Adhesion Improvements of Nanocellulose Composite Interfaces

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Attention has recently become focused on the performance advantages of nanocomposites, and particularly polymer-based nanocomposites with respect to incumbent "neat" polymers or metallic materials for lightweighting initiatives. In the interest of sustainability, the specific use of bio-reinforced nanocomposite parts and nanostructured coatings within automotive, aerospace, construction, medical, and packaging applications is accelerating. These "green" nanocomposites can provide high mechanical strength at low density, low weight, and potentially low cost. However, there are interfacial surface adhesion challenges with these and other nanocomposites, in addition to particle distribution and stability issues, which can inhibit full realization of their mechanical performance advantages. This paper will profile polymeric nanocomposites and nanocoatings, as well as define surface modification protocols using atmospheric pressure plasma technologies to optimize interfacial adhesion to similar and dissimilar materials.

Introduction

New efforts are underway to develop and apply sustainable nanocomposites to improve structural properties for applications in the automotive, aerospace, packaging, and medical fields. Typical properties which are improved include, but are not limited to, dimensional stability, structural strength, thermal resistance, chemical resistance, weight reduction, and electrical conductivity.[1]

Prior art and current state-of-the-art composites involve the employment of aliphatic/aromatic polyesters, glass fiber reinforcements, carbon fiber reinforcements, nanoclay additives, CNTs, and other materials for producing nanocomposites. Many of these are impacted by market supply and pricing volatility of hydrocarbon-based resources, as well as their contribution to global environmental effects at the "cradle and grave."[2-6] It is these sets of issues which have given rise to the search for biobased nanocomposite solutions which maintain (or exceed) the properties desired for the aforementioned industries and applications.

The utilization of polymer nanocomposites from sustainable sources, termed bio-nanocomposites, has advantages over synthetic sources, most particularly the opportunity for biodegradability and reductions in CO_2 emissions. Recent use of certain blends of poly-

Table 1: List of Natural Fibers and Their Properties

Fiber Source	Treatment	% Cellulose	Tensile Strength MPa	Elastic Modulus GPa	% Elongation
Banana	NS	NS	779	32	2
Cotton	Alkaline boiling modified with carbomethyl-cellulose	NS	NS	82	13.57
Bark of cotton stalks	NaOH treatment	79	377	18.7	3
Sisal	NS	NS	600-700	38	2.3
Flax	NS	NS	800-1500	60-80	1.2-1.6
Hemp	NS	NS	550-900	70	1.6
Jute	NS	NS	400-800	30-Oct	1.8
Coir (coconut husk)	NS	NS	220	6	1.5-2.5
Velvet Leaf	Alkaline treatment	69	325–500	18-38	1.6-2.6
Switch grass leaves	Simple alkaline treatment	61.2	715	31	2.2
Switch grass stems	Simple alkaline treatment	68.2	351	9.1	6.8
Stinging nettle	NS	NS	1594	87	2.11
Kenaf	Alkaline treatment	NS	130	11	1.3
Ramie	Untreated	68.6–76.2	560	24.5	2.5
Soybean straw	Alkaline treatment	85	351	12	3.9
Flax	NS	NS	1339	54	3.27
Wheat straw	Mechanical processing	47.55	58.7	3.7	NS
Wheat straw	Microbial retting	NS	139.9	4.8	NS
Wheat straw	Chemical processing	63.14	146	7.9	NS
Hop stem	Alkaline treatment	84	53.3	20	3.3
Cornstalks	Alkaline treatment	52	286	16.5	2.2

lactic acid, polycaprolactone, and thermoplastic starch as composites has been reported by Sarazin *et al.*[7] Increases in the concentration of thermoplastic starch used in PLA resulted in an increase in strain at break with a decrease in elastic modulus and maximum strength, introducing the potential for integration of these nanocomposites in higher performance stress applications, such as within automotive and aerospace. Natural rubber has also been blended with starch to form nanocomposites.[8]

The leveraging of natural fibers for physical load-bearing additives in composite materials is gaining more notice. Table 1[9] shows the list of natural fibers that have been applied as reinforcement for composites and nanocomposites. Key determinants of the performance properties of natural fiber-reinforced composites include fiber–matrix adhesion, the mechanical properties of the fiber, moisture content, physical impact and fatigue, thermal stability, and production of fiber-based nanocomposites. Optimization of interfacial adhesion between a reinforcing biobased nanoparticle and a polymer-based matrix is critical for appropriate transfers of stress from loading. It has been demonstrated and well-known that when matrix polymer chains are grafted directly to the reinforcement surface, entanglement occurs with the matrix bulk polymer chains, causing strong interfacial adhesion.[10]

Cellulose nanomaterials (CNs) have garnered widespread interest as a renewable reinforcing phase for polymers to increase their modulus, strength, and heat-distortion temperature.[13] Two of the most highly studied CN particles are cellulose nanofibrils (CNFs) and cellulose nanocrystals (CNCs); both are fiber-like particles with high aspect ratios. CNFs are produced via high mechanical shear processes of the starting cellulose materials (typically wood or plant pulp) with or without chemical treatment. CNCs are extracted via acid hydrolysis and result in a high fraction of crystalline cellulose. Both particles are pure cellulose, with cellulose chains aligned along the long axis of the particle. The surfaces of the CN particles have accessible –OH groups upon which chemical modification can take place. CNs have a high mechanical properties, similar to Kevlar™, and low density and thermal expansion. Additionally, CNCs have a rigid rod-like nature in solution and surface charge resulting in lyotropic liquid crystalline behavior when they are dispersed in polar solvents.

Interfacial Bonding

Emerging from the development of structurally-performing bio-reinforced nanocomposite structures is the need for interfacial bonding strength between polymeric nanocomposites and similar (or dis-similar) substrate surfaces. One must first keep in mind that nanocomposites have an exceptionally high surface area to volume ratio, increasing their reinforcement efficacy. The significant amount of reinforcement surface area means that only a relatively small amount of nanoscale reinforcement material can have, for example, a macro effect on the overall mechanical properties of the nanocomposite. However, nanoscale dispersion of nanostructures in the polymer matrix will introduce new physical properties as well as a variation in the composition of the exposed surface that will be different than with unfilled matrices, effectively changing the nature of interfacial adhesion with an adhesive, for example, and another substrate.

As inferred above, differences in the surface properties of a bio-nanocomposite are largely determined by the gradient concentration of biobased nanoparti-

cles from the surface to the interior in the polymer matrix. The special properties of nanocomposites basically stem from the interaction of the polymer matrix and nanocomposite "filler" at the interface which constitutes a major amount of the bulk. This is in contrast to the interfaces of typical composites which constitute a small fractional volume relative to the bulk material.

It is well known that the surface tension of polymeric materials contributes significantly to adhesive forces. The concentration and dispersion of biobased nanoparticles within polymer matrices will also change surface-tension dynamics relative to bondable interfaces. For example, a high volume concentration of a biobased nanoparticle with high surface hardness and hydrophilicity could indicate the need for a change in surface modification protocols relative to a low volume concentration of the same nanoparticle, assuming for both that the dispersions are equal. Hence, proper control of interfacial surface energy must be achieved through optimization of nanoparticle interaction with the polymer matrix, as well as through optimization of surface tension of the nanocomposite relative to its interface. It is the latter which hereto has not been well analyzed.

Bio-nanoparticles, such as nanocellulose, are one-dimensional and form elongated structures with high aspect ratios (relationship between its width and its height). As can be seen in *Figure 1*, the surface roughness of a polymer nanocomposite with cellulose whisker reinforcement is significantly increased. As such, the wettability rate of an adhesive applied to an interface is impeded by this roughness and the surface tension of the polymer matrix. Other nanocomposites, such as epoxy-based cellulose nanocrystal composites (CNCs), can have particle lengths ranging from 0.05 to 0.5 microns, and 3 to 5 nm in width and height. It is common for surfaces with high concentrations of CNCs to have a higher mean surface roughness.

As mentioned above, nanocelluloses are generally recognized to be effective in reinforcing polymers due to interactions between the nano-scale elements that form a binding network interconnected by hydrogen bonding. And adhesion theories have been extensively reviewed in the bonding of nanocellulose fibers within matrixes, including mechanical interlocking, adsorption, diffusion, and weak boundary layer theory. However, no preliminary studies have heretofore been conducted which explore the surface dynamics of green nanocomposite films relative to interfacial adhesion.

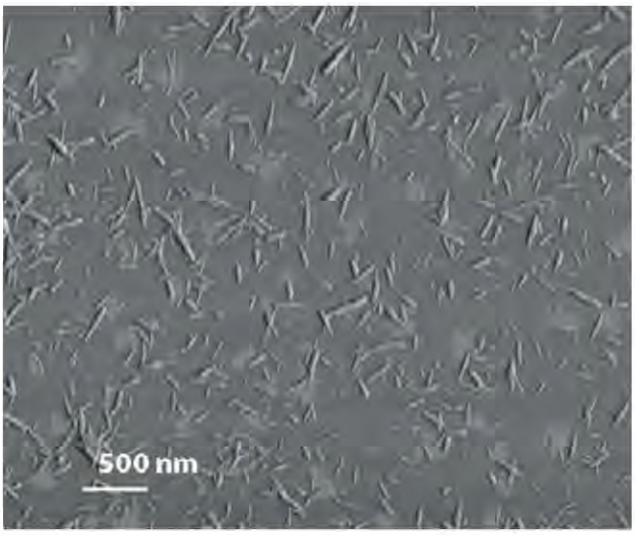

Figure 1: AFM phase image of cellulose whiskers at polymer nanocomposite surface (Image courtesy of Anand Paul Mangalam, Oregon State Univ.[11])

To clarify the impact that green nanocomposite surface properties may have on interfacial adhesion, a first-phase study of these surface properties was conducted with the use of 100% nanocellulose structures, as well as epoxy-cellulose CNC composite structures.

Experimental

Materials: Ancarez AR555 and Anquamine 401 were kindly provided by Air Products (Allentown, Pennsylvania), and used as received. AR555 is a solid epoxy emulsion in water (55 wt%) via a nonionic surfactant with D50 = 0.5 um and an epoxy equivalent weight of 550. Anquamine 401 is a polyamine dispersed in 30% water having an amine hydrogen equivalent weight of 200. CNCs, 8.75 wt% suspensions in water, were provided by Richard Reiner and Alan Rudie of the USDA Forest Products Laboratory (Madison, Wisconsin). These CNCs were derived from mixed southern yellow pine, dissolving pulp via 64% sulfuric acid digestion as described elsewhere.[12] The resultant CNCs have sulfate functionality due to residual sulfate esters on their surfaces. The CNCs were determined to contain 0.72 wt% sulfur on a dry cellulose basis by inductively coupled plasma/mass spectroscopy (ICP/MS). CNCs from this process are typically 4-5 nm in diameter and 150-200 nm long.[13]

Films: Two epoxy and four epoxy-nanocellulose films were fabricated and one microfibrillated cellulose film provided by Verso Paper Corporation in Bucksport, Maine, USA. The AR555 and 401 were added at a stoichiometric ratio. Because nanoparticle dispersion is critical not only for uniform reinforcement of the bulk film but also for accurately measuring and assessing interfacial adhesion, two dispersion techniques were included in the design of experiment for the epoxy-based films. Table 2 details the composition of all subject films, inclusive of the CNC weight by volume of each film. High-speed mixing denotes the use of a cowl's blade at 800 rpm to disperse the CNCs in the epoxy. The resultant films exhibited only diffuse birefringence. The magnetic stir dispersion method used a lab magnetic stir to disperse the CNCs. The resultant films exhibited distinct domains of birefringence.

Table 2: Experimental Nanocomposite Samples

Identifier	Material	CNC Wt.	Dispersion
A	Epoxy	0%	High Speed Mix
B	Epoxy CNC	5%	High Speed Mix
C	Epoxy CNC	10%	High Speed Mix
D	Epoxy	0%	Magnetic Stir
E	Epoxy CNC	5%	Magnetic Stir
F	Epoxy CNC	10%	Magnetic Stir
G	MFC	n/a	Casting

Surface Modification: An Enercon atmospheric pressure glow discharge plasma system (60-inch Plasma3™ Model) for films was used to modify the surface of the cellulose and nanocomposite films. Plasma treatment trials were subsequently conducted at a base power density of 10 watts min/ft^2.

Surface Activation and Adhesion Measurements: Contact angles were measured with a Tantec Model Cam-Film using distilled water via the advancing method. 180° tape peel values were obtained using 3M 800 acrylic tape per ASTM D3330/D3330M tape tester.

Results and Discussion

One of the key objectives of this study is to examine the adhesion-promotion effects of an environmentally friendly, low-temperature, and highly uniform technique for the surface modification of cellulose-based nanocomposite materials. Two functionalizing gas mixtures were initially pre-tested, argon/oxygen and nitrogen/hydrogen, to identify the most adhesion-optimizing protocol for the primary design of experiment using epoxy CNC films. Peel adhesion testing confirmed that the argon/oxygen gas mixture at a standardized power density provided elevated peel adhesion relative to the nitrogen/hydrogen mixture.

The results of contact angle (CA) measurements and peel testing experiments for the films before and after plasma treatment are shown in Table 3. The epoxy films and MCC film were generally hydrophilic both before and after plasma treatment, based on the contact angle values obtained. Additionally, the trends in contact angle values were not systematic with respect to CNC loading. However, the sample preparation technique did appear to have an effect of the efficacy of the plasma treatment because the contact angle values for the samples produced by magnetic stirring were decreased more with plasma treatment than the samples produced by high-speed mixing. The trend in contact angle with plasma treatment for the MCC film was more similar to the samples made by magnetic stirring.

The peel testing results indicated higher adhesion between the films and the substrates after plasma treatment for all of the films, and again the trends in peel testing results were not systematic with respect to CNC loading. Overall, lower values were obtained from

Table 3. Plasma Surface Modification Data

Identifier	Initial CA	Post CA	Initial Peel (grams/in)	Post Peel (grams/in)
A	55°	49°	566.0	885.7
B	69°	59°	714.0	846.5
C	50°	47°	372.0	721.2
D	61°	32°	556.0	789.0
E	58°	39°	276.0	440.1
F	46°	24°	288.0	483.1
G	68°	47°	457.0	802.0

the peel testing for the samples produced by magnetic stirring than for the samples produced by high-speed mixing.

Taken together, these results suggested that the processing method employed, for composite and neat films, had impacts on the surface attributes and surface modification capabilities. While the processing method employed to produce a discontinuously reinforced composite is commonly accepted to influence bulk physical properties through the particle dispersion and distribution attained, the link between processing and surface properties is not as intuitive. In these samples, the CNC dispersion attained was more homogeneous in the samples produced by high-speed mixing than in the samples produced by magnetic stirring. Given the change in both contact angle values and peel testing results for the epoxy and composite samples, the size of the CNC domains seem to have an effect on the surface properties and surface treatment efficacy. The authors are continuing to examine the processing-structure-property relationships in these materials, and the results of these experiments will be published in a future manuscript.

Conclusions

As related by the data in Table 3, contact angles universally decreased and peel values universally increased, indicating successful surface activation. Curiously, the average increase in peel adhesion between samples A-C (high-speed mix dispersion) and D-F (magnetic stir dispersion) was nearly identical at 56.1% and 56.3%, respectively, potentially indicating that both dispersion methods for forming epoxy CNC films can offer similar interfacial adhesion despite achieving different levels of CNC dispersion. However, the lowest and highest change in peel adhesion were recorded within high-speed mix dispersion techniques at 18.5% (5% weight) and 93.9% (10% weight). Given that the high-speed mix epoxy control sample achieved a peel adhesion of over 56%, the wide peel strength variation between the 5% and 10% CNC weights may indicate dispersion and/or anchorage issues at the film surface. Magnetic stir dispersion films had fairly consistent peel values ranging from 41.9% (0% weight) to 67.7% (5% weight), perhaps indicating a more consistent surface topography. The MFC film had a peel adhesion increase of 75.5% following plasma activation, second-highest among all films tested and indicating the potential for good adhesive wetting for interfacial bonding.

With all green nanocomposite films indicating excellent surface wettability and interfacial bond-strength potential following oxidative plasma treatment, broader studies are warranted to explore methods which can optimize both dispersion techniques applied in this

study, as well as interfacial bonding performance utilizing plasma surface modifications.

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