Available online at www.sciencedirect.com
ScienceDirect
Composites: Part B 38 (2007) 360–366
composites
Part B: engineering
www.elsevier.com/locate/compositesb

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*

Received 5 April 2006; accepted 4 July 2006
Available online 15 November 2006

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.
Published by Elsevier Ltd.

Keywords: A. Fiber; A. Polymer–matrix composites (PMCs); B. Strength; Nanocellulosics

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).

1359-8368/$ - see front matter Published by Elsevier Ltd.
doi:10.1016/j.compositesb.2006.07.008

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

three times and on average had a standard deviation of 2.3°.

2.5. Electron microscopy

Transmission electron microscope (TEM) observation was conducted on a JEOL 100C TEM machine with an accelerating voltage of 100 kV. The samples were prepared by casting a drop of diluted aqueous dispersion onto a 200 mesh holey copper grid covered with a carbon film. The samples were then stained by casting a drop of 2 wt% uranyl acetate solution. Scanning electron microscopy (SEM) observation was conducted on a LEO 1530 thermally assisted field emission (TFE) scanning electron microscope with an acceleration voltage of 4 kV. The samples were coated with a thin layer of Au/Pd prior to SEM observation.

2.6. Atomic force microscopy (AFM) analysis

A silicon cantilever tip was used with a Digital Instruments 3100 Scanning Probe Microscope to evaluate the surface morphology of the composite film. All images were collected with tapping mode in air, and height, amplitude and phase images were taken. For each sample, height images were used to provide the roughness measurements in nm^2 for each sample by using Eq. (1) [26]

$$R_{rms} = R\left(F\sum_{i=1}^{N}(Z_i - Z_{ave}), N\right) \quad (1)$$

where N is the number of points in the area examined, Z_i is the current height value, Z_{ave} is the average height value, and R_{rms} is the root-mean square of the standard deviation for the height (Z) data.

2.7. Mechanical testing

T-film samples were cut into dimensions of 120 × 15 mm (length × width) and G-films of 70 × 15 mm. Samples were conditioned at 50.0% ± 2.0% relative humidity and 23.0 ± 1.0 °C for 1 day. The conditioned samples were tested on an Instron 4400R Universal Testing machine (Model 1122, Instron Corp., USA) with a cross-head speed of 250 mm/min at 23.0 ± 1.0 °C temperature. The applied load (f) was recorded as a function of sample elongation ($l - l_0$). The tensile strength σ and strain ε of the material was calculated as $\sigma = f/a$, and $\varepsilon = (l - l_0)/l_0$, respectively, where a was the sample cross-sectional area, l_0 the sample initial length and l the length at breaking. The averages of tensile energy absorption (TEA), tensile strength and strain were obtained using four specimens for each measurement.

3. Results and discussion

Fig. 1 shows the TEM image of cellulose whiskers which were observed to have a rod-like structure. The rod-like whiskers were shown to have length values of 100–250 nm and width on the order of 5–15 nm, leading to an aspect ratio of 20–50. Fig. 2 shows the SEM image of cellulose nanoball particles. The cellulose nanoball had an average diameter of ~80 nm and aspect ratio of ~1.1.

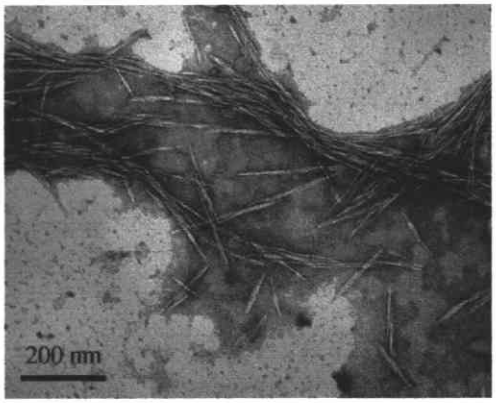

Fig. 1. Transmission electron microscope image of cellulose whiskers.

Acrylic latexes have been employed for a variety of applications including painting and adhesion. Since these materials are prepared via aqueous-based polymerization techniques and utilized in an aqueous suspension, this makes them an especially attractive candidate to combine with nanocellulosics dispersed in water. In this study a series of composites were prepared using nanocellulose particles prepared from a fully bleached pine kraft pulp. In addition, a fully bleached acacia kraft fiber was used to prepare composite acrylic films. This fiber was selected for comparison with the nanocellulosics reinforced composites since it is one of the smallest commercially available pulp fibers with a weight-weighted length of 0.62 mm and width of ~0.02 mm, and yet is approximately 4000 orders of magnitude larger than the cellulosic whiskers employed.

The contact angles of the acrylic latex and cellulosic composites dispersion against a glass plate were determined and these results are summarized in Fig. 3. The data showed that the dispersions containing cellulosics had

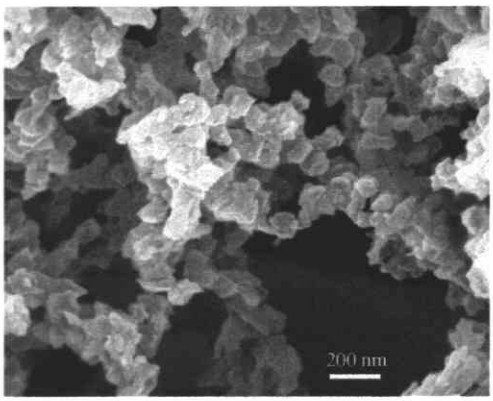

Fig. 2. Scanning electron microscope image of cellulose nanoballs.

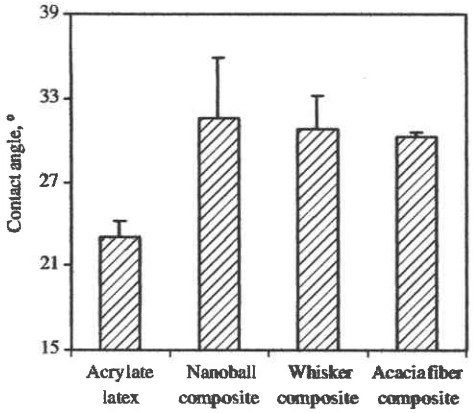

Fig. 3. Contact angle for acrylic latex and composites prepared with 5 wt% nanoball, cellulose whiskers and acacia fibers.

higher contact angle. To further explore this relationship, the contact angles for cellulose whisker latex dispersion were further examined as summarized in Fig. 4. The latex composite dispersion had a higher contact angle as an addition of cellulose whiskers increased. It is clear that the greatest benefit is in the range of 5–10% cellulose whiskers and then the increase in contact angle values levels off.

To ascertain the impact on the physical strength properties of the latex-cellulose composites, the TEA, tensile strength and strain for the cured T-films were determined and these results are presented in Figs. 5–7. Interestingly, the composites reinforced with cellulose whiskers exhibited a threefold increase in TEA whereas the addition of acacia fibers had a negative effect and the nanocellulose balls had no effect on TEA values. The cellulose whisker reinforced composite also exhibited higher tensile strength and strains than nanoball and acacia composites films. This indicates that nanocellulosic composites have enhanced strength properties in comparison to the acacia pulp fiber and nanoball composite. The acacia pulp fiber composite exhibited decrease TEA, strain and slightly increased tensile strength. The absence of reinforcing effect with the cellulose nanoballs in comparison to the cellulose whiskers could be attributed to its aspect ratio approaching a value of 1. These results clearly suggested that whisker composite had better reinforcing strength properties than nanoball

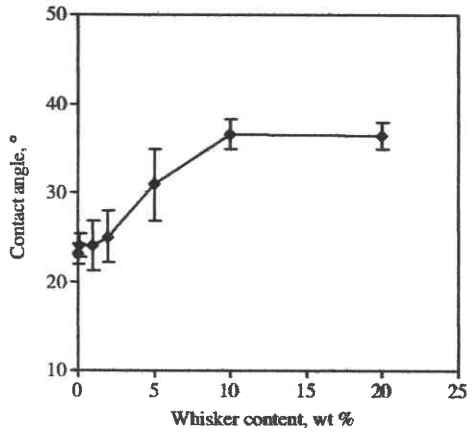

Fig. 4. Contact angles of acrylic latex composites with cellulose whiskers.

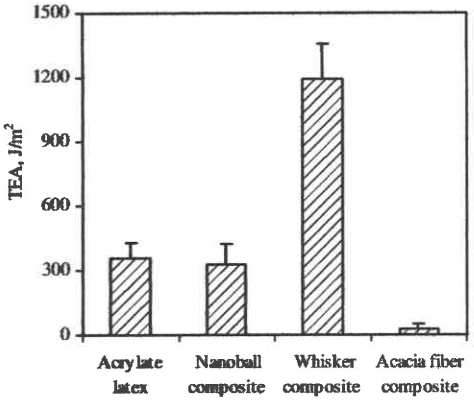

Fig. 5. TEA analysis of acrylic latex and composites prepared with 5 wt% nanoball, cellulose whiskers and acacia fibers.

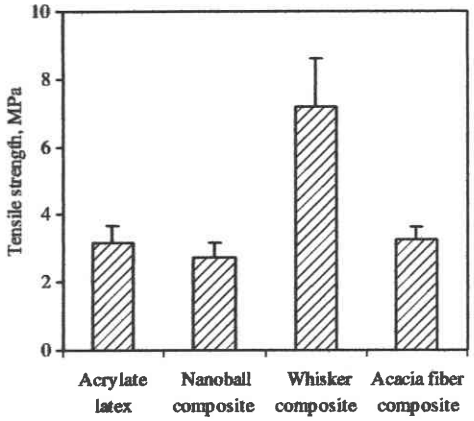

Fig. 6. Tensile strength analysis of acrylic latex and composites prepared with 5 wt% nanoball, cellulose whiskers and acacia fibers.

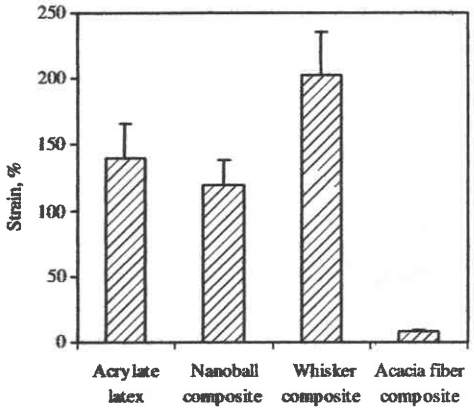

Fig. 7. Strain analysis of acrylic latex and composites prepared with 5 wt% nanoball, cellulose whiskers and acacia fibers.

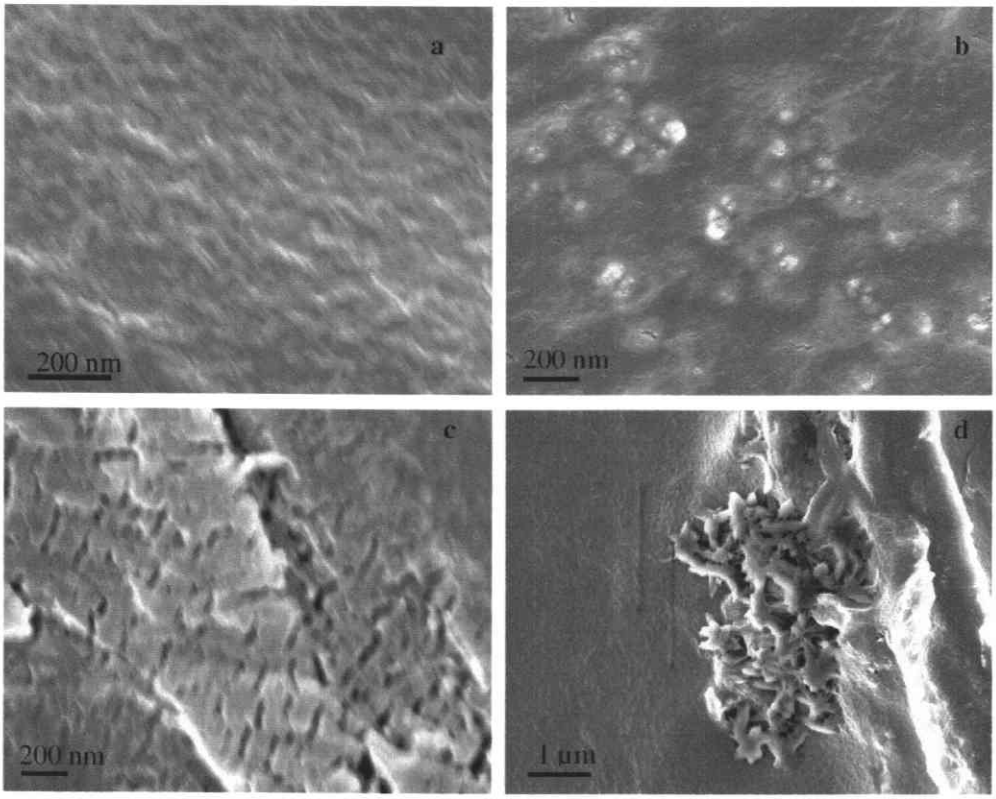

Fig. 8. Scanning electron microscope images of acrylic latex (a) and composites prepared with 5 wt% cellulosics (b: nanoball; c: cellulose whiskers; d: acacia fibers).

and pulp fiber composites which were attributed to cellulose whisker's unique structure. Since the initial report by Favier et al. [11] of improvements in physical properties of latex films reinforced with cellulose whiskers, a series of publications have documented these benefits in several composites. As recently reviewed by Samir et al. [20], the improvements in mechanical properties can be attributed to the formation of rigid hydrogen-bonded network of cellulose whiskers in the composite that is governed by a percolation mechanism. These considerations and the importance of the fillers aspect ratio are undoubtedly contributing factors to the mechanical properties reported in this study. SEM observation of the acrylic latex and cellulosic composite films shows that nanoballs and whiskers had relatively uniform distribution in the latex matrix, while acacia fiber was observed to aggregate in the matrix (Fig. 8). The aggregation of acacia fiber in the latex might result in the lower strain and TEA of the acacia fiber composite. These results are the first to report the different reinforcing effects that resulted from the addition of mass equivalent amounts of acacia fiber, cellulose whiskers and nanoballs.

The beneficial effects of acrylic films reinforced with cellulosic whiskers were subsequently further explored by varying the portion of whiskers from 0% to 20% by mass. As a control, a second set of acacia fiber acrylic composite films were prepared in exactly the same manner. The composite films (G-films) were then characterized for physical properties including TEA, tensile strength, and strain as summarized Figs. 9–11. These analyses clearly demonstrate distinct strength benefits for reinforcing acrylic films with cellulose whiskers in the 5–10% range. The addition of more than 10% cellulosic whiskers to latex resulted in a gradual decrease in strength properties. These results indi-

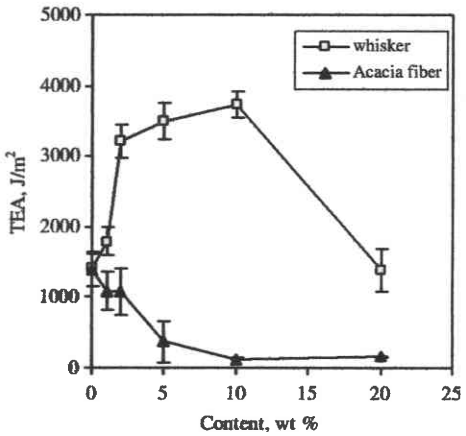

Fig. 9. TEA analysis of acrylic – cellulosics composite films.

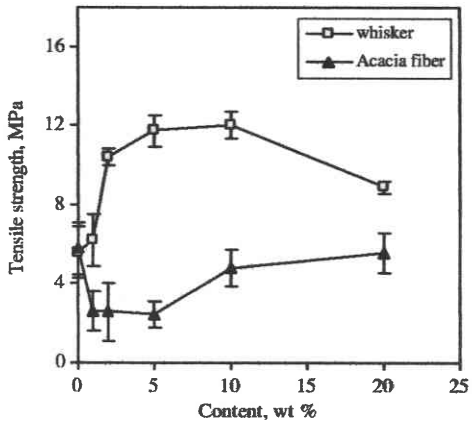

Fig. 10. Tensile strength analysis of acrylic – cellulosics composite films.

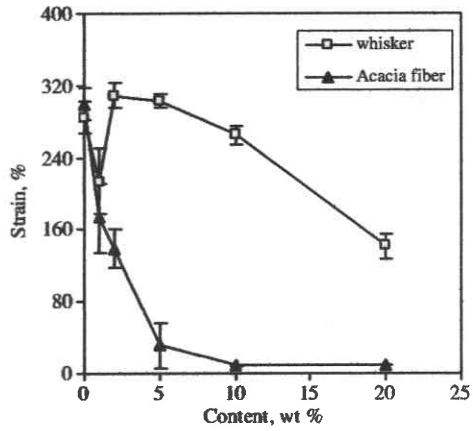

Fig. 11. Strain analysis of acrylic – cellulosics composite films.

cate there is an optimal range for the addition of cellulosic whiskers for strength improvement, which if surpassed results in a detrimental effect on the composite film strength properties. At no time were the acacia fibers able to provide comparable strength benefits under the conditions studied. The acacia fiber acrylic composites exhibited lower TEA, tensile strength and strain than the original acrylic latex, indicating that the addition of acacia fiber led to a detrimental effect on the composite strength properties. These results suggest that the observed strength properties of latex films reinforced with cellulosic whiskers is due, at least in part, to the size dimensions of the whiskers.

To further explore the fundamental interactions between cellulosic whiskers and acylates, composite films containing 0%, 5% and 20% whiskers were analyzed by atomic force microscopy (AFM). The results are presented in Fig. 12. These results clearly demonstrate a re-organization of the

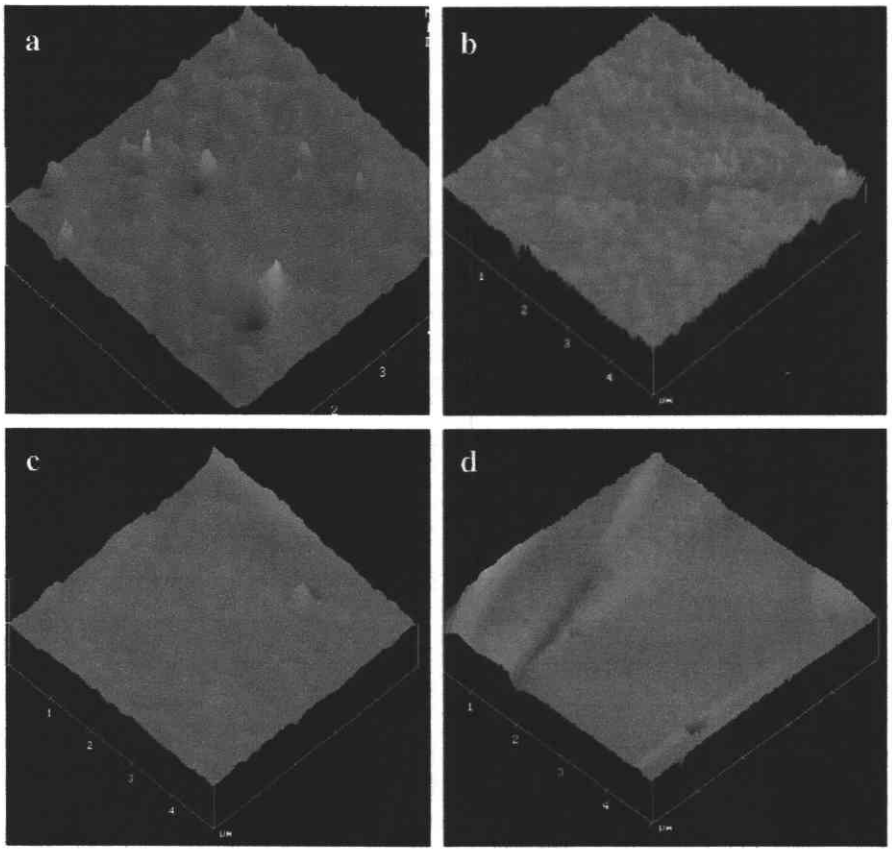

Fig. 12. AFM amplitude mode analysis of acrylate films with (a) 0%, (b) 5%, (c) 20% by cellulose whiskers and (d) 5% nanocellulose balls.

surface of the composite films. In contrast to the relatively rough surface of the acrylate film the incorporation of cellulosic whiskers dramatically decreased surface roughness. In addition, a comparison of the composite films with 5% cellulose whiskers versus 5% nanocellulose balls exhibits significant differences in surface properties. The inclusion of nanocellulose balls into the latex provides a rougher surface.

The interpretation of the amplitude data was further confirmed by surface roughness measurements which provided values of 8.86, 1.86, 3.99 and 2.87 for the control, 5%, 20% cellulosic whisker and 5% nanocellulose balls reinforced films, respectively.

4. Conclusion

Three closely related cellulosic acrylic films were prepared employing acacia pulp fibers, cellulose whiskers and nanocellulose balls. Latex films reinforced with cellulosic whiskers had an enhanced strength properties compared to acacia pulp and nanoball composite. AFM analysis indicated that the cellulose whisker reinforced composite exhibited decreased surface roughness.

Acknowledgements

The authors would like to thank the National Science Foundation (EEC-0332554), Georgia Research Alliance, Gunnar Nicholson Fellowship program and the member companies of the Institute of Paper Science and Technology at Georgia Institute of Technology for their financial support and guidance of this study. YP thanks Dr. Q. Sun for help with the TEM observation.

References

[1] Baekeland LH. On soluble, fusible, resinous condensation products of phenols and formaldehyde. J Ind Eng Chem 1909;1:545–9.
[2] Pardos F. Engineering and specialty plastics in the world 2000–2010. In: Proceedings of annual technical conference – society of plastics engineers, San Francisco, May, 2002. p. 2736–40.
[3] Bunsell AR, Berger M-H. Inorganic fibers. Surface characteristics of fibers and textiles, surfactant science series, vol. 94. New York: Marcel Dekker; 2001. p. 161–202.
[4] Smith PA. Carbon fiber reinforced plastics-properties. In: Polymer matrix composites. Oxford: Elsevier; 2001. p. 107–50.
[5] Puglia D, Biagiotti J, Kenny JM. A review on natural fibre-based composites – Part II: Application of natural reinforcements in composite materials for automotive industry. J Nat Fibers 2004;1(3):23–65.
[6] Pritchard G. Two technologies merge: wood plastic composites. Plast Additives Compound 2004;6(4):18–21.
[7] Mazumdar SK. Composites manufacturing: materials, product, and process engineering. USA: CRC Press; 2001.
[8] Klason C, Kubat J, Gatenholm P. Wood fiber reinforced composites. In: Wolfgang GG, Hatakeyama H, editors. Viscoelasticity of Biomaterials, ACS Symposium Series, vol. 489. Washington, DC: ACS; 1992. p. 82–98.
[9] Artzi N. Why nano-composites are in? A glimpse into polymer based nanocomposites. Rev Chem Eng 2005;21(5):307–45.
[10] Kvien I, Tanem BS, Oksman K. Characterization of cellulose whiskers and their nanocomposites by atomic force and electron microscopy. Biomacromolecules 2005;6(6):3160–5.
[11] Favier V, Canova GR, Cavaille JY, Chanzy H, Dufreshne A, Gauthier C. Nanocomposite materials from latex and cellulose whiskers. Polym Adv Technol 1995;6(5):351–5.
[12] Chazeau L, Paillet M, Cavaille JY. Plasticized PVC reinforced with cellulose whiskers. I. Linear viscoelastic behavior analyzed through the quasi-point defect theory. J Polym Sci Polym Phys 1999;37(16):2151–64.
[13] Chazeau L, Cavaille JY, Terech P. Mechanical behaviour above T_g of a plasticized PVC reinforced with cellulose whiskers; a SANS structural study. Polymer 1999;40(19):5333–44.
[14] Chazeau L, Cavaille JY, Canova G, Dendievel R, Boutherin B. Viscoelastic properties of plasticized PVC reinforced with cellulose whiskers. J Appl Polym Sci 1999;71(11):1797–808.
[15] Ljungberg N, Bonini C, Bortolussi F, Boisson C, Heux L, Cavaille JY. New nanocomposite materials reinforced with cellulose whiskers in atactic polypropylene: effect of surface and dispersion characteristics. Biomacromolecules 2005;6(5):2732–9.
[16] Samir MASA, Alloin F, Gorecki W, Sanchez JY, Dufresne A. Nanocomposite polymer electrolytes based on poly(oxyethylene) and cellulose nanocrystals. J Phys Chem B 2004;108(30):10845–52.
[17] Samir MASA, Alloin F, Sanchez JY, Dufresne A. Cross-linked nanocomposite polymer electrolytes reinforced with cellulose whiskers. Macromolecules 2004;37(13):4839–44.
[18] Samir MASA, Alloin F, Sanchez JY, Dufresne A. Cellulose nanocrystals reinforced poly(oxyethylene). Polymer 2004;45(12): 4149–57.
[19] Angles MN, Dufresne A. Plasticized starch/tunicin whiskers nanocomposites, 1. Structural analysis. Macromolecules 2000;33(22): 8344–53.
[20] Samir MASA, Alloin F, Dufresne A. Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. Biomacromolecules 2005;6(2):612–26.
[21] Ruiz MM, Cavaille JY, Dufresne A, Graillat C, Gerard J-F. New waterborne epoxy coatings based on cellulose nanofillers. Macromol Symp 2001;169:211–22.
[22] Jana AK, Jain A, Kumar J. Volatile organic compounds (VOCs) in paints and its reduction. Paintindia 2005;55(12):67–8.
[23] Beck-Candanedo S, Roman M, Gray DG. Effect of reaction conditions on the properties and behavior of wood cellulose nanocrystal suspensions. Biomacromolecules 2005;6(2):1048–54.
[24] Araki J, Wada M, Kuga S, Okano T. Flow properties of microcrystalline cellulose suspension prepared by acid treatment of native cellulose. Colloid Surface A 1998;142(1):75–82.
[25] Zhang J, Elder TJ, Pu Y, Ragauskas AJ. Facile synthesis of spherical nanocellulose particles, Carbohyd Polym, submitted for publication.
[26] Vander Wielen LC, Elder T, Ragauskas AR. Analysis of the topochemical effects of dielectric-barrier discharge on cellulosic fibers. Cellulose 2005;12(2):185–96.