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Film morphology and orientation of amino silicone adsorbed onto cellulose substrate

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ABSTRACT

A series of amino silicones with different amino values were synthesized and adsorbed onto surfaces of cotton fibers and cellulose substrates. The film morphology, hydrophobic properties and surface composition of the silicones are investigated and characterized by field emission scanning electron microscope (FESEM), atomic force microscope (AFM), contact angle measurement, X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance infrared (ATR-IR). The results of the experiments indicate that the amino silicone can form a hydrophobic film on both cotton fibers and cellulose substrates and reduce the surface roughness significantly. Furthermore, the roughness becomes smaller with an increase in the amino value. All these results suggest that the orientation of amino silicone molecule is with the amino functional groups of amino silicone molecule adsorbed onto the cellulose interface while the main polymer chains and the hydrophobic Si–CH_3 groups extend toward the air.

1. Introduction

Silicones are special materials that impart desired mechanical performance properties of fabrics such as softness, bounciness and anti-wrinkle properties to fabrics and related materials [1–3]. In practice, amino silicones exhibit superior softening benefit and mechanical properties, possibly owing to their excellent film forming ability and morphology [4,5]. It was proposed that a film of amino silicone forming on the cellulose not only lowers the friction coefficient of the cellulose surface, but also minimizes the clearance between the wool squamae, and thus makes the surface smoother [6]. This morphology can affect the tactile properties of surfaces, and reveal the film forming mechanism, which has become a hot spot in recent research of polysiloxane [7]. An et al. [8] have investigated the film morphology and orientation of amino silicone on cotton fiber by FESEM and XPS, and proposed that the orientation of amino silicone on cotton fiber substrate is in such an approach that the hydrophobic Si–CH_3 groups project outward into air, while Si–O dipole bonds as well as the polar amino groups point to the interface between amino silicone and cellulose. Burrell et al. [9] examined the thin layers of amino silicones on cellulose surface by angle-dependent XPS to study the orientation of the amino endgroup relative to the main polymer chain, and proposed the model with the endgroups adsorbed onto the cellulose interface and the polymer chains forming loops that extend toward the air. But amino silicones with different amino values provide different softening benefits and properties of textiles, which indicate that their film morphology and roughness are diverse [10–12]. Luo et al. [13] proposed that high amino content could increase the affinity between silicones and fabrics and regulate the polymer molecular arrangement, thus provide superior softness and smoothness.

To investigate the softening mechanism of amino silicone and reveal the correlations between the amino value, the structure and film morphology, a series of N-β-aminoethyl-γ-aminopropyl polydimethylsiloxane (APS) with various amino values were synthesized. The film morphology and orientation of amino silicone on the cellulose surfaces are characterized by FESEM, XPS, AFM, ATR-IR and other instruments.

2. Experimental

2.1. Materials

N-β-aminoethyl-γ-aminopropyl methyldimethoxylsilane and α,ω-dihydroxypolydimethylsiloxane ($n = 45$), both industrial grade, were purchased from Nanjing Shuguang Inc. and Dow Coming Inc. respectively. Acetic acid, isopropanol, toluene, acetone, hexane and acetic ether, all A.R., were from Hangzhou Chemicals, China. The alkaline catalyst was prepared in our laboratory. Absorbent cotton fibers, cellulose films, were obtained

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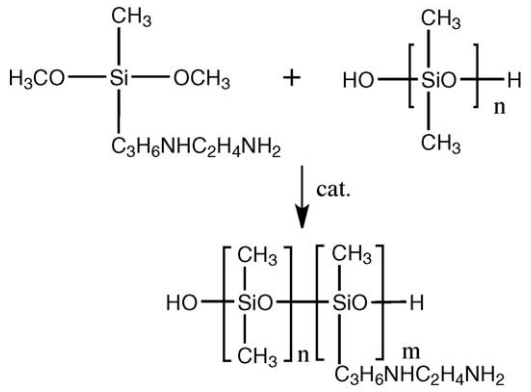

Scheme 1. Synthesis route to APS.

from Jiaozuo Medical Material Co. and Shangyu Cellophane Co. respectively. All the chemicals were used as received.

2.2. Synthesis of APS

To a four-necked flask equipped with a nitrogen purge, a vacuum device, a stirrer and a thermometer, were added in the following order 90 g (0.027 mol) of α,ω-dihydroxypolydimethylsiloxane, a proper amount of N-β-aminoethyl-γ-aminopropyl methyldimethoxylsilane corresponding with the desired amino value and 3.6 ml of the alkaline catalyst. The reaction mixture was slowly heated to 90 °C and kept at this temperature for 5 h. A glutinous, colorless and transparent fluid, N-β-aminoethyl-γ-aminopropyl polydimethylsiloxane (shown in Scheme 1), was obtained with a yield of 98% (confirmed by ^{1}H NMR measurements [14]).

2.3. Techniques

2.3.1. Characterizations of APS

The APS amino value was estimated by chemical titration, of which the details are available elsewhere [15]. The average molecular weight was determined by measuring the intrinsic viscosity [η] [16]. Infrared (IR) spectrum was acquired on a Nicolet 560 spectrometer. ^{1}H NMR spectra were recorded at 25 °C on an Avance DMX 500 with $CDCl_3$ as the solvent and tetramethylsilane (TMS, $\delta = 0$) as the internal standard.

2.3.2. Field emission scanning electron microscope (FESEM)

The best way to research the morphology of amino silicone softener on fibers is to observe the treated fiber surface directly. Therefore, SEM was first utilized to investigate the treated fiber surface in the experiment.

Amino silicone softeners are usually used in textile industry in emulsion. In accordance with this, a 7.5% APS emulsion (6 g APS emulsified with 4 g fatty alcohol polyoxyethylene ether and 70 g H_2O) was used as a sample in the experiment to finish the fibers and form the desired siloxane film on the fiber surface.

Absorbent cotton fiber samples were impregnated in a diluted aqueous bath (bath ratio, 7.5% APS emulsion:H_2O = 2:3) containing a circa 3% APS emulsion sample, padded to wet pick-up at about 70% on the weight of the dry fibers. The padded fibers were then dried at 100 °C for 10 min, cured at 120 °C for 2 min and finally kept in a desiccator overnight.

The surface morphology of the fiber samples treated with APS emulsion was evaluated with FESEM (SIRION-100, FEI, Holland) after the samples were coated with gold in a vacuum.

2.3.3. Preparation of APS film on cellulose substrate

Natural fibers are fixed with difficulty in contact angle measurement, XPS, AFM and ATR-IR observation, and the cellulose substrate allows a better morphological characterization of coating on the nanoscale than the rugged surface of a fiber. We therefore used cellulose film (cellophane) as a model surface.

The cellulose films were cleaned sequentially with water, acetone, isopropanol and hexane by ultrasound. This operation was developed to remove surface contaminants (due to processing and handling), and minimize the wrinkling while drying.

The APSs were dissolved in isopropanol (0.05 wt.%) and applied to the cellulose substrates by dip coating. Then the samples were dried at 100 °C for 10 min, cured at 120 °C for 2 min and finally kept in a desiccator. These samples were ready to be used for contact angle measurement, XPS, AFM and ATR-IR observation.

2.3.4. Contact angle measurements

The hydrophobicity/hydrophilicity of cellulose substrates treated with APSs with different amino values was estimated via contact angle measurement using the OCA20. Reported water contact angles are the average of 5–7 measurements using pure water drops.

2.3.5. X-ray photoelectron spectroscopy (XPS)

The chemical composition of the APS layers was determined by a PHI-5000C ESCA system (PHI Enterprises, USA) equipped with Mg Kα radiation ($h\nu$ = 1253.6 eV). The base pressure of the analyzer chamber was about 5×10^{-8} Pa. All spectra were charge corrected by setting the energy of the C_y–H_x bond to 284.6 eV. The data analysis was carried out by using the XPSPeak4.1 software.

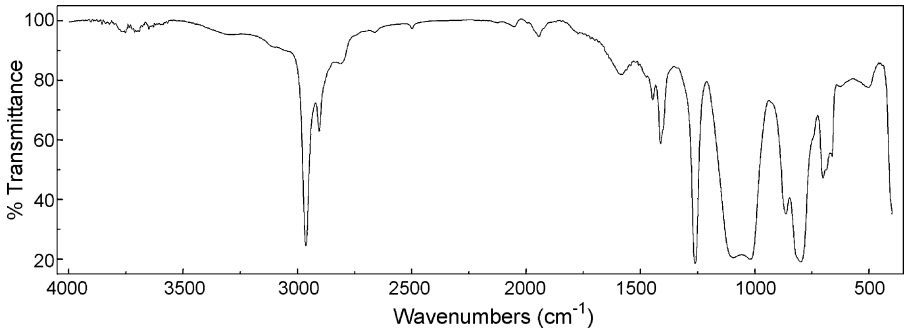

Fig. 1. Infrared spectra of amino silicone with amino value 0.6 mmol/g.