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Full Length Article

Microscopic mechanism of amino silicone oil modification and modification effect with different amino group contents based on molecular dynamics simulation

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ABSTRACT

The microscopic mechanism of amino silicone oil (ASO) modification of natural fiber was investigated for the first time using molecular dynamics (MD) simulation at the atomic and molecular levels. The MD simulation results indicated that the ASO molecular interacted with the cellulose molecular within the natural fiber, mainly by intermolecular forces of N—H—O and O—H—N hydrogen bonds and the molecular chain of ASO absorbed onto the natural fiber in a selective orientation, i.e., the hydrophobic alkyl groups ($—C_nH_{2n+1}$) project outward and the polar amino groups ($—NH_2$) point to the surface of natural fiber. Consequently, the ASO modification changed the surface characteristic of natural fiber from hydrophilic to hydrophobic. Furthermore, the modification effects of the ASO modification layer with different amino group contents (m:n ratio) were also evaluated in this study by calculating the binding energy between the ASO modifier and natural fiber, and the cohesive energy density and free volume of the ASO modification layer. The results showed that the binding energy reached a maximum when the m:n ratio of ASO was of 8:4, suggesting that a good bonding strength was achieved at this m:n ratio. It was also found that the cohesive energy density enhanced with the increase in the amino group content, and the higher the cohesive energy density, the easier the formation of the ASO modification layer. However, the fraction free volume decreased with the increase in the amino group content. This is good for improving the water-proof property of natural fiber. The present work can provide an effective method for predicting the modification effects and designing the optimized m:n ratio of ASO modification.

1. Introduction

In recent years, natural fiber reinforced polymer composites have attracted much interest in the field of composites because of a greater concern for environmental protection and energy saving around the world [1–3]. Natural fiber reinforced polymer composites, as a kind of green composites, have many applications in construction, automobile, and packaging industries [1,4,5]. However, natural fiber contains a large number of polar hydroxyl groups, which normally lead to a very poor compatibility between the hydrophilic natural fiber and hydrophobic polymer matrix [6]. Therefore, in order to improve the overall properties of natural fiber reinforced composites, it is essential to improve the compatibility between natural fiber and polymer matrix by surface modification. Recently, many chemical treatments have been used to improve the interfacial adhesion between natural fiber and polymer matrix, such as sodium hydroxide, silane, acetic anhydride, oxidation modification, maleic anhydride and graft copolymers [6–9]. Treatment with amino silicone oil (ASO) is one of the natural fiber surface modification methods, which can decrease the surface hydrophilicity of natural fiber and effectively improve the overall properties of natural fiber/polymer composites [10]. In recent years, modification of natural fiber with ASO has become a research focus [11–13]. An et al. investigated the film morphology and orientation of ASO on cotton fiber by the field-emision scanning electron microscopy (FESEM) and X-ray photoelectron spectroscopy (XPS) [14]. Burrell et al. analysed the layer of ASO on the surface of cellulose by the angle-dependent XPS to determine the orientation and adsorption of ASO on the cellulose surface [15]. Xu et al. investigated the film morphology and orientation

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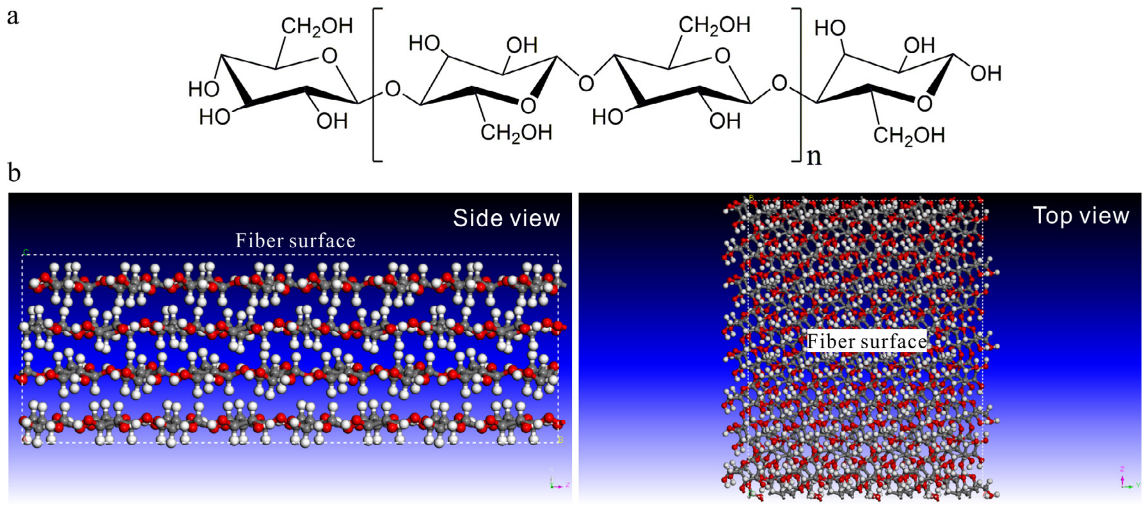

Fig. 1. Structures of cellulose. a: Molecular formula, b: molecular model (C: grey, O: red, H: white). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of ASO on the cellulose surfaces by experimental test. The results indicated that the amino groups of ASO adsorbed onto the cellulose surface and the hydrophobic alkyl groups extended toward the air on the surface [16]. However, the microscopic mechanism of ASO modification and microscopic structures and properties of ASO modification layer at the atomic and molecular levels have been rarely studied. On the other hand, molecular dynamics simulation is an effective method to study the surface and interface of materials. For example, Cui et al. used molecular dynamics simulation to investigate the surface and interface properties of some materials in depth, and achieved many interesting results [17,18]. Thus, in this study, molecular dynamics (MD) simulation was applied to study the microscopic structure and characteristics at the interface modified with ASO and further to elucidate the microscopic mechanism of ASO modification at the atomic and molecular levels. Additionally, this work also evaluated the effects of amino group content (m:n ratio) on the modification effects of ASO treatment using the MD method based on the quantitative calculation results of the binding energy between the ASO modifier and natural fiber, and the cohesive energy density and free volume of the ASO modification layer.

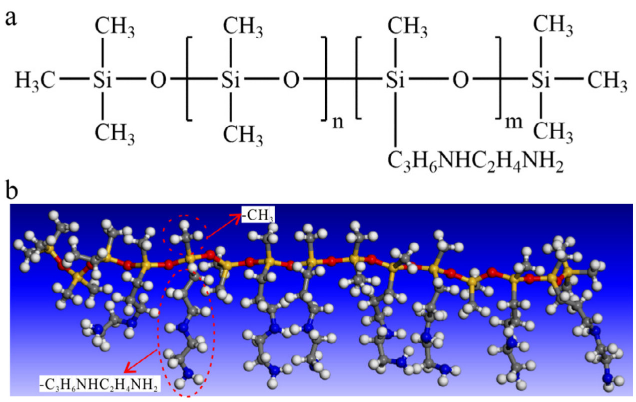

Fig. 2. Structures of amino silicone oil. a: Molecular formula, b: molecular model (C: grey, O: red, N: blue, Si: yellow, H: white). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2. Modeling and MD simulation

In this study, modeling and simulations were performed using the Materials Studio 4.0 software from Accelrys Inc. The Condensed-Phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) force field was used to conduct force field computations. COMPASS force field has been widely used in simulations for studying the surface and interface properties of materials, and it is expressed as a sum of valence (or bonding), cross-terms, and non-bonding interactions. So the total potential energy of simulation system includes the valence terms, cross-terms, and non-bonding terms, which are given by the following functions [19]:

$$\begin{aligned}E_{total} = &\sum_{b}[k_2(b-b_0)^2+k_3(b-b_0)^3+k_4(b-b_0)^4]\\&+\sum_{\theta}[k_2(\theta-\theta_0)^2+k_3(\theta-\theta_0)^3+k_4(\theta-\theta_0)^4]\\&+\sum_{\varphi}[k_1(1-\cos\varphi)+k_2(1-\cos 2\varphi)+k_3(1-\cos 3\varphi)]\\&+\sum_{\chi}k_2\chi^2+\sum_{b,b'}k(b-b_0)(b'-b'_0)+\sum_{b,\theta}k(b-b_0)(\theta-\theta_0)\\&+\sum_{b,\varphi}(b-b_0)[k_1\cos\varphi+k_2\cos 2\varphi+k_3\cos 3\varphi]\\&+\sum_{\theta,\varphi}(\theta-\theta_0)[k_1\cos\varphi+k_2\cos 2\varphi+k_3\cos 3\varphi]\\&+\sum_{b,\theta}k(\theta'-\theta'_0)(\theta-\theta_0)+\sum_{\theta,\theta,\varphi}k(\theta-\theta_0)(\theta'-\theta'_0)\cos\varphi\\&+\sum_{i,j}\frac{q_iq_j}{r_{ij}}+\sum_{i,j}\varepsilon_{ij}\left[2\left(\frac{r_{ij}^0}{r_{ij}}\right)^9-3\left(\frac{r_{ij}^0}{r_{ij}}\right)^6\right]\end{aligned} \tag{1}$$

2.1. Construction of natural fiber surface model

It is known from the literature that the main constituent of natural fiber is cellulose [20]. In this study, In order to simplify the simulation model, the cellulose Iβ crystal was used, and its initial structure was built from the experimental test data [21]. The initial dimension of the simulation model box was set as 7.784 Å × 8.210 Å × 10.380 Å with $\alpha = 90$, $\beta = 90$ and $\gamma = 96.55$. Then the fiber surface was constructed by making a supercell with a (5 × 6)