# Molecular Modeling Simulation Study of Interactions in Starch/Poly(acrylic acid) Blend

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**Abstract**

In this work we have studied the nature of interactions between starch and poly(acrylic acid) by using  semi-empirical AM1 and PM3 methods. Theoretical computations involved the determination of optimal  geometries, binding energies and vibrational frequencies of the blended polymers. Calculations are  performed for four pairs of complexes of glucose (Glu) in starch and acrylic acid (mAA) in poly(acrylic acid) PAA. Based on results of calculation, the binding energies show negative values, which indicate that the interactions of glucose and acrylic acid are favorable at the lower energy. This means that the interactions of starch and PAA are stable. Vibrational frequency analysis of hydroxyl OH and carboxyl C=O groups of the 1Glu–1mAA, 1Glu–2mAA and 1Glu–3mAA complexes with single hydrogen bond showed that the stretching of these groups shifts to a lower wave number due to the formation of hydrogen bonds.

**Keywords**:Polymer blends, AM1, PM3.

## 1.Introduction

Blending of chemically different polymers is an important tool in industrial production of tailoring products with optimized  material properties(Sionkowska 2001). Another route, polymer blending is a simple  yet attractive method to provide combined physical and mechanical properties. Blends of synthetic polymers and starches have been extensively studied since these blends can be prepared so they are biodegradable. Among all  natural biopolymers, starch has been considered as one of the most promising materials because of its easy availability, biodegradability and lower cost.

Starch is the major form of stored carbohydrate in plants such as corn, wheat,rice and potatoes. Starch is composed of a mixture of two polymers of glucose – linear amylose and a highly branched amylopectin(Tang&Alavi 2011). To impart  biodegradability to polymers, starch has been blended with common polymers such as poly(vinyl chloride)(Westhoff et al 1974), polyethylene,(Griffin1974&Otey et al 1987) alpoly(ethylene-*co*-acrylic acid),(Fanta et al 1992)and poly(ethylene-*co*-vinyl alcohol)(George et al 1994). Biodegradable films from starch and ethylene–acrylic acid (EAA) copolymers with the aim of improving their water resistance and preventing them from becoming brittle with age were studied(Otey et al 1977). Compatible mixtures containing up to 90% starch and EAA copolymer were milled or casted from aqueous dispersions into flexible, non-supported films without the aid of a conventional plasticizer. These films were water resistant and appeared to have acceptable physical properties for a variety of packaging and agricultural mulch applications. The added EAA may be associated with the starch molecules enough to hold them in their expanded, flexible states. As the amount of EAA is decreased, this association can be partially disrupted, especially with age or in the presence of a solvent such as water. A technique for blending gelatinized starch and poly(ethylene-*co*-acrylic acid) (EAA) to produce flexible blown films that contain high levels of starch was studied (Otey  *et al* 1980). Starch is a highly hydrophilic macromolecule. It is often used as the degradable additive in the preparation of biodegradable polyethylene film. Polyethylene is resistant to microbial breakdown(Leja et al 2010). The great difference between starch and polyethylene in their properties results in poor compatibility of starch/polyethylene blends (Shujun et al 2006). The use of compatibilizer containing groups capable of hydrogen bonding with starch hydroxyls increases the compatibility in starch-polyethylene blends. Ethylene/acrylic acid copolymer (EAA) is such an example (Yin et al 2008,Jasberg et al 1992, Fanta et al 1990&Villart et al 1995).

The interactions between starch (amylose portion) and poly-propylene carbonate by employing DFT based B3LYP and semi-empirical AM1 and PM3 methods on five complexes were studied (Joshi&Mebel 2010). Meanwhile, the use of  semi-empirical AM1 method to study the interaction on three pairs of starch and poly vinyl alcohol was carried out(Saleh et al 2009).

Recently,  semi-empirical AM1 (Austin Model 1) and PM3 (Parameterized Austin Model 3) methods to study the hydrogen bonding interactions between poly vinyl alcohol and starch were employed(Sin et al 2010). In this study, molecular modeling simulations have been studied to understand the compatibility and interactions between starch and poly(acrylic acid) . In addition to these computational methods, the interactions between these two polymers have also been evaluated using vibrational frequency analysis.

In this work,we have investigated theoretically four pairs of complexes of glucose (Glu) in starch and acrylic

acid (mAA) in poly(acrylic acid) PAA by using the semi-empirical AM1 and PM3 methods. We aimed to evaluate the interaction between glucose (Glu) in starch and acrylic acid (mAA) in poly(acrylic acid) PAA through the formation of hydrogen bonds between them.

**2. Theoretical Methods**

Geometrical optimizations were carried out by using the AM1 & PM3 semi-empirical methods as implemented in the Hyperchem 8 package. All structures were fully optimized at the Restricted Hartree – Fock (RHF). Geometrical optimizations were carried out by using a conjugate gradient method (Polka – Ribiere lgorithm) .The self-consistent-field SCF convergence was set to 0.1 Kcal mol$^{-1}$ in the calculations. Also, Hyperchem was used to generate binding energy and vibrational frequency analysis to produce infrared absorption of the complexes. Three pairs of complexes consisting of increasing numbers of glucose (Glu.) and PAA monomers (mAA) have been studied. The geometrically optimized structures for all the three complexes at different levels of theory are represented in Figs.1-3.

**3. Results and Discusion**

**3.1 Hydrogen bonds**

The important factor that determines the properties of a blend is the compatibility/miscibility of polymer pairs. The chemical structures of the polymeric components have a significant effect on the interactions between the polymers resulting in miscibility of the polymer blend. For starch and PAA blends,both the Carbonyl functional groups of AA have the potential to interact with the hydroxyl groups of Starch via hydrogen bonding. In general, the hydrogen bond is a directed, attractive interaction between electron-deficient hydrogen and a region of high electron density. Most frequently, a hydrogen bond is of the X–H/Y type, where X and Y are electronegative elements and Y possesses one or more lone electron pairs. In most cases, X and Y are F, O and N atoms. The hydrogen bonds are generally much weaker than covalent bonds or other polar bonds, but much stronger than the vander Waals interaction(He et al 2004). For polymer scientists, the hydrogen bond in polymer blends is also an important issue. The presence of inter-associated hydrogen bonds between the components in a blend can promote compatibility and also miscibility and has significant effects on the properties of the blends. In fact, now-a-days the introduction of hydrogen bonds is a routine and effective strategy to achieve the compatibility and to modify the properties of blends (Wiswanathan&Dadmum 2003,2002). A hydrogen bond is formed if the hydrogen-donor distance is less than 3.2 Ångstroms and the angle made by covalent bonds to the donor and acceptor atoms is less than 120 degrees(Hypercube 2002). Figs. 1-3 Show the geometrical optimized structures with the presence of hydrogen bonding between mAA and Glu.

**3.2Binding energy**

The binding energy of each complex was calculated using the following formula:

$$\Delta E = E_{complex} - (E_{Glu.} + E_{mAA})$$

Here, $E_{complex}$, $E_{Glu.}$, $E_{mAA}$ represent total energies of the Glu.-mAA complex, the individual Glu. and mAA molecules, respectively. The computed AM1and PM3 binding energies are presented in Table 1. The negative energies imply a favorable interaction between the two polymers. Also, binding energies show an increasing trend with increasing polymer length for most complexes. Thus ,one can conclude that the interactions between the two polymers are energetically favorable. On the other hand, as the binding energies increase with the polymer length, the interaction between the polymers increases with increasing polymer length.

**3.3Vibrational frequency analysis**

The vibrational frequencies were calculated by using the AM1 and PM3 methods for the 1:1, 1:2 and 1:3 (Glu:mAA) complexes. The computed carbonyl C=O grup frequencies of pure mAA, hydroxyl OH
 group frequencies of pure Glu. and the corresponding frequencies for the complexes are given in Tables 2 and 3. Both systems exhibit a decrease in the carbonyl and hydroxyl bond stretching frequencies in the complex as compared to the corresponding frequencies in mAA and Glu. This clearly indicates a specific interaction between the carbonyl group of mAA and the hydroxyl group of Glu. It can also be seen that the PM3 method overestimates the decrease in the frequencies as compared with the AM1 method.

**4.Conclusion**

The semiemprical AM1 (Austin Model 1) and PM3 (Parameterized Austin Model 3) methods are very useful to understand the interaction in starch/Poly(acrylic acid) blend. The geometrically optimized structures of all

complexes showed the formation of hydrogen bonding between glucose in starch and acrylic acid in poly(acrylic acid). Also,the vibration frequency for C=O and O-H groups was reduced in complexes than that  in acrylic acid and glucose. Theoretical calculation from binding energy showed  that the blend of the complexes has good compatibility between two components  .

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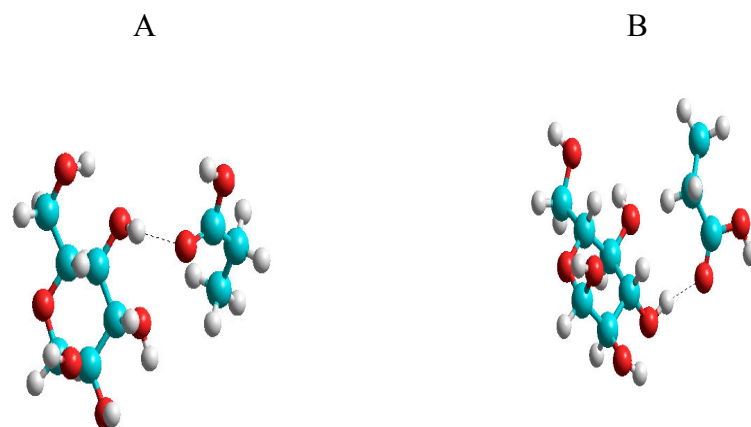Hypercube. HyperChem[®] Release 7 for Windows[®]. United States: Hypercube;2002, chapter 2.

A                                           B



Fig. 1. Geometrically optimized structures of  hydrogen bond Glu–1mAA at (A) AM1 and (B) PM3.

A                                                        B



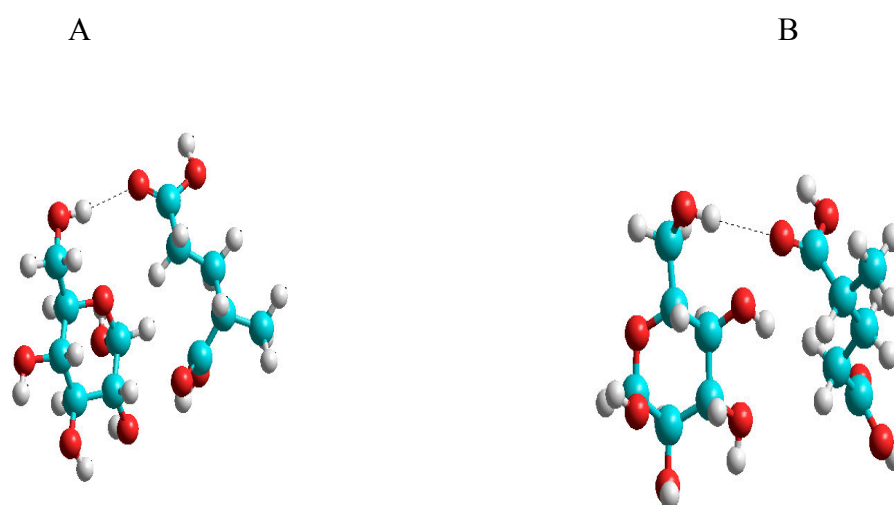Fig. 2. Geometrically optimized structures of hydrogen bond Glu–2mAA at (A) AM1 and (B) PM3.

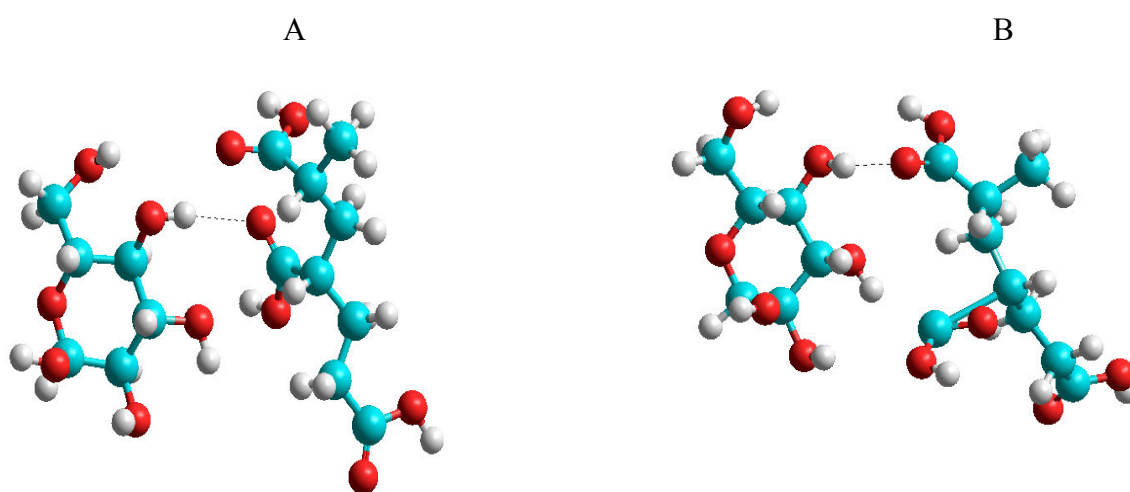A                                                        B



Fig. 3. Geometrically optimized structures of hydrogen bond Glu–3mAA at (A) AM1 and (B) PM3.

Table 1 Binding energies ΔE  (kJ/mol) and hydrogen bond HB distance (Å)at AM1and PM3 of the 1Glu:1mAA, 1Glu:2mAA and 1Glu:3mAA complexes

| Complexes | 1Glu:1mAA | | 1Glu:2mAA | | 1Glu:3mAA | |
|---|---|---|---|---|---|---|
| Model | ΔE | HB distance | ΔE | HB distance | ΔE | HB distance |
| AM1 | -3.67 | 2.13 | -4.53 | 2.23 | -4.26 | 2.34 |
| PM3 | -1.88 | 1.8 | -1.05 | 2.75 | -4.53 | 1.82 |

Table 2 Vibrational frequencies(cm$^{-1}$) of the carbonyl C=O groups at AM1 and PM3 of the 1Glu:1mAA, 1Glu:2mAA and 1Glu:3mAA complexes.

| Complexes | AM1 | | PM3 | |
|---|---|---|---|---|
| | H bond | V.F. | H bond | V.F. |
| 1Glu:1mAA | with without | 2074.83 2074.93 | with without | 2128.13 2128.22 |
| 1Glu:2mAA | with without | 2077.06 2080.32 | with without | 1971.8 1972.31 |
| 1Glu:3mAA | with without | 2066.25 2066.93 | with without | 2128.26 2129.1 |

H Bond=Hydrogen bond; V.F.= Vibrational frequency.

Table 3 Vibrational frequencies(cm$^{-1}$) of the hydroxyl OH groups at AM1 and PM3 of the 1Glu:1mAA, 1Glu:2mAA and 1Glu:3mAA complexes.

| Complexes | AM1 | | PM3 | |
|---|---|---|---|---|
| | H bond | V.F. | H bond | V.F. |
| 1Glu:1mAA | with<br>without | 3461.01<br>3461.76 | with<br>without | 3527.86<br>3552.48 |
| 1Glu:2mAA | with<br>without | 3454.03<br>3460.45 | with<br>without | 3867.25<br>3871.16 |
| 1Glu:3mAA | with<br>without | 3426.12<br>3443.12 | with<br>without | 3530.21<br>3566.05 |

H Bond=Hydrogen bond; V.F.= Vibrational frequency.