



Scalable processing of thermoplastic polyurethane nanocomposites toughened with nanocellulose



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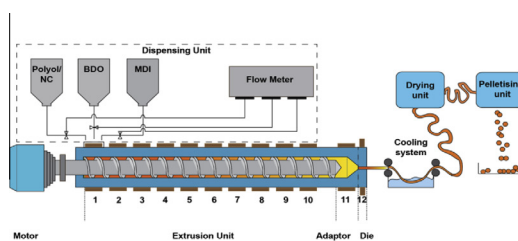
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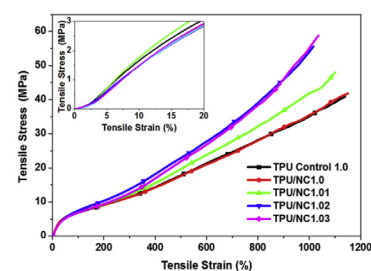
HIGHLIGHTS

- Thermoplastic polyurethane (TPU) is toughened with high aspect ratio nanocellulose.
- Scalable approach of processing nanocomposites is shown *via* reactive extrusion.
- The 'polyol-nanocellulose dispersion route' could reduce the usage of organic solvent.
- With 0.5 wt.% spinifex nanocellulose, TPU showed up to 43% improvement in tensile strength.
- It can be an attractive approach for polymerisable/curable systems.

GRAPHICAL ABSTRACT



Reactive extrusion of polyurethane/nanocellulose nanocomposite



Improvement in tensile properties

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ABSTRACT

The production of strong and elastic polyurethane nanocomposites toughened with nanocellulose (NC) and their widespread application in many engineering fields are currently limited by poor processability *via* classical industrial processing methods and/or the usage of large amount of solvents. In this report, we demonstrate a scalable, organic solvent-free incorporation of nanocellulose into thermoplastic polyurethane (TPU) and a remarkable reinforcement without compromising elastic properties. The nanocomposites were prepared *via* water-assisted dispersion of nanocellulose in polyether polyol by bead milling, drying and reactive extrusion of this dispersion with comonomers. Upon the incorporation of nanocellulose (0.5 wt.%), as observed from infrared spectroscopic and thermal analysis, the phase mixing of hard and soft-segments in the TPU matrix and the primary relaxation temperature have slightly increased due to the hydrogen bonding, interfacial area and nucleation-enhanced by long polar nanocrystals. The TPU/nanocellulose nanocomposites prepared with an appropriate stoichiometric ratio (determined through appropriate process control) showed a remarkable improvement (up to 43%) in ultimate tensile strength without compromising the elastic properties including elongation, creep and hysteresis.

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1. Introduction

Thermoplastic polyurethanes (TPUs) are versatile polymers which readily allow properties to be controlled by altering the compositions of soft and hard segments and structural morphologies. Due to their versatility in structure and (mechanical and

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physical) properties, they have found a vast array of applications ranging from soft medical tubing to moulded automotive parts, and from breathable clothing to ski boots [1]. Although they account for less than 6% of total polyurethane products, TPUs have experienced one of the highest market segment growth rates due to their unique combination of properties such as melt-processability, high elasticity and high abrasion resistance. In TPU copolymers, filler particles have sometimes been incorporated to increase the strength and stiffness of the host polymer and to reduce the production cost. However, any increase in strength and modulus values observed in conventional TPU composites has almost always been associated with a sacrifice in elastic (reduced elongation and toughness) and optical properties (discoloration and haze) [2–4]. Recent advancements in nanoscience and nanotechnology have offered a wide variety of nanoscale particles including clay, carbon nanotubes, metals and metal oxides as reinforcing fillers for polyurethane. Due to the increasing awareness of environmental issues, the residual fossil feedstock economy, and also occupational health considerations, the demand for products made from renewable and sustainable resources is increasing.

Cellulose is the most abundant natural polymer on the planet; it is widely explored as a potential source for nanomaterials in many areas (biomedical, engineering, and industrial) due to its renewability, biodegradability, excellent specific properties, and possible additional functionalities. The nanocellulose can be isolated into filament-like cellulose nanofibres (CNF) or rod-like or elongated rice-like cellulose nanocrystals (CNC), previously known as whiskers, from lignocellulosic plant biomass [5,6], and some marine animals [7,8]. According to Moon et al. [5], which further categorises nanocellulose types by their dimensions, typical CNF have a length between 0.5 and 2 μm and a width of about 4–20 nm, whereas a rod-like cellulose nanocrystal (CNC) show a length around 0.05–0.5 μm and width of 1–30 nm. A CNF are usually produced via mechanical shearing methods like ultrasonication, homogenisation, grinding, microfluidisation or milling in combination with enzymatic and/or chemical pre-treatments [9–11], whereas CNCs are isolated via acid hydrolysis, enzymatic treatment, hydrothermal treatment, ultrasonication and mechanical methods, or combinations thereof [12–14]. The reinforcing potential of nanocellulose has been exploited not only due to its sustainability and reliability but more so due to its virtuous individual mechanical properties such as high specific strength and modulus, and the potential to retain transparency in the nanocomposite materials [5,15,16]. Up until now, nanocellulose based thermoplastic polymer nanocomposites have typically been prepared via solvent based methods (casting, in-situ polymerisation, organogel template route), melt compounding and compression-moulding of alternating layers of polymer and nanofibre films [14,17–23].

Wu et al. [24] reported polyurethane (PU) nanocomposites reinforced with microcrystalline cellulose (MCC) particles and prepared via in-situ solution polymerisation. This study demonstrated that with an assistance of “pre-swelling” in DMF solvent combined with two-step solution polymerisation, significant improvements in stiffness, strain-to-failure, and strength are possible. For example, at an optimum concentration (5 wt.%) of MCC, the tensile strength was improved by three fold, albeit from a very modest baseline, from 8 MPa to 24 MPa, whereas the ‘conventional’ solution polymerised cellulose composite failed to significantly improve the tensile strength (8 MPa to 9 MPa), but still resulted in significant stiffening [24]. These contrasting results were attributed to the differences in solution processing affecting the degree of in-situ defibrillation of MCC (bundles) into nanofibres, and in turn, enhanced stress transfer because of the nano-scale reinforcement. In another study nanocomposites using rod-like or elongated rice-like cellulose nanocrystals were prepared by dispersing them in a waterborne polyurethane host polymer [25], or dispersing

the organogel of CNC in a thermoplastic polyurethane solutions [26]. These nanocomposites demonstrated remarkable improvements in stiffness, for example the nanocomposites via waterborne methods showed an improvement in Young modulus from 0.5 to 344 MPa with 0–30 wt.% CNC, whereas, the organogel based TPU/CNC nanocomposites showed an improvement in tensile storage modulus from 14 MPa to 1076 MPa with high loadings of 2–20% v/v of CNC. However, they failed to demonstrate improvements in tensile strength, due to the high loading of nanoparticles that sacrifice the rubbery properties of TPU materials. With high-aspect ratio (>100) filament-like cellulose nanofibrils, the nanocomposites were developed by compression moulding of the stacks comprising polyurethane films and mats of cellulose nanofibrils [17,19,27]. They have also shown increase in stiffness of nanocomposites. In reading these particular studies some pragmatic questions must be posed; what is the point of turning a thermoplastic elastomer into a plastic and wouldn't there be more utility in trying to engineer a TPU-nanocellulose nanocomposite with maximum strength, toughness, compliance and resilience? It appears that others are pursuing this objective.

When the nanocomposites were prepared via in-situ polymerisation using a low concentration of CNC (1% v/v), these nanocomposites achieved an 8-fold increase in tensile strength with only a small increase in tensile modulus. This improvement indicates that at low volume fraction, these low-aspect ratio rod-like nanocrystals can enhance the stress-transfer dramatically between polymer and filler particles due to the high interfacial surface area and a reduced number of complex agglomerates or bundles [28]. However, all of these studies rely on solvent-based methods. For large-scale production, wet processing methods are limited by the use of large-amounts of solvents causing environmental issues and greatly increasing the nanocomposites production-cost to unacceptable levels. Compounding methods using existing extrusion and moulding facilities are favoured by the industry as they are economically viable and environmentally friendly. Hence, this study communicates a significantly more attractive route for processing nanocellulose reinforced TPU nanocomposites via a classical extrusion method i.e. ‘reactive extrusion’.

The reactive extrusion builds up the polymer chains via in-situ bulk copolymerisation of monomers or precursors in a co-rotating twin-screw extruder. This method remains the preferred commercial process for making the majority of PU materials sold globally today, as it provides a greater ability to convey, shear and polymerise the precursors, adjust the processing temperature, tune the composition, molecular weight and thereby the performance (properties). Also, developing a route for introducing nanocellulose into the supply-chain in the non-reactive liquid polyol precursor materials will provide an economic “drop in” solution for the polyurethane industry regarding materials handling and large-scale processing. Hence, herein, we demonstrate a large-scale processing strategy for polyurethane/cellulose nanocomposites, by isolating nanocellulose from *Triodia pungens* (*T. pungens*), dispersing this very unique cellulose in polyol and subsequently performing twin-screw reactive extrusion. *T. pungens*, more commonly known as “spinifex” is a soft resinous grass that is dominant vegetation which covers nearly one-third of the Australian continent. We have recently explored spinifex as a source of high-aspect ratio nanofibrils capable of being extracted using comparatively green methods and very low energy consumption [10,11].

2. Experimental

2.1. Materials

Triodia pungens (*T. pungens*) grass was collected directly from plants growing around Camooweal, Queensland, Australia. The

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