



Cellulose nanocrystal: A promising toughening agent for unsaturated polyester nanocomposite



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ABSTRACT

New nanocomposites of an unsaturated polyester resin (UPR) and cellulose nanocrystals (CNCs) were prepared. Effects of CNC silane surface treatment on the morphology, mechanical and thermal properties, viscoelastic behavior and water absorption of CNC reinforced UPR have been studied. The results showed that the crystallinity index of the CNCs reduced after the surface treatment. However, it did not impact the size and aspect ratio of the rod-like nanoparticles. Tensile tests showed that both the strength and stiffness of the UPR improved upon the incorporation of silane treated CNCs (STCNCs), whereas no significant changes were observed on the impact energy after the treatment. Interestingly, the impact energy increased significantly with the addition of untreated CNCs. The viscoelastic behavior and thermal degradation for both the CNC and STCNC-reinforced nanocomposites were improved. The water-absorption behavior of the UPR was found to decrease upon incorporation of CNCs, and a further reduction was observed with STCNCs.

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1. Introduction

Cellulose nanocrystal (CNC) is one of the most important biopolymers and has attracted a great deal of interest in the nanocomposite field because of its appealing intrinsic properties such as nanoscale dimensions, high surface area, unique morphology, low density, and high mechanical strength. In addition, it can be easily modified and is readily available, renewable, and biodegradable. Acid hydrolysis to produce CNCs is the most well-developed technique [1–4]. CNCs are rod-like particles, and their dimensions depend on the source of the cellulose and the hydrolysis conditions; however, their length generally ranges between 100 and 1000 nm [5]. Thus, CNCs with different aspect ratios have been isolated from different sources such as tunicin [6], kenaf [4], sisal [7], banana fiber [8], and rice husk [9], and evaluated as a reinforcing phase in nanocomposites using different polymer matrices such as poly(lactic

acid [10], poly(vinyl alcohol [11], acrylic latex [12], polyethylene [13], polyurethane [14], thermoplastic starch [15], and rubber [16].

Unsaturated polyester resin (UPR) is one of the most popular thermoset polymers for use as a matrix in composites for applications in the marine and aerospace industries because of its unique properties such as high strength and modulus, high resistance to water, room temperature cure capability, and transparency. However, its low toughness limits its usage, and an improvement in this regard is greatly desired.

The addition of elastomeric particles into thermoset resins is a well-known approach to overcome their low toughness. However, the high stiffness and strength of thermoset resins are inevitably reduced by the addition of an elastomer with low stiffness and strength [17,18]. To avoid the loss of the inherent stiffness and strength of the UPR, reinforcing fillers such as fibers or layered silicates such as montmorillonite, with a fairly large aspect ratio, have been extensively studied [19–23]. Other nanoparticles such as alumina [24,25], zinc oxide [26], carbon black [27], and carbon nanotubes [28,29] have been used to prepare nanocomposites. However, to the best of our knowledge, there has been no research on the application of CNCs to the UPR.

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One disadvantage of CNCs in terms of their industrial application is the strong hydrophilicity of their surfaces, which inhibits homogeneous dispersion in most nonpolar polymer matrices and causes a weak interface, thus reducing the mechanical performance of the composites. Indeed, good dispersion of CNCs in the polymer matrix is an important prerequisite to benefit from its large surface area and to obtain good mechanical properties for the resulting composites [30]. One effective way to prevent the aggregation of CNCs and improve their dispersion and compatibility with the matrix material is surface chemical modification using coupling agents [31–33]. Many types of coupling agents have been reported, namely, anhydrides, maleated polymer isocyanates, triazines, and alkoxy silanes [34]. Phenyl isocyanate (PI), alkenyl succinic anhydride (ASA), 3-iso-propenyl- α , and α -dimethylbenzyl isocyanate (TMI) were also used to chemically modify the surface of chitin nanocrystals [35]. Coupling nanocellulose with *N*-octadecyl isocyanate via a bulk reaction in toluene has also been reported to enhance its dispersion in organic media and its compatibility with polycaprolactone, which significantly improved the stiffness and ductility of the resulting nanocomposites [36]. Among all the mentioned coupling agents, silanes are the most effective and widely used. Goussé et al. [33] stabilized tunicin nanocrystals in tetrahydrofuran (THF) by partial silylation of their surface. Grunnert and Winter [37] reported the preparation of topochemically trimethylsilylated bacterial cellulose nanocrystals. The resulting nanoparticles were dispersed in acetone to process nanocomposites with a cellulose acetate butyrate matrix. The surface trimethylsilylation of nanocellulose from bacterial cellulose and their resulting composites with cellulose acetate butyrate [31] were also investigated.

Most studies on CNC-reinforced composites have been based on thermoplastics [13,38–40], with very few using a thermosetting resin, specifically, the UPR. In this work, cellulose nanocrystals were extracted from the kenaf bast fiber, which is a natural source [4], and applied as a reinforcing agent in a UPR matrix to replace inorganic nanoparticles, for improving the impact properties. Nanocomposites were prepared by reinforcing the UPR matrix with untreated and silane-treated CNCs. The effect of the surface treatment on the mechanical properties, thermal behavior, and morphology of the nanocomposites was evaluated and discussed.

2. Materials and methods

2.1. Materials and chemicals

Raw kenaf bast (*Hibiscus cannabinus*) fibers were kindly supplied by KFI Sdn. Bnd. (Malaysia). The UPR used was ortho-phthalic-based polyester resin containing 30% styrene, with the molecular weight of 2×10^3 – 3×10^3 , supplied by Revertex (M) Sdn. Bhd. *N*-(β -aminoethyl)- γ -aminopropyltrimethoxysilane (APS) was purchased from Dow Corning Singapore Pte. Ltd. All other chemicals used were purchased from SYSTERM Bhd. Chemical structure of UPR and APS are illustrated in Fig. 1.

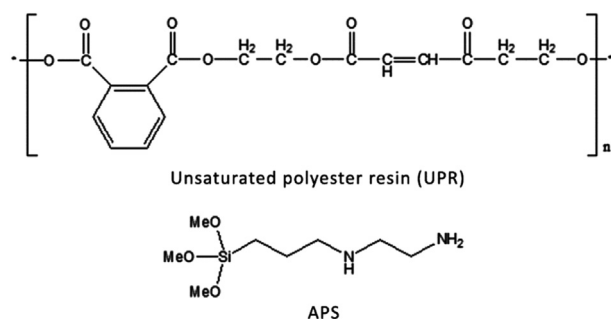


Fig. 1. Chemical structure of unsaturated polyester resin and APS.

2.1.1. Cellulose nanocrystal preparation

Colloidal suspensions of CNCs in water were prepared from the kenaf bast fiber [4]. Alkali and bleaching treatments were used to extract the cellulose, and acid hydrolysis was conducted for 40 min at 45 °C under mechanical stirring using 65% H₂SO₄.

2.1.2. Surface treatment of cellulose nanocrystals

The treatment of neutralized, freeze-dried CNCs was carried out with a dilute aqueous solution of APS (0.5 wt%). The aqueous solution was prepared by adding APS to a mixture of water–ethanol, 80/20 (v/v %), under stirring, followed by acidification to pH 3–4.5 with acetic acid to improve the performance of the reinforcing CNC. The CNC was then added, and the solution was sonicated for 3 min to prevent the aggregation of the CNC and produce a homogenous suspension. The mixture was kept for 2 h at room temperature. The suspension was then washed with distilled water using centrifugation at 4000 rpm to remove any excess silane from the CNC before lyophilization. The obtained silane-treated CNCs were abbreviated as STCNCs.

2.1.3. Nanocomposite preparation

The freeze-dried CNCs were redispersed in styrene using an ultrasonic vibrator for 30 min in an ice bath. The CNC suspension in styrene was mixed with the UPR, and the mixture was sonicated for 30 min. The resulting mixture was stirred with a mechanical stirrer and heated at 60 °C to evaporate excess styrene. The mixture was then cooled to room temperature before an initiator (1.5% of the resin) was added, and the solution was stirred for 2 min. The mixture was poured into molds and cured at room temperature for 24 h. Nanocomposites with different CNC contents were prepared. A similar technique was used for the STCNC-based nanocomposites. Nanocomposites prepared with CNCs and STCNCs were abbreviated as CNC-UPR and STCNC-UPR, respectively.

2.2. Characterization

2.2.1. Infrared spectroscopy

Infrared spectroscopy with attenuated total reflectance (ATR) was used to examine the changes in the functional groups induced by the surface treatment of the CNC. Freeze-dried samples were analyzed in the transmittance mode within the range 4000–600 cm⁻¹.

2.2.2. Microscopy

The morphology of the fractured surface of the nanocomposites was examined using a Zeiss Supra 55VP field emission scanning electron microscope (FESEM). All samples were sputter-coated with gold before observation to prevent charging.

Transmission electron microscopy (TEM) was conducted using a Philips CM30 microscope to investigate the morphology of the CNCs before and after the surface treatment and in the nanocomposite as well. A droplet of a diluted suspension was deposited on a Cu grid covered with a thin carbon film. For the nanocomposites, a thin nanocomposite film (70-nm thickness) was prepared using cryo-ultramicrotomy (Leica EM, FC6) under liquid nitrogen. To enhance the contrast, the nanocrystals were negatively stained with 1 wt% uranyl acetate solution in deionized water for 30 s and then dried at room temperature.

2.2.3. Tensile tests

Tensile testing was carried out using an Instron Universal Testing Machine model 5567 according to ASTM D-638-91 with a cross-head speed of 5 mm/min. The specimens were cut from cured sheets to dimensions of 160 mm × 13 mm × 3 mm. The tensile values were taken from an average of 10 specimens.

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