å)	1.87	1.87	1.86
Number of dipole–dipole interactions ≤3.00 Å	202	200	216
Avg dipole–dipole length of 200 shortest dipole–dipole (Å)	2.94	2.94	2.93

For every case where the % PLLA of one blend equals the % PDLA of another blend, the two blends have about the same potential energy before hydrolysis as shown in Fig. 2. In addition, for a given blend, the potential energy after hydrolysis for cleavage of a PLLA is within 0.01% of that for cleavage of a PDLA. The two blends in each of these cases also have approximately equal ΔU values as shown in Fig. 1. Two blends therefore, have approximately the same resistance to hydrolysis if they are mirror images of each other, which occurs when the weight percentage and molecular weight distribution of PLLA in one blend is equal to that of PDLA in the other blend. Blends that are mirror images of each other have about the same resistance to hydrolysis because they have nearly identical hydrogen-bonding and dipole–dipole interactions as demonstrated in Table 3 for pure PLLA and PDLA.

4. Conclusion

Molecular modeling has been used to explain how the percentages of PLLA and PDLA in PLA blends affect its resistance to hydrolysis. The 50/50 PLLA/PDLA blend is found to have the greatest resistance to hydrolysis among the blends included in this study, and this finding is supported by an earlier study that found that a 50/50 blended film is hydrolyzed to a lesser extent than a pure PLLA or PDLA film. The high potential energy of all the PLLA/PDLA blends before hydrolysis (9116–9156 kcal/mol) indicates that PLA is very unstable. The change in potential energy for hydrolysis, ΔU, is found to decrease linearly (−83 to −45 kcal/mol) with increasing % PLLA or % PDLA within the range 0–50%. Two blends have the same ΔU when the % PLLA of one blend equals the % PDLA of the other blend, and for a given blend, the ΔU for cleavage of one PLLA is equal to that for cleavage of one PDLA. This indicates that two blends have the same resistance to hydrolysis when the weight percentage and molecular weight distribution of PLLA in one blend is identical to that of PDLA in the other blend because the blends are mirror images of each other. Blending PLLA and PDLA in equal amounts improves the resistance of PLA to hydrolysis because the 50/50 blend is the most energetically stable blend before hydrolysis. The greater resistance to hydrolysis of the 50/50 blend is due to its stronger hydrogen-bonding and dipole–dipole interactions compared to pure PLLA and PDLA. This is based on the finding that the differences between the 50/50 blend and the pure homopolymers with respect to the $\Delta U_{\text{electrostatic}}$ (42–44 kcal/mol), which account for the potential energy of the hydrogen-bonding and dipole–dipole interactions but not that of the dispersion forces or dipole-induced dipole interactions, are larger than their differences with respect to the $\Delta U_{\text{van der Waals}}$ (3–4 kcal/mol). Additionally, the $\Delta U_{\text{electrostatic}}$ is less negative for the 50/50 blend (-38 and -37 kcal/mol) than for pure PLLA (-80 kcal/mol) and PDLA (-81 kcal/mol). The stronger hydrogen-bonding and dipole–dipole interactions in the 50/50 blend are also based on the greater number of hydrogen-bonds and dipole–dipole interactions of lengths within 2.00 and 3.00 Å for the 50/50 blend and the shorter average length for its hydrogen-bonds and dipole–dipole interactions before hydrolysis. Of these intermolecular interactions, the hydrogen-bonding possibly has a greater effect than the dipole–dipole interactions on giving the 50/50 blend greater resistance to hydrolysis because the 50/50 blend has more hydrogen-bonds than dipole–dipole interactions by a factor of about 9, and the average length of the 1952 shortest hydrogen-bonds (2.71 Å) in the 50/50 blend is lower than the average length of the 200 shortest dipole–dipole interactions in that blend (2.93 Å).

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