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Investigation into nanocellulosics versus acacia reinforced acrylic films

Yunqiao Pu [a], Jianguo Zhang [b], Thomas Elder [c], Yulin Deng [d], Paul Gatenholm [e], Arthur J. Ragauskas [b,*]

[a] Institute of Paper Science and Technology, Georgia Institute of Technology, 500 10th St., Atlanta, GA 30332, USA
[b] School of Chemistry and Biochemistry, Georgia Institute of Technology, 500 10th St., Atlanta, GA 30332, USA
[c] Southern Research Station, USDA-Forest Service, 2500 Shreveport Highway, Pineville, LA 71360, USA
[d] School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, 500 10th St., Atlanta, GA 30332, USA
[e] Department of Chemical and Biological Engineering, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

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Abstract

Three closely related cellulosic acrylic latex films were prepared employing acacia pulp fibers, cellulose whiskers and nanocellulose balls and their respective strength properties were determined. Cellulose whisker reinforced composites had enhanced strength properties compared to the acacia pulp and nanoball composites. AFM analysis indicated that the cellulose whisker reinforced composite exhibited decreased surface roughness.
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1. Introduction

The revolution in synthetic plastics that started in 1909 has dramatically impacted modern society [1]. Indeed, total world plastics consumption has been estimated at over 150 million tons [2]. Although the design of new resins and polymers remains an active field of study, it is now well established that for a variety of materials their performance-cost requirements can be more readily accomplished with the formulation of composites. A variety of notable composites have been successful transferred from the laboratory into commercial applications, including plastics reinforced with glass fibers [3], carbon fibers [4], natural fibers [5], wood [6] and other materials [7]. Two notable trends over the past decade have been the design of composites utilizing natural fibers and nanocomposites. The former frequently provides enhanced performance at a lower cost, lower densities, and reduced abrasion to processing equipment than what can be achieved with synthetic fibers. In addition, composites reinforced with natural fibers can simplify disposal issues at the end of their product lifetimes [8]. The application of nanoparticles with polymers for novel composites is a rapidly developing field of study and has become one of the most promising means of dramatically enhancing the physical properties of plastics [9]. Along these lines, cellulose whiskers, which are derived from cellulosic fibers and typically have dimensions of 3–50 nm in cross-section and have lengths of 100 nm to several hundred nm have exhibited promising behavior in several synthetic and natural plastics [10]. Favier et al. [11] were the first to demonstrate the benefits of reinforcing a polymer with cellulose whiskers. By employing 6% cellulose whiskers derived form tunicate cellulose in a latex polymerized from styrene and butyl acrylate, the composite films exhibited a twofold increase in the shear modulus over control films containing no whiskers. Following this discovery several other synthetic and natural polymers including poly(vinylchloride) [12–14], polypropylene [15],

* Corresponding author. Tel.: +1 404 894 9701; fax: +1 404 894 4778.
E-mail address: arthur.ragauskas@chemistry.gatech.edu (A.J. Ragauskas).

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polyoxyethylene [16–18], starch [19] and cellulose acetate butyrate have been beneficially reinforced with cellulose whiskers. The results of these studies and others have been recently summarized in a timely review by Samir et al. [20].

Typically, the preparation of cellulose whiskers is accomplished by aqueous hydrolysis of cellulose fibers with sulfuric acid yielding a water-based stable suspension. Hence, the application of cellulose whiskers with water-borne polymeric systems has taken on a special emphasis. For example, Ruiz et al. [21] has reported that low-level addition of tunicin cellulose whiskers to an epoxy emulsion yielded improvements in the composite modulus in the rubbery state of the matrix which cannot be accomplished with other cellulose-based fibers. The improvements in physical properties of polymeric films derived from aqueous suspensions is of special significance since many coating and painting technologies are being converted to water-based solvent systems to reduce volatile organic compounds emissions and other harmful environmental pollution issues [22]. Among the various latex systems employed, 100% acrylic latex paints have been shown to be especially durable, highly flexible and exhibit high adhesion to a variety of surfaces.

Prior studies have demonstrated that the structure of cellulose whiskers is dependent, to some extent, on the source of cellulose employed. For example, the length and lateral dimensions of cellulose whiskers derived from cotton and tunicin have been reported to be approximately 200×5 nm and 1000×15 nm, respectively. Until recently, the application of wood pulp as a resource for cellulosic whiskers and their inclusion in composites has been understudied. A report by Candanendo et al. demonstrated that acid hydrolysis of bleached sulphite black spruce yielded whiskers ranging in size between 147 and 105 nm in length with a diameter of ~5 nm [23]. These results are consistent with prior studies by Araki et al. [24]. In this study, the physical properties of an acrylic latex film reinforced with cellulose whiskers, nanocellulose balls and bleached acacia kraft fibers were examined.

2. Experimental

2.1. Materials

Fully bleached commercial pine and acacia kraft pulps were used in this study. All pulps were washed with distilled water until the effluents were pH neutral and colorless. The pulps were air-dried and stored at 0 °C prior to use. Acrylic latex (UCAR™ 625, 50%, w/v, $T_g = 12$ °C) was kindly provided by Dow chemicals. Sulfuric acid (95–98%) was purchased from EMD™ and used as received.

2.2. Nanocellulosics

Cellulose whiskers were prepared by sulfuric acid hydrolysis according to the literature methods [23]. In brief, fully bleached pine kraft pulp was refined in a Wiley mill to pass a 40-mesh screen. The ground pulp (40.00 g) was treated with sulfuric acid (700 ml, 64 wt%) at 45 °C for 45 min. After hydrolysis, the mixture was diluted 10-fold with distilled water and then concentrated by centrifugation. The concentrated sample was dialyzed against water for several days until the pH remained constant. The mixture was subject to repeated sonication (Branson Sonifier, Model 350) for 7 min intervals for a total of 35 min, while cooling in an ice bath (3 min) between steps to avoid overheating. The mixture was then allowed to stand over a Sigma mixed bed resin for 48 h and then filtered through ashless Whatman 541 filter paper.

Cellulose nanoballs were prepared following the procedure described by Zhang et al. [25]. This methodology involves initially refining the pulp to 0.35 mm in a Willy mill. This material was then soaked in 5.0 M NaOH solution for 3 h at 75 °C, washed and treated with DMSO for 3 h at 75 °C. The swollen cellulose particles were then washed with deionized water and then acid hydrolyzed with a 12.1 N HCl–36.0 N H_2SO_4 solution at 75 °C in a sonicator for 10 h. The resulting hydrolyzed cellulose particles were purified by centrifugation at 2750 rpm followed by dialysis with Spectra/Por membranes having molecular weight cut-off of 1000. The acidic sonication treatment was repeated for a second time for 4 h at 75 °C. After purification by centrifugation and dialysis, particle size analysis with a Zetasizer 3000 indicated that the cellulose particles (~70% yield) had an average diameter of ~80 nm.

2.3. Composite films

Cellulose whisker and nanoball suspensions were freeze dried, re-dispersed into water and ultrasonicated to form a colloidal suspension. Two sets of composite films, *T-films* and *G-films*, were made. The *T-films* were made by adding a 5 wt% suspension of cellulosics (30 ml) to an aqueous acrylic latex (30 ml, 15%) and mixed vigorously for 30 min. The resulting mixture was cast into a teflon mold and kept for two days at room temperature and then heated for 12 h at 50 °C. For the *G-films* the cellulosics suspension or acacia pulp fiber (20 ml) was added into aqueous acrylic latex (30 ml, 15%) and mixed vigorously for 30 min. The resulting mixture was cast into glass dishes and kept for two days at room temperature and then heated for 12 h at 50 °C. The T-film had a thickness of 0.14 ± 0.02 mm, G-film 0.19 ± 0.03 mm for whisker composites, and 0.36 ± 0.11 mm for acacia fiber composites. The films were then used for physical testing, scanning electron microscopy (SEM) and atomic force microscopy (AFM) analyses.

2.4. Contact angle measurement

The mixture of cellulosics and aqueous acrylic latex was dropped onto a glass plate for contact angle measurements using a FTA 200 Dynamic contact angle analyzer (First Ten Angstrong, Inc., USA). Measurements were recorded