Theoretical Insights into Three Types of Oxidized Starch-Based Adhesives: Chemical Stability, Water Resistance, and Shearing Viscosity from a Molecular Viewpoint

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To better understand the origin and difference associated with chemical stability, water resistance, and shearing viscosity of three types of different oxidized modified starch-based adhesives, a detailed theoretical investigation from a molecular viewpoint has been performed using the AM1 semiempirical level and the DFT-B3LYP level, respectively. As a result, our findings suggest that, by Mulliken population analysis (MPA), frontier orbital analysis, and electrostatic potential (EP) analysis based on B3LYP/6-31G calculations, the chemical stability, water resistance, and shearing viscosity of the oxidized modified starch-based adhesives are uniformly improved and corresponding difference for each property presents an identical order: the oxidized grafted cross-linked starch-based adhesive > the oxidized grafted starch-based adhesive > the oxidized starch-based adhesive, which is well consistent with experimental results.

1. Introduction

Starch, the most important energy source and most abundant carbohydrate as common biopolymers, possesses inexpensive and naturally renewable characteristics and is extensively applied in the diverse areas of polymer science [1–6]. At present, starch has been used successfully as an additive in papermaking, as well as an adhesive [7]. In recent years, with the enhancement of people’s awareness to environmental protection and health, the starch-based adhesive has been considered as the most potential adhesive in the application and development [8–12]. However, compared with the “native starch” extracted directly from the plant, the so-called “modified starch” with one or more chemical modifications can reach specific properties [13, 14]. Therefore, a large number of studies have been devoted to exploring the effect of the modification methods on the properties of the starch-based adhesives [15–17], such as gelatinization [18], oxidizing [19], cross-linking [20], and grafting [21]. Meanwhile, the physical properties of these modified starch-based derivatives have also been widely discussed [22, 23], indicating lower hydrophilicity and higher intensity.

Among a great deal of investigations of the modified starches, those after chemical modification like the oxidation attract our great interest, in which carboxyl and carbonyl functional groups can be introduced into the starch chains [24]. The modification had been studied in detail by Wing and Parvuori et al. [25, 26] who proposed that chemical stability, water resistance, and shearing viscosity are improved. Nevertheless, it should be pointed out that a theoretical investigation is very important in understanding the origin of the characteristic variation so as to conclude the regular reasons. Unfortunately, to the best of our knowledge, no theoretical study has reported the oxidized derivatives with different properties so far. Thus, in this paper, we would complete a detailed computational investigation to analyze the properties of three types of oxidized modified starch-based adhesives, aiming at the origin and difference of chemical
stability, water resistance, and shearing viscosity. Note that our theoretical investigation should be very reasonable for this studied system because of the existence of some small glucopyranose residues derived from the partial breakage of starch molecular chains by acid hydrolysis, as visualized in Scheme 1. Consequently, our calculations presented here can provide comprehensive and authentic information, thereby giving a suitable explanation to the experimental results; meanwhile, the results obtained can also predict the properties of analogous species for some known and/or as yet unknown systems.

2. Computational Methods

All equilibrium geometries in this paper have been fully optimized at the AM1 semiempirical level without any symmetry restriction [27], which is very favorable to treat the macromolecule. For each optimized stationary point, vibrational frequency analysis obtained at the same theoretical level was performed to determine its character as minima (zero imaginary frequencies). To obtain more reliable theoretical data, the geometries of three types of key starch molecules (the oxidized starch molecule, the oxidized grafted starch molecule, and the oxidized grafted cross-linked starch molecule, resp.) were further optimized at the DFT-B3LYP [28, 29] level with the 6-31G basis set (B3LYP/6-31G) by using the AM1 semiempirical optimized geometries. All calculations reported here have been carried out with Gaussian 03 [30] program package.

To describe the oxidized starch–based adhesives’ chemical stability preventing degradation due to oxygen erosion, the mean square displacement (MSD) was performed via the 10 ps total simulation with time step of 0.5 fs which is defined as

\[
\text{MSD} = \langle [r_i(t) - r_i(0)]^2 \rangle, \quad (1)
\]

where \(r_i(t)\) is the displacement vector at \(t\) time and \(\langle \rangle\) is the ensemble average.

The increase of MSD with time is related to the diffusion coefficient \(D\) [33]:

\[
D = \frac{N_a}{6} \lim_{t \to \infty} \frac{d}{dt} \sum_{i=1}^{N_a} \langle [r_i(t) - r_i(0)]^2 \rangle \quad (2)
\]

where \(N_a\) is the number of diffusive atoms in the system; in Forcite module, the MSD is already averaged over all atoms and the relationship between MSD and time has been fitted as a straight line: \(y = ax + b; D\) then follows as

\[
D = \frac{a}{6}. \quad (3)
\]

Finally, shearing viscosity \(\eta\) was calculated to simulate the shearing for the oxidized starch–based adhesives. Shear rate as an input to the simulation was set as 0.1 s\(^{-1}\). Herein, shearing viscosity is defined as

\[
\eta = \frac{\sigma}{\gamma}. \quad (4)
\]

where \(\sigma\) is the shear stress and \(\gamma\) is the shear rate.

All MD simulation was performed under the NVE ensemble with the COMPASS force field at 298 K utilizing Forcite modules in the version of Materials Studio 6.0 [34].

3. Results and Discussion

We have carried out a series of computational investigations at the AM1 level based on the constructed model (Starch-OH)\(_n\) and comparatively discovered that the analogous charges distribution appears in the different starch molecules when \(n\) is designated from 7 to 20. As we all know, it is difficult to carry out a DFT calculation for the starch system due to the extremely expensive computational price. Accordingly, it is very rational for our research objects when \(n = 8-9\) to be investigated by DFT-B3LYP method as an illustrative example in this paper, so as to explore how and to what extent the
small molecules derived from the oxidized starches influence the properties of the modified starch-based adhesives, such as chemical stability, water resistance, and shearing viscosity, although only few amount of the small molecules can be detected in the starch-based adhesives after the oxidization.

3.1. Formation and Structure of the Oxidized Starch Molecule. The results of MPA are listed in Scheme 2. As shown in Scheme 2(a), the charges located on O\textsuperscript{26}, O\textsuperscript{25}, and O\textsuperscript{24} atoms of the amylopectin molecule are −0.285, −0.256, and −0.248 a.u., respectively. Note that charges of the carbon atoms associated with the above-mentioned oxygen atoms were clearly negative, taking (a.u.) −0.029 on C\textsuperscript{15}, −0.022 on C\textsuperscript{26}, and −0.013 on C\textsuperscript{1}, respectively. It can be strongly suggested that the starch crystalline structures can be largely damaged due to the bursting of the granule structures presented in the breakage of molecular chains taking place in the C\textsuperscript{1}−O\textsuperscript{27}, C\textsuperscript{15}−O\textsuperscript{16}, and C\textsuperscript{26}−O\textsuperscript{25} bonds when the starch pastes were oxidized. Comparatively, in the amylose molecule as observed in Scheme 2(b), the intermolecular

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\end{itemize}
breakage should happen in the bonds $C^1-O^{26}$ and $C^{25}-O^{24}$, respectively. Those support that hydroxyl groups in starch, primarily at the C-2, C-3, and C-6 positions, are transformed into carbonyl or carboxyl groups via oxidation [35, 36]. Therefore, the original starch pastes after the oxidation, regardless of the amylpectin or amyllose, should all cover three-polysaccharide molecules due to depolymerization of the molecular chains, which decreased the molecular weight. Obviously, the hydroxyl groups in the starch also decreased with oxidation, which can effectively improve the water resistance of the adhesive. Moreover, based on the consideration of dual effect from the charges distribution and the steric effect, the $C^{10}$ atom in the amylpectin molecule and the $C^2$, $C^{19}$, and $C^{23}$ atoms in the amylose molecule with certain amount of positive charges should be the most active sites during the oxidation. It means that further oxidation can make the hydrogen bonds between the starch chains weakened, showing the oxidation of the hydroxyl groups associated with $C^{10}$, $C^{19}$, $C^{23}$, and $C^2$ atoms, so leading to higher thermoplasticity and hydrophobicity for the starch pastes. Here, the hydroxyl groups bonded $C^2$, $C^{10}$, and $C^{19}$ are oxidized to the ketone groups while the hydroxyl groups bonded $C^{23}$ is did the carboxyl groups; namely, hybridization state of the $C^{10}$, $C^{19}$, $C^{23}$, and $C^2$ atoms was changed from $sp^3$ to $sp^2$, inducing further molecular stability. Additionally, the ketone group neighbored with $C^{19}$ atom is oxidized to carboxyl group. As a result, the net proportion between the carboxyl and the ketone group is 4:3, which is consistent with the results measured in experiment [19], finding that the amount of carboxyl groups exceeds that of ketone groups. Moreover, it can be seen that there are two parts with positive charges indicated by arrow as shown in Figure 1 that are presented in the oxidized molecules (a) and (b), respectively, which is easy to be further oxidized. Here, (a) involves the formation of two carboxyl groups via oxygenation process, while in (b) two hydroxyl groups are firstly oxidized to form corresponding ketone groups; subsequently one ketone group originated from the oxidized hydroxyl group just now and another neighboring ketone group; both are further oxidized to yield two carboxyl groups. Thus, when the oxidized starches are deeply oxidized, the amount of carboxyl groups will increase progressively as compared to that of ketone groups, reflecting that the crystalline structures of the starch granules are further damaged. This is in good agreement with the experimental results [26]. Therefore, with the increase of the oxidants added to the reactions, more carboxyl groups being available in starch increase the hydration capacity of starch pastes and result in formation of more glucose residues which contains a lot of inorganic components.

3.2. Formation of the Oxidized Grafted Starch Molecule and Determination of the Oxidized Grafted Cross-Linked Starch
As shown in Scheme 2, on basis of consideration of the steric effect, the maximal positive charges distributions are located on C^{10} (0.029 a.u.) in the amylopectin molecule and on C^{33} (0.062 a.u.) in the amyllose molecule, respectively. It means that the C^{10} and C^{33} positions of the species are much easier to be attacked by nucleophiles. So, the vinyl alcohol, acting as a kind of stronger nucleophile molecule, firstly attaches to C^{10} and C^{33}, followed by concerted oxygenation, to generate the oxidized grafted starch molecule in which the obtained proportion between the carboxyl and the ketone group is closely equal to 4:3 [37]. Thus, compared with the single oxidized starch pastes, the starch pastes after grafted oxidized treatment do not essentially change the proportion, in turn keeping the same values. Furthermore, in the molecule (c), there are two parts with positive charges indicated by arrow as shown in Figure 1, which imply the further oxygenation of the hydroxyl groups. More important, with further oxygenation of the oxidized grafting starch molecule, the amount of ketone groups is increasing; namely, the water resistance of corresponding starch emulsion is increased because of presence of a great deal of hydrophobicity groups. It is presumable that molecule (c) is instable and thus unfavorable model in theoretics to construct geometry of the oxidized grafted cross-linked starch molecule. However, in the molecule (d), there is no part with positive charges; that is, the molecule (d) is not further oxidized and thus considered as a steady molecule. As a result, we have presented rationally geometry of the oxidized grafted cross-linked starch molecule (e) on the basis of the structure of molecule (d) via the cross-link by epoxichloropropene so as to compare its characteristics with the other modified starch molecules [38], which can scientifically provide comprehensive and authentic information, thereby interpreting the difference in properties of the different oxidized modified starch adhesives presented here.

3.3. Chemical Stability of Three Types of Oxidized Starch-Based Adhesives. According to the molecular orbital theory [39–43], chemical stability of all modified starch molecules is very high because the energy values of corresponding HOMO and LUMO are negative. Moreover, the difference in stability is easily understood in terms of the HOMO (Lewis base)-LUMO (Lewis acid) interaction; namely, a smaller HOMO-LUMO gap (ΔE) helps in more electrotransition in general, so it is unfavorable for the formation of a Lewis steady molecule. Our theoretical result indicates that ΔE value of the oxidized starch molecule is less than that of the oxidized graft starch molecule as shown in Table 1. Consequently, it is reasonable that the chemical stability of the oxidized grafted starch molecule is higher than that of the oxidized starch molecule. In other words, the composite modified starch-based adhesive possesses higher chemical stability than the single modified starch-based adhesive, which are analogues to the results of the graft modification enhanced the thermal stability [32]. Moreover, as mentioned before (see Section 3.1), the hydroxyl groups associated with the carbons with positive charges indicated by arrow in molecule (b) are oxidized to form one ketone group and three carboxyl groups, respectively, as compared with those in molecule (a) that contains two ketone groups and one carboxyl group, respectively. Therefore, the water resistance of the starch paste associated with molecule (a) was improved and thus itself chemical stability for corresponding adhesive was rationally increased. This is fully confirmed by our theoretical calculations. As shown in Table 1, there is the order of ΔE_{b(a)} > ΔE_{e(a)}. Furthermore, compared to the modified starch molecules (a), (b), and (c), it can be seen that the oxidized grafted cross-linked starch molecule (e) presents less value for ΔE gap. This seems plausible that the chemical stability of the composite modified starch-based adhesives is lower than that of the other modified starch-based adhesives. In fact, based on the electrostatic potential (EP) analysis, we have found that chemical stability of the oxidized grafted cross-linked starch-based adhesive itself is also related to corresponding molecules’ water-solubility, which is mentioned in Section 3.4. Moreover, diffusion coefficient of oxygen molecules in the modified starch-based adhesive might give us a reasonable explanation why chemical stability of the composite modified adhesive is higher than that of the single modified cases with respect to preventing degradation according to the simulation of oxygen erosion. The relationships between MSD and time are shown in Figure 2. The diffusion coefficients (cm^2 s^{-1}) of oxygen in the modified starches equal 2.1 \times 10^{-5} (a), 2.1 \times 10^{-5} (b), 1.7 \times 10^{-5} (c), 1.8 \times 10^{-5} (d), and 1.6 \times 10^{-6} (e), respectively. Therefore, the composite modified starch-based adhesive with the higher stability due to better oxygen resistance performance can be ascribed to the lower diffusion coefficient of oxygen molecules.

3.4. Water Resistance and Shearing Viscosity of Three Types of Oxidized Starch-Based Adhesives. As known, the electrostatic potential (EP) acted as the most informative property can describe visually charges distribution in molecule, favoring the determination of active regions of corresponding molecule. In this paper, the models as shown in Figure 3, showing the EP (blue = positive, red = negative) mapped onto the van der Waals surface, are reported as the representative examples, displaying that the largest positive density (deepest blue) is concentrated on the oxidized grafted cross-linked starch molecule (e), as compared with the other oxidized modified starch molecules (a), (b), (c), and (d), and a decreasing trend can be found in the order of (e) > (c) > (d) > (a) > (b). Thus, the oxidized grafted cross-linked starch molecule is much easier to be attacked by water molecule; namely, chemical stability of the oxidized grafted cross-linked starch-based adhesive is greatly high because more water enter and combine. Nevertheless, as shown in Figure 3, the oxidized grafted cross-linked starch molecule’s surface is easier to be hydrated, as compared to the oxidized starch molecule taking place in molecule’s interior and the oxidized grafted starch molecule occurred in molecule’s interior and surface. In other words, with the rising of temperature, the water molecules bonded the oxidized grafted cross-linked starch molecule will be easier to be lost because the interaction between them only exists at the molecules
Figure 2: Continued.
Figure 2: The relationship between MSD and time corresponding to annealed amorphous cell embraced five oxygen molecules in ten oxidized modified starch molecules. (a) and (b) are cases of the oxidized starch molecules, respectively; (c) and (d) are cases of the oxidized grafted starch molecules, respectively; and (e) is case of the oxidized grafted cross-linked starch molecule.

Table 1: Orbital energies (a.u.), dipole moment (D), viscosity (MPa s), and shear stress (MPa) of the oxidized modified starch molecules.

<table>
<thead>
<tr>
<th></th>
<th>Oxidized starch molecule (a)</th>
<th>Oxidized starch molecule (b)</th>
<th>Oxidized grafted starch molecule (c)</th>
<th>Oxidized grafted starch molecule (d)</th>
<th>Oxidized grafted cross-linked starch molecule (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO</td>
<td>–0.3972</td>
<td>–0.3364</td>
<td>–0.3957</td>
<td>–0.4027</td>
<td>–0.3927</td>
</tr>
<tr>
<td>LUMO</td>
<td>–0.0169</td>
<td>–0.0089</td>
<td>–0.0008</td>
<td>–0.0132</td>
<td>–0.0152</td>
</tr>
<tr>
<td>( \Delta E = E_{\text{LUMO}} - E_{\text{HOMO}} )</td>
<td>0.3803</td>
<td>0.3275</td>
<td>0.3949</td>
<td>0.3895</td>
<td>0.3775</td>
</tr>
<tr>
<td>Dipole moment</td>
<td>2.3485</td>
<td>1.3664</td>
<td>1.8523</td>
<td>2.6105</td>
<td>5.8061</td>
</tr>
<tr>
<td>Viscosity</td>
<td>3.897</td>
<td>1.370</td>
<td>3.587</td>
<td>7.342</td>
<td>58.190</td>
</tr>
<tr>
<td>Shear stress</td>
<td>0.5267 [0.5](^{a})</td>
<td>1.0929 [1.12 ± 0.07](^{b})</td>
<td>5.8190 [5.6](^{a})</td>
<td>5.45 ± 0.06(^{b})</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\)Reference [31].
\(^{b}\)Reference [32].

The strong support that the water resistance of the oxidized grafted cross-linked starch-based adhesives will be progressively improved with rising of the temperature. So, it is reasonable if we consider the decrease in water resistance for the oxidized modified starch-based adhesives presented here, exhibiting the following order: oxidized grafted cross-linked starch-based adhesive > the oxidized grafted starch-based adhesive > the oxidized starch-based adhesive, in excellent agreement with Zhang et al.’s conclusion that water resistance of the starch-based adhesive was significantly improved via the graft modification of oxidized starch [32].

Furthermore, a common use of the shearing simulation is to calculate and provide a wealth of insights into the shearing viscosity of the liquid. As shown in Table 1, the shear stress
data for those oxidized starch-based adhesives are found to be 0.5267, 1.0929, and 58.190 MPa for the (a) + (b), (c) + (d), and (e) residues, respectively, in excellent agreement with our previous experiential predictions [31, 32]. According to the high-viscosity adhesive emulsion that prevented the spreading and permeation of the adhesive emulsion on the material surface [44], we suggest that the difference of shearing viscosity for the modified starch-based adhesives should be the oxidized grafted cross-linked starch-based adhesive > the oxidized grafted starch-based adhesive > the oxidized starch-based adhesive, which is in good agreement with the experimental results [23]. Moreover, the modified starch-based adhesives are very polarizable as revealed by corresponding EP and thus very sensitive to mutual polarization effects. This is fully confirmed by our theoretical calculations. For instance, the dipole moments (D) obtained for the modified starch molecules are 2.3485 (a), 1.3664 (b), 1.8523 (c), 2.6105 (d), and 5.8061 (e), respectively, as listed in Table 1. Thus, it is reasonable for the above-mentioned decrease order in shearing viscosity for the oxidized modified starch-based adhesives. Evidence also supports the conclusion that the higher polarization resulted in the higher shear stress [45].

4. Conclusions

In the present work, a detailed theoretical investigation has been performed to characterize formation of the small molecules from the oxidized modified starch-based adhesives and rationally explain corresponding adhesives’ origin and different in chemical stability, water resistance, and shearing viscosity. With the above analysis in mind, some intriguing results were elicited as follows: (1) the small glucose molecules derived from the partial breakage of starch molecular chains in the oxidized modified starches can determine the properties of the corresponding adhesives;
(2) Structural destruction in the starch-based adhesives was very important to change the chemical stability; namely, the more serious destruction made in crystalline regions, the better chemical stability appeared; (3) Based on the Mulliken population analysis (MPA), the frontier orbital analysis, and the electrostatic potential (EP) analysis, respectively, we have confirmed that chemical stability, water resistance, and shearing viscosity of three types of oxidized modified starch-based adhesives are uniformly improved and presented an identical order of the oxidized grafted cross-linked starch-based adhesive > the oxidized grafted starch-based adhesive > the oxidized starch-based adhesive, which is well consistent with available experimental results.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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