Rheological properties of cellulose nanocrystal-embedded polymer composites: a review

Yern Chee Ching · Md. Ershad Ali · Luqman Chuah Abdullah · Kai Wen Choo · Yong Ching Kuan · Sabariah Julai Julaihi · Cheng Hock Chuah · Nai-Shang Liou

Received: 11 September 2015 / Accepted: 28 January 2016 © Springer Science+Business Media Dordrecht 2016

Abstract Nanotechnology provides useful insights into the behavioural properties of materials from the nanoscale point of view, enabling researchers to develop new materials that were previously inconceivable. Cellulose is an ideal candidate for nanomaterial for nanotechnology because of its nanofibrillar structure, abundance, renewability, biodegradability and eco-friendly nature. Nanocrystalline cellulose materials have become the focus many studies related to these materials and their applications. This review summarises the current knowledge on the field of nanomaterials, focussing mainly on the rheological behaviour of polymer nanocomposites embedded with nanocrystalline cellulose. This review will enable better understanding of the use of nanocrystalline cellulose for the development and applications of cellulose nanocrystal-based nanocomposites.

Keywords Cellulose nanocrystals (CNCs) · CNC-matrix composites · Rheological properties

Introduction

There has been an increasing interest in using natural fibres to replace synthetic ones in polymeric composites as they are eco-friendly and renewable (Eichhorn et al. 2010; Ching et al. 2013; Yong et al. 2015a). The automotive, construction, paper, textile and packaging industries have indeed shown enor-mous interest in developing new natural
fibre-reinforced composites as engineering materials (Nurfatimah et al. 2014, 2015; Yong et al. 2015b; Ashiqur et al. 2015). These natural fibre-reinforced composites possess acceptable mechanical properties and also offer a number of well-known advantages including light weight, low density, low cost, availability, biodegradability, high specific stiffness and mechanical strength, low hardness, renewability and recyclability, and they are non-hazardous (Azizi Samir et al. 2005; Belgacem and Gandini 2008; Boldizar et al. 1987; Ershad et al. 2015; Gousseé et al. 2004; Seng et al. 2014; Tan et al. 2015a, b; Woodhams et al. 1984; Zadorecki and Michell 1989). Many studies have recently been carried out to improve the physico-mechanical and rheological properties of fibre-reinforced polymer composites with the addition of nanofillers into various polymers. Interest in developing lignocellulosic fibre-reinforced composites has also grown enormously.

Cellulose mainly occurs naturally in plants and is also synthesised by algae, tunicates and certain types of bacteria (Henriksson and Berglund 2007; Iwamoto et al. 2007). Cellulose nanocrystals (CNCs) are ideal candidates as nanomaterials for nanotechnology because of their nanofibrillar structure, abundance, biodegradability, renewability and multi-functionality and can replace high-cost, non-biodegradable synthetic fibres, for example, carbon nanotubes (Moon et al. 2011). CNCs can be synthesised from native cellulose source materials by various means, for example acid hydrolysis, enzymatic hydrolysis and mechanical treatment. The term cellulose nanoparticle (CN) is used to broadly define several cellulose particle types that have at least one dimension on the nanoscale, such as nanofibrillated cellulose (NFC), cellulose nanocrystals (CNC) and bacterial nanocellulose (BNC). In this article, we will use the term CNCs for all types of cellulose: nanocrystalline, cellulose whiskers, cellulose nanowhiskers (CNWs) and cellulose microcrystals.

Many studies have been devoted to understanding nanocrystalline cellulose isolated from native cellulose source materials by various means and their applications in polymer nanocomposites (Habibi et al. 2010). Impressive mechanical, reinforcement and other properties make CNCs the ideal materials for processing polymer nanocomposites (Dufresne 2006, 2013). CNCs have been found to be good reinforcement fillers in a wide range of polymeric matrices because of their high specific moduli, stiffness, nanoscale dimensions and high aspect ratio (Šturcová et al. 2005; Ching and Ng 2014). CNCs are hydrophilic, which makes them suitable for combining with hydrophilic polymers. Moreover, various chemical modification methods make it possible to combine cellulose with a range of polymer matrices including hydrophobic organic polymers. Additionally, enormous efforts have been directed towards the chemical modification of cellulose, use of surfactants as stabilising agents for obtaining cellulose dispersions in organic nonpolar matrices and incorporation into new polymeric matrices (Gousseé et al. 2002; Ng et al. 2014). Surface modification also helps to introduce new functionalities and produce “active” CNCs that can produce possible interaction sites with polymer surfaces resulting in good adhesion between the polymer and fibre. Other potential CNC applications include biomedical implants, pharmaceuticals, drug delivery, templates for electronic components, separation membranes, batteries, supercapacitors, flexible displays, barriers, and antimicrobial and transparent films (Moon et al. 2011). CNCs are also used as the rheology modifier in polymers, paint, cosmetics and pharmaceutical products because of the above-mentioned properties (Turbak et al. 1983). Recently, CNCs were reported to be used as an effective rheological modifier in drilling fluids and cement (Li et al. 2015a, b; Cao et al. 2015).

Generally, the addition of nanofillers to a polymer modifies the rheological properties of the resulting composites because they embed themselves between the polymer chains. The CNCs induce polymer chain anchors/cross-links to different CNCs as well as the same CNCs, providing stability to the network structures (Yang et al. 2013a). Study of the rheological properties is very important in the field of polymer nanocomposites. Rheology is a powerful tool for gaining an integrated picture of nanocomposite materials since it may provide information on the influence of nanofillers on the local deformation rate of the polymer, influence of the nanofiller orientation, state of nanomaterial dispersion, degree of polymer-filler interactions and structure-property relationships in polymer nanocomposites (Rubentheren et al. 2015a). Furthermore, rheology also provides critical insights into the processing characteristics of these materials and could help to predict the effect of nanofillers on the final composite materials.
This review summarises the current knowledge and findings on the rheological properties of CNC-embedded polymer nanocomposites. It aims to provide better understanding and knowlege of rheology in the field of cellulose nanocomposites.

Rheological properties of cellulose nanocrystal suspensions

The rheological behaviour of CNC suspensions is significantly influenced by the physico-chemical properties of the particles. The occurrence of phase transitions in the suspensions is controlled by the dimensions and surface properties of rod-like CNCs and the ionic strength of the system (Dong et al. 1996; Dong and Gray 1997; Beck-Candanedo et al. 2005; Shafiei-Sabet et al. 2013). Commonly, cellulose whisker suspensions have been used to study the rheological behaviour of rigid rod-like particles (Azizi Samir et al. 2004; Bercea and Navard 2000). The whiskers can be easily oriented, and the flow properties above a critical concentration are similar to those of liquid crystal polymer solutions. Three well-defined regions are observed for aqueous suspensions of cotton linter. At a low shear rate (<1 s⁻¹), the viscosity is high and decreases monotonically with the shear rate. This shear thinning shows the alignment of whiskers under flow as observed by Ortz et al. (1995) and Ebeling et al. (1999) in aqueous medium. At an intermediate shear rate (1–10 s⁻¹), the viscosity decrease is slighter. It is ascribed to a high level of order of cellulose whiskers because of interparticle interactions. These interactions can result in a high resistance to flow and explain this shear-rate-independent behaviour. At higher shear rates (>10 s⁻¹), this ordered structure breaks down and the whiskers become individualised. This rheological behaviour is typical of liquid crystalline polymers. Urena-Benavides et al. (2011) reported that the rheological properties and phase behaviour of cellulose nanocrystal suspensions are mainly related to the concentration and temperature. Tzoumaki et al. (2010, 2011) reported that with the same rod-like morphology, chitin nanowhiskers exhibit a similar rheological behaviour as cellulose nanocrystals.

Li et al. (2015a) investigated the structure-morphology-rheology relationships for cellulose nanoparticles (CNPs), including cellulose nanocrystals (CNCs). They observed that the viscosity of CNC suspensions gradually increases as the concentration increases because of the growth in the collision possibility of CNCs. However, the viscosity monotonically declines as the shear rate increases over the whole investigated shear rate ranges, exhibiting a typical shear thinning behaviour. The viscosity of CNC suspensions is strongly dependent on the shear rate, CNC concentration and CNC aspect ratio. Two transitions in the rheological behaviour are observed here: a transition from isotropic to liquid crystal and from liquid crystal to gel with increasing CNC concentrations of the suspension in water. An isotropic sample shows a Newtonian plateau at low shear rates, followed by shear thinning at intermediate shear rates as the nanocrystals are aligned parallel to the shear direction. At high shear rates, there is another plateau in the viscosity where all the particles are aligned (Bercea and Navard 2000; Shafiei-Sabet et al. 2012, 2013, 2014). As the formation of the liquid crystal phase suspension above the first critical concentration, the viscosity profile changes to the three-region profile, typical of the liquid crystal of polymer solutions (Onogi and Asada 1980). This viscosity profile comprises three different regions: a shear thinning region (region I) at low shear rates because of alignment of chiral nematic liquid crystal domains, a plateau (region II) at the intermediate shear rates as all the domains have been deformed and aligned along the shear direction, and a second shear thinning (region III) at high shear rates, where the liquid crystal domains are destroyed and freed because of the high shear stress, so that the particles essentially align themselves along the shear flow direction. As the phase reaches above the second critical concentration, it behaves like a gel-like structure. In this region, the viscosity profile shows a single shear thinning region over the whole range of shear rates.

Wu et al. (2014) also reported similar findings in their work on using CNCs prepared from switchgrass and cotton fibres. The viscosity, storage and loss modules increased with increasing CNC concentration. The two critical concentrations depended on the aspect ratio and corresponded to the overlap and gelation concentration. Because of their higher aspect ratio, the switchgrass CNC suspension transitioned into a biphasic state and formed a hydrogel at lower concentrations than those of cotton CNC suspensions. Similar observations on the phase transition of CNC
suspensions were also reported by Urena-Benavides et al. (2011), Beck-Candanedo et al. (2005) and Bercea and Navard (2000).

The surface charge density of CNCs is affected by the degree of sulphation on the CNC surface, which then determines the stabilisation of the suspension. A stable suspension is indicated by the presence of significant negative surface charges on CNC particles. However, the addition of inorganic salt, such as NaCl, reduces the absolute value of the zeta potential of CNC particles because of the adsorption of Na\(^+\) counterions onto negatively charged CNC surfaces. The sulphuric acid-treated cellulose nanocrystals showed some shear thickening and no time-dependent behaviour because of the influence of the surface charge, whereas hydrochloric acid-extracted nanocrystals showed much higher shear thinning behaviour, thixotropy at high concentrations and anti-thixotropy at dilute concentrations (Araki et al. 1998; Boluk et al. 2011).

The effects of NaCl addition on suspension rheology at constant CNC concentrations and varied NaCl concentrations have been studied. For isotropic samples, the viscosity of suspensions decreased as the ionic strength increased. This trend was expected as the presence of the inorganic salt compresses the thickness of electrical double layers and thus decreases the electro-viscous effects on the charged CNC suspension. For anisotropic samples, the viscosity reduces at high shear rates as expected, although it increases in the low shear rate region with the addition of NaCl up to 5 mM. At low shear rates, the trend can be due to the structural changes in the chiral nematic domains. At higher salt concentrations (10 and 15 mM), the viscosity increases significantly and shows a single shear thinning behaviour resulting from the large aggregation of particles due to the reduced repulsive forces. Thus, the suspension becomes unstable. For the gel samples, the viscosity decreases with the addition of NaCl up to 5 mM because of the disturbance of hydrogen bonding interactions among the CNC particles. This results in the formation of a weaker gel structure with lower viscosity. By further addition of NaCl (10 and 15 mM), the viscosity increases because of the aggregation of CNC particles.

The viscosity of the suspension is also significantly decreased by applying critical ultrasound energy (1000 J/g of CNC) because of the breakage of aggregates in the system, which in turn become ready for testing the rheological properties. Although this decreased the viscosity level for intermediate and high shear rates above a critical energy level, it continued to greatly affect the viscosity at low shear rates. It was also deduced that the structure of chiral nematic liquid crystal domains was broken with increases in the applied ultrasound energy, thus reducing the viscosity of CNC suspensions (Shafiei-Sabet 2013).

**Rheological properties of cellulose nanocrystal-reinforced polymer nanocomposites**

Rheology extends the classical disciplines of the viscoelasticity of materials whose mechanical behaviour cannot be defined by classical theories. Rheology is mainly the study of non-Newtonian fluids such as butter, mayonnaise and different kinds of polymers. Newtonian fluids have a single coefficient of viscosity for a specific temperature. Even though the viscosity changes with temperature, it remains unchanged with the strain rate. But non-Newtonian liquids show changes in viscosity with the relative velocity of flow or strain rate. Polymers usually do not behave like normal Newtonian liquids, so the study of rheology is really important for understanding the fluid mechanics of various polymers. The rheological properties of cellulose-based polymer nanocomposites are crucial for arriving at a fundamental understanding of the processibility and structure-property relationship. The nanoscale dimensions and large aspect ratios are often common in cellulosic nanoparticles employed in composites, resulting in some interrelated characteristics (Krishnamoorti 2007).

A general rule is that the viscosity of the polymer-natural organic fibre composites is more than that of the neat polymer and it increases with the fibre concentration (La Mantia et al. 2004, 2005; Li and Wolcott 2004). The viscoelastic behaviour of nanocomposite materials can be evaluated by measuring the viscoelastic components, elastic components or storage modulus, \(G'\), and viscous components or loss modulus, \(G''\), in which the viscoelastic behaviour is strongly dependent on the nanofibre content. In most of the nanocomposite systems, the neat matrix and/or small fibre loading exhibits a typical viscoelastic liquid-like behaviour with a loss modulus higher than the storage modulus (\(G'' > G'\)). On the other hand, the storage modulus is higher than the loss modulus (\(G' > G''\)) in case of higher
fibre loading. Both $G'$ and $G''$ increase with increasing nanofibre content. However, $G'$ increases more rapidly than $G''$ as the storage modulus is particularly strongly dependent on the nanoparticle concentration. Liquid-like behaviour is observed in case of $G' < G''$. On the other hand, the material behaves like a gel when $G'$ becomes larger than $G''$. In brief, the system shows a liquid-like character at the beginning. There is a monotonic increase in both $G'$ and $G''$ with an increase in nanofibre content. As a result, they culminate in a “crossover” called the transition point or percolation threshold, corresponding to the onset of the gel point, and begin to exhibit a solid-like character. The viscoelastic character can also be quantified using the loss tangent value, which is the ratio of the storage and loss moduli ($\tan \delta = G''/G'$). The sample behaves like a viscoelastic liquid when the value is higher than one, while a value smaller than one means that the sample behaves more like a viscoelastic solid. Complex viscosity and melt fluidity are two significant parameters that affect the structural relationship in polymer composites (Verney and Michel 1989). It has been shown that complex viscosities, $\eta^*$, of all nanocomposites increase when nanofibres are added to a polymer matrix (Durmus et al. 2007) and the resulting composites have higher $\eta^*$ than a virgin polymer. Incorporation of fibres into the matrix may increase the fibre-matrix interaction that in turn increases $\eta^*$. It may also increase wall slips because of the presence of longitudinally oriented fibres along the wall melt interface, decreasing the $\eta^*$.

The rheological properties of polymer composites containing fibres have been studied by numerous researchers because of scientific interest as well as industrial applications. A brief summary of CNC-based nanocomposites having different polymer matrices and their reported rheological properties are provided in Table 1.

**Effect of fibre content on the rheological properties of CNC-polymer composites**

Effects on viscosity

Generally, the viscosity of the polymer-nanofibre composites is higher than that of the neat polymer and the viscosity further increases with increasing filler content. Previous studies reported increases in viscosity with cellulose nanocrystal content in polymer composites (Hill 2008; Liu et al. 2011; Marcovich et al. 2006). Liu et al. (2011) investigated the rheological behaviours of CNC colloid and observed that viscosity was enhanced as the concentration of CNCs increased from 0.91 to 2.03 % and to 3.17 %. In addition, Hill (2008) reported that the viscosity of microfibrillar cellulose gels increased with increasing CNC concentrations. A study by Marcovich et al. (2006) also showed that the addition of small amounts of cellulose crystals to the liquid mixtures of polyols was sufficient to increase their viscosity by 6100 and 20 times compared to that of the neat polymer mixture at low frequency and high frequency ranges respectively (Fig. 1).

Effect on viscoelastic properties/components

Several studies reported that the storage modulus, $G'$, and loss modulus, $G''$, increased with increases in shear frequency $\omega$ and fibre content (Hasani et al. 2008; Ten et al. 2012). Hasani et al. (2008) reported that the storage and loss moduli both increased with increasing CNC concentration. At higher suspension concentrations, it behaved elastically. However, at lower concentrations, viscous fluid behaviour appeared in the suspension. The increasing values of the loss tangent value ($\tan \delta$), from 0.39 for the 5.0 % w/w suspension to 2.2 for the 1.9 % w/w suspension over all angular frequencies, indicated that the CNC suspension behaviour shifted from viscous fluid to elastic gel as the concentration increased. Ten et al. (2012) conducted research on the effect of CNCs on the rheological properties of the CNC/poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) composite. They reported that the $G'$ and $G''$ of the composites increased with CNCs. The most rapid change seemed to occur when the CNW content was between 0.5 and 2 wt%. They also observed that 1.2 wt% was the transitional CNW content where $G'$ and $G''$ had similar values. The composites were dominantly elastic when the CNW content was higher than 1.2 wt%. This transition was also demonstrated by the dissipation factor $\tan \delta$. The factor was significantly reduced at 1.2 wt% CNW content, implying that the material became substantially more elastic and dissipated much less energy during shear deformation compared to the samples with lower CNW contents.

A study reported by Aranguren et al. (2013) indicated that a viscoelastic liquid behaviour was observed with the addition of a low concentration of
<table>
<thead>
<tr>
<th>Type of CNC</th>
<th>Matrix</th>
<th>CNC loading (wt%)</th>
<th>Surface modification</th>
<th>Measurement parameters</th>
<th>Reported rheological properties</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNC (pulp fibres)</td>
<td>Polyacrylamide</td>
<td>0–3</td>
<td>γ-Methacryloxypropyltrimethoxysilane</td>
<td>25 °C, viscoelastic region</td>
<td>2 Order of magnitude increase in $G'$</td>
<td>Yang et al. (2013a)</td>
</tr>
<tr>
<td>MCC</td>
<td>Poly(vinyl alcohol)</td>
<td>0–8</td>
<td></td>
<td></td>
<td>2.4-Fold increase in $G'$</td>
<td>Lee and Deng (2012)</td>
</tr>
<tr>
<td>CNC (Cassava bagasse)</td>
<td>Natural rubber latex</td>
<td>0–10</td>
<td></td>
<td>25 °C, glassy state</td>
<td>70-Fold increase in $G'$</td>
<td>Pasquini et al. (2010)</td>
</tr>
<tr>
<td>CNC (beech pulp)</td>
<td>Poly (vinyl acetate) latex</td>
<td>0–3</td>
<td>Carboxymethylated</td>
<td>80 °C, glassy state</td>
<td>867-Fold increase in $G'$</td>
<td>López-Suevos et al. (2010)</td>
</tr>
<tr>
<td>CNC (beech pulp)</td>
<td>Poly (vinyl acetate)</td>
<td>0–30</td>
<td></td>
<td>0 °C, glassy state</td>
<td>1.8-Fold increase in $G'$</td>
<td>López-Suevos et al. (2010)</td>
</tr>
<tr>
<td>MCC</td>
<td>Phenolic resins</td>
<td>7.5</td>
<td></td>
<td>275 °C, glassy state</td>
<td>32 % increase in $G'$</td>
<td>Liu and Labotie (2011)</td>
</tr>
<tr>
<td>CNC (cotton)</td>
<td>Polyurethane</td>
<td>0–20</td>
<td></td>
<td>25 °C, rubbery state</td>
<td>77-Fold increase in $G'$</td>
<td>Mendez et al. (2011)</td>
</tr>
<tr>
<td>Tunicine</td>
<td>Poly(styrene-co-butylacrylate) latex</td>
<td>0–6</td>
<td></td>
<td>52 °C, glassy state</td>
<td>1000-Fold increase shear moulus</td>
<td>Favier et al. (1995)</td>
</tr>
<tr>
<td>MCC</td>
<td>Poly(vinyl acetate)</td>
<td>0–10</td>
<td></td>
<td>100 °C, viscoelastic region</td>
<td>2-Fold increase in $G'$</td>
<td>Gong et al. (2011)</td>
</tr>
<tr>
<td>MCC</td>
<td>Poly(methyl methacrylat)</td>
<td>0–10</td>
<td></td>
<td>85 °C, glassy state</td>
<td>3.3-Fold increase in $G'$</td>
<td>Liu et al. (2010)</td>
</tr>
<tr>
<td>Bacterial cellulose</td>
<td>Cellulose acetate butyrate</td>
<td>0–10</td>
<td>Silyated</td>
<td>124 °C, glassy state</td>
<td>1.9-Fold increase in $G'$</td>
<td>Grunert and Winter (2002)</td>
</tr>
<tr>
<td>MCC</td>
<td>Poly(lactic acid)</td>
<td>0–5</td>
<td>Acetylation</td>
<td>170 °C, glassy state</td>
<td>2-Fold increase in $G'$</td>
<td>Mukherjee et al. (2013)</td>
</tr>
<tr>
<td>CNC (pulp fibre)</td>
<td>Poly(ethylene glycol)</td>
<td>0–1.5 (%v/v)</td>
<td></td>
<td>Room temperature</td>
<td>3-Fold increase in $G'$</td>
<td>Yang et al. (2013b)</td>
</tr>
<tr>
<td>NFC</td>
<td>Poly(methyl methacrylate) (PMMA)</td>
<td>0–15</td>
<td>PMMA grafted</td>
<td>210 °C, viscoelastic region</td>
<td>1000-Fold increase in $\eta^*$</td>
<td>Littunen et al. (2013)</td>
</tr>
<tr>
<td>CNC (cotton seed)</td>
<td>Nitrile rubber</td>
<td>0–20</td>
<td></td>
<td>80 °C, glassy state</td>
<td>2.3-Fold increase in $G'$</td>
<td>Cao et al. (2013)</td>
</tr>
<tr>
<td>Type of CNC</td>
<td>Matrix</td>
<td>CNC loading (wt%)</td>
<td>Surface modification</td>
<td>Measurement parameters</td>
<td>Reported rheological properties</td>
<td>References</td>
</tr>
<tr>
<td>------------</td>
<td>--------</td>
<td>------------------</td>
<td>---------------------</td>
<td>------------------------</td>
<td>-------------------------------</td>
<td>------------</td>
</tr>
<tr>
<td>CNC (tunicine)</td>
<td>Poly(vinyl acetate)</td>
<td>0–10</td>
<td>Propylamine</td>
<td>37 °C, glassy state</td>
<td>20-Fold increase in $G'$</td>
<td>Dagnon et al. (2013)</td>
</tr>
<tr>
<td>CNW (commercial)</td>
<td>Poly(3-hydroxy-co-3-hydroxyvalerate)</td>
<td>0–5</td>
<td></td>
<td>175 °C, viscoelastic region</td>
<td>Significant increase in $\eta^*$</td>
<td>Ten et al. (2013)</td>
</tr>
<tr>
<td>CNW (ramie fibres)</td>
<td>50/50 (w/w) polycaprolactone (PCL) and polylactide (PLA)</td>
<td>0–2</td>
<td>Co-grafted (PCL and PLA)</td>
<td>160 °C, glassy state</td>
<td>$G'$ increases 1–2 order of magnitude compared to ungrafted composite</td>
<td>Goffin et al. (2012)</td>
</tr>
<tr>
<td>CNW (ramie fibres)</td>
<td>Poly(ε-caprolactone) (PCL)</td>
<td>0–8</td>
<td>Co-PCL grafted</td>
<td>20 °C</td>
<td>$G'$ of grafted composite 350 and 230 % higher compared to neat PCL and PCL/CNW composites respectively</td>
<td>Goffin et al. (2011)</td>
</tr>
<tr>
<td>CNC (cotton)</td>
<td>Poly oxyethylene</td>
<td>0–9</td>
<td></td>
<td>Room temperature</td>
<td>Significant change in $G'$ value</td>
<td>Ben Azouz et al. (2011)</td>
</tr>
<tr>
<td>CNW (tunicine)</td>
<td>Unsaturated polyether/polyoxyethylene</td>
<td>0–6</td>
<td></td>
<td>170 °C, rubbery state</td>
<td>Significant change in $G'$ and tan $\delta$ with temperature</td>
<td>Azizi Samir et al. (2004)</td>
</tr>
<tr>
<td>CNC (ramie fibre)</td>
<td>Polyvinyl alcohol</td>
<td>0–15 %</td>
<td></td>
<td>125 °C, rubbery state</td>
<td>Significant decrease of $G'$ value with temperature</td>
<td>Peresin et al. (2010)</td>
</tr>
<tr>
<td>CNC (pulp fibres)</td>
<td>Poly(acrylic acid)</td>
<td>0–0.5 %w/v Silyated with γ-methacryloxypropyltrimethoxysilane</td>
<td></td>
<td>65 °C, viscoelastic region</td>
<td>$G'$ increases with CNC</td>
<td>Yang et al. (2012)</td>
</tr>
<tr>
<td>CNC (commercial MCC)</td>
<td>Polyacrylamide (PAM)</td>
<td></td>
<td></td>
<td>20 °C</td>
<td>Enhanced $G'$ and tan $\delta$ value compared to pure PAM</td>
<td>Zhou et al. (2011a, 2011b)</td>
</tr>
<tr>
<td>CNW (commercial)</td>
<td>Poly(3-hydroxy-co-3-hydroxyvalerate)</td>
<td>0–4.6</td>
<td></td>
<td>60 °C</td>
<td>$G'$ increases 3 order of magnitude compared to neat matrix</td>
<td>Ten et al. (2012)</td>
</tr>
<tr>
<td>CNW (ramie fibres)</td>
<td>Poly(oxyethylene)</td>
<td>0–30</td>
<td></td>
<td>90 °C</td>
<td>Considerably different $G'$ for two different methods of film processing</td>
<td>Alloin et al. (2011)</td>
</tr>
<tr>
<td>Type of CNC</td>
<td>Matrix</td>
<td>CNC loading (wt%)</td>
<td>Surface modification</td>
<td>Measurement parameters</td>
<td>Reported rheological properties</td>
<td>References</td>
</tr>
<tr>
<td>------------</td>
<td>--------</td>
<td>------------------</td>
<td>---------------------</td>
<td>------------------------</td>
<td>--------------------------------</td>
<td>------------</td>
</tr>
<tr>
<td>CNW (commercial MCC)</td>
<td>Poly(lactic acid)</td>
<td>0–5</td>
<td>Beycostat A B09 (CECCA S.A., France)</td>
<td></td>
<td>Minor improvement of $G'$ for presence of surfactant</td>
<td>Bondeson et al. (2006)</td>
</tr>
<tr>
<td>CNC (ramie fibres)</td>
<td>Poly(ε-caprolactone) (PCL)</td>
<td>0–7.5</td>
<td>PCL diol</td>
<td>40 °C</td>
<td>Significant increase in $G'$ for unmodified CNC</td>
<td>Zoppe et al. (2009)</td>
</tr>
<tr>
<td>CNC (commercial MCC)</td>
<td>Polyurethanes (castor oil based)</td>
<td>0–3</td>
<td></td>
<td></td>
<td>$G'$ increases 5 order of magnitude and $\eta^*$ increases 400 times compared to neat matrix</td>
<td>Wik et al. (2011)</td>
</tr>
<tr>
<td>CNC (commercial MCC)</td>
<td>Polyurethanes</td>
<td>0–5</td>
<td></td>
<td>135 °C/glassy state</td>
<td>500 fold increase in $G'$</td>
<td>Aranguren et al. (2013)</td>
</tr>
<tr>
<td>CNF (commercial MCC)</td>
<td>Polyurethane</td>
<td>0–15</td>
<td>Polyaniline</td>
<td>160 °C, viscoelastic region</td>
<td>100-Fold increase in $\eta^*$</td>
<td>Auad et al. (2011)</td>
</tr>
<tr>
<td>CNW (commercial MCC)</td>
<td>Poly(styrene-co-hexylacrylate) copolymer</td>
<td>0–5</td>
<td>$\gamma$-Methacryloxypropyltrimethoxysilane</td>
<td>180 °C</td>
<td>Significant increase in $G'$ and $\eta^*$</td>
<td>Mabrouk et al. (2011)</td>
</tr>
<tr>
<td>CNC (commercial MCC)</td>
<td>Ethylene vinyl acetate</td>
<td>0–10</td>
<td></td>
<td>40 °C</td>
<td>Significant increase in $G'$ and $\eta^*$ at low frequency</td>
<td>Zoppe et al. (2009)</td>
</tr>
<tr>
<td>CNC (commercial MCC)</td>
<td>Polyurethane</td>
<td>0–5</td>
<td></td>
<td></td>
<td>61,000 and 20-fold increase in $\eta^*$ at low and high frequency respectively</td>
<td>Marcovich et al. (2006)</td>
</tr>
<tr>
<td>CNC (softwood)</td>
<td>Ethylene vinyl acetate</td>
<td>0–10</td>
<td></td>
<td>190 °C</td>
<td>$G'$ increases significantly</td>
<td>Mahi and Rodrigue (2012)</td>
</tr>
<tr>
<td>CNC (cottonseed linter pulp)</td>
<td>Waterborne polyurethane (WPU)</td>
<td>0–10</td>
<td></td>
<td></td>
<td>Significant increase in $G'$ compared to neat matrix</td>
<td>Cao et al. (2009)</td>
</tr>
</tbody>
</table>
CNCs to a mixture of polyols and 4,4’-diphenylmethane diisocyanate. However, as expected, the unreacted mixture behaved as a Newtonian liquid with zero storage modulus. Initially, $G''$ shows a higher value than $G'$ at a low fibre loading and frequency range. However, at higher CNC loading, the composite had a higher elastic component than the viscous one ($G' > G''$) and had solid-like behaviour in all frequency ranges (Fig. 2).

Previous studies of these types of composite systems suggested that percolation occurs at around 1 wt% (Marcovich et al. 2006). Above this concentration, the well-dispersed nanocrystals will be in contact with each other and form large percolating structures of H-bonded “rods”. These structures could easily be destroyed by shearing the sample outside the analysed linear viscoelastic range. This enhanced rigidity can be attributed to the increased amount of the crystalline part in the nanocomposites and reinforcing effect from the CNCs (Cao et al. 2009).

In another study on ethylene vinyl acetate (EVAc) and CNC composites, it was observed that the moduli $G'$ and $G''$ showed non-terminal behaviour at low frequencies, while in viscosity the appearance of yield stress was observed at higher CNC content (Mahi and Rodrigue 2012). Considering the nano-scale of the filler, the effect of the particles themselves is not significant at high frequency, which is the range associated with shorter dynamics. At low frequencies, EVAc chains can relax and the polymer exhibits a typical terminal behaviour for both $G'$ and $G''$. With increasing CNC content, the terminal behaviour disappears and the dependence of $G'$ and $G''$ on frequency is also weakened. These findings indicate a pseudo solid-like rheological behaviour related to the formation of the nano-particle network as a result of hydrogen bonds between the cellulose particles.

Dagnon et al. (2013) reported the effect of rheological properties on the reinforcement of the carboxilated CNC and polyvinyl acetate (PVAc) nanocomposites. The rheological study of the dry nanocomposite PVAc films indicated that the incorporation of CNC nanofillers resulted in the reinforcement of the PVAc matrix, which was not significantly affected by the charge density on the CNCs.

Zoppe et al. (2009) reported that the storage modulus increased significantly with fibre loading in CNC-filled poly(e-caprolactone) (PCL) compared to neat PCL. Another study reported by Wik et al. (2011) showed a significant increase in $G'$ with incorporation of CNCs in castor oil-based polyol (COPO) composites. Typical solid-like viscoelastic behaviour was observed even at the lowest concentration (0.5 wt%) in all analysed frequency ranges. However, the neat polyol behaved like a viscoelastic liquid and consequently there was no equilibrium modulus at low frequencies.
frequencies. This report was consistent with the finding of Marcovich et al. (2006) investigation where 1 wt% cellulose nanocrystal addition to a commercial polyol resulted in a suspension that could achieve an equilibrium modulus at low frequencies. The rheological behaviour of these two composites explained that the concentration of the cellulose crystals was above the critical percolation threshold, so that even at low CNC concentrations, more elastic behaviour was observed. However, it is evident from the result obtained by Mukherjee et al. (2013) that 1.5–2.5 wt% of microrystalline cellulose nanocrystal loading enhanced the storage modulus of polylactic acid (PLA)-CNC composites compared to raw PLA. Thus the percolation threshold for uniform dispersion of CNCs in the PLA matrix was 2.5 wt%. They also suggested that at lower frequency, the composites behaved more like a solid, whereas at a higher frequency, the composites behaved more like a liquid. This was probably due to the fact that cellulose was highly deformable at a higher frequency, which led to a reduction in the storage modulus. On the other hand, low deformation of cellulose led to an increase in the storage modulus at lower frequency. A similar trend was observed in CNC/PEG (polyethylene glycol) nanocomposite hydrogels where the $G'$ increased with an increase in CNC loading up to a certain level. After that level, $G'$ exhibited a pronounced declining trend considered to result from the structural inhomogeneity at high CNC loadings (Yang et al. 2013b).

Generally in CNC-polymer sol-to-gel transitions both $G'$ and $G''$ were frequency dependent and increased during the gelation process. The phenomenon indicated that the systems became more elastic compared to initial aqueous state (Yang et al. 2012). A study on CNC-PAM (polyacrylamide) nanocomposite hydrogels showed that the elastic modulus of hydrogels was highly dependent on the CNC content and an increase in CNC content increased the hydrogels’ elastic modulus, indicating that CNCs mainly determined the rubbery elasticity of the systems. This pronounced increase in $G'$ with CNC content indicated that strong interactions between the matrix and CNCs existed where the polymer chains were anchored on the surface of CNCs, their free motion was restricted and hydrogels exhibited an efficient energy dissipation process (Yang et al. 2013a). In fact, this phenomenon is the result of the orientation of the CNCs and relaxation of the grafted chains between different CNC-polymer clusters during the deformation process, where the reversible movement of polymer chains and cluster conformational rearrangements may be responsible for the rubbery elasticity and high toughness of the nanocomposite hydrogels. It has also been reported that the viscosity and $G'$ of CNC colloids and suspensions elevated with an increase in shear rate $\omega$ and CNC concentration (Liu et al. 2011; Marcovich et al. 2006; Urena-Benavides et al. 2011).

Effect on the glass transition temperature

The characteristic of one $T_g$ in the nanocomposite samples shows the good interaction of cellulose fibres and polyvinyl alcohol (PVA) in the amorphous phase. The $T_g$ of the PVA depends on some of its characteristics (hydrolysis degree, polymerisation degree and others) and especially on the moisture content, a wide temperature range (58–85 °C) being reported for this property (Wiria et al. 2008). The $T_g$ decreases as the humidity content increases because of the plasticising effect of water molecules in the aqueous PVA composite (Roohani et al. 2008). Previous study showed that the observed $T_g$ value for all the PVA/5 wt% cellulose nanofibre composites showed no significant changes owing to the nanometre-sized fibres, which did not cause massive breaks of hydrogen bonds in PVA (Ching et al. 2015). The expected interactions between these nanocellulose fibres and PVA will not affect the supramolecular structure of the amorphous phase. The macromolecules’ rubbery properties and increase in mobility happened at around the same temperature. Nevertheless, it seemed that these newly formed interactions were not strong enough to slow the chain mobility associated with the glass transition since the $T_g$ values measured on PVA/nanocellulose fibre composite samples were close to those of neat PVA. A study also indicated the $T_g$ value decreased with the addition of larger size nanocellulose fibres (tens of microns in diameter and hundreds of microns in length) into the composite because of the broken hydrogen bonds in PVA. This characteristic is caused by the reduction of the cohesive energy density in the amorphous phase of the composite compared to the neat PVA. In addition, a recent study reported that the addition of cellulose had no effect on the glass transition temperature ($T_g$) of polylactide/cellulose (PLA/CELL) composites.
(Šumigin et al. 2012). The thermogram analysis showed a small endothermic peak at around 60 °C, typically indicating the stress relaxation on heating. The material moved into glassy behaviour after fast cooling to the temperature below $T_g$ and tended to reduce its excess enthalpy to reach the equilibrium glassy state.

The thermal glass transition temperatures of the polyethylene oxide (PEO)/CNC and poly(methyl methacrylate) (PMMA)/CNC fibres increased slightly with increased CNC content (Zhou et al. 2011a, b; Dong et al. 2012). The effects of the addition of CNCs to the $T_g$ of the matrix polymer PEO or PMMA were explained by the interactions between CNCs and the polymer limiting the molecular chain movement. On the contrary, the $T_g$ of polystyrene fibres with added CNCs (and surfactant) tended to decrease with CNC loading, caused by the plasticising effect of the surfactant (Rojas et al. 2009).

The reinforcing effects of CNCs on the storage modulus at temperatures either above or below $T_g$ were demonstrated by several nanocomposite fibres. The storage modulus of poly(ε-caprolactone) (PCL) fibres with several CNC loadings is shown in Fig. 3, and the reinforcement effect was related to both the loading of CNCs and fibre diameter (Zoppe et al. 2009). A significant increase in the storage modulus was observed in PCL fibres filled with unmodified CNCs (2.5 and 7.5 %) in comparison to the neat PCL. The reinforcement of 2.5 % CNCs was attributed to both the filler loading and smaller fibre diameters rather than PCL fibres resulting in a higher interfibre bonding area.

The increased storage modulus at 7.5 % CNC loading was brought about by the reinforcing contribution of CNCs within the fibre, despite the diameter of the nanocomposite fibre being larger than that of the neat PCL fibres. In another study, uniaxially oriented arrays of PEO/CNC fibres were prepared with CNC contents of 5, 10 and 15 %, respectively (Changsarn et al. 2011). All the fibres had similar diameters in the range of 400–500 nm. The reinforcement of CNCs on PEO fibres was apparent, and the storage moduli of the PEO/CNC nanofibre arrays along the fibre axis were 1.5–2 times greater than the neat PEO fibre array. It is worth noting that the effect of interfibre bonding on mechanical properties was largely eliminated because of disconnection among fibres in the transverse direction.

![Fig. 3 Storage modulus curves for the nanofibre webs of neat PCL (open square) and PCL loaded with 2.5 % (open circle), 5 % (open triangle) and 7.5 % (open inverted triangle) unmodified CNCs](image)

Effect on tangent delta (tan $\delta$)

As stated earlier, the viscoelastic character can also be quantified using the loss tangent value. The loss factor value is the ratio of dissipated energy to stored energy ($\tan \delta = G''/G'$). The system behaves like a viscous liquid at $\tan \delta > 1$ and acts as an elastic solid at $\tan \delta < 1$.

In a recent study, the CNC-PAM nanocomposite hydrogel showed a gel-like behaviour even at low CNC contents (0.2 wt%); the $\tan \delta$ decreased with an increase in CNC content and approached 0.01 at high CNC contents (>3 wt%; Yang et al. 2013b). The frequency sweep results of a sample containing carboxylated cellulose nanocrystal and PVAc nanocomposite showed a frequency dependence of $\tan \delta$. The sample with 10 wt% CNCs showed a decrease in $\tan \delta$ followed by an increase with an increase in frequency, with the $\tan \delta (<1)$ behaviour indicating a dense elastic network and even more solid-like behaviour (Dagnon et al. 2013). Urena-
Benavides et al. (2011) reported that the 10.4 vol% aqueous CNC suspensions behaved predominantly as viscous fluids (tan δ > 1), whereas in the 12.1 and 12.6 vol% samples, an elastic behaviour was dominant (tan δ < 1).

Effect on complex viscosity

Complex viscosity (η*) is one of the main parameters affected by the structure of polymer composites (Verney and Michel 1989). It was evident that the complex viscosity of all composites increases with increasing filler content in all frequency ranges and all composite samples have a higher η* than a virgin polymer (Durmus et al. 2007; Ten et al. 2013). At the low frequency region, the neat polymer had a Newtonian plateau with a constant viscosity regardless of the frequency. CNC addition at a low concentration produced a non-Newtonian response. Moreover, all composites containing CNCs displayed a significant shear-thinning behaviour with increasing frequency, indicating that the viscosity is a function of the frequency (Auad et al. 2011). Clearly, the viscosity curves of higher concentration composites do not show a Newtonian plateau at low frequencies. The increase in the complex viscosity within the terminal zone and non-Newtonian behaviour clearly indicated the alteration of polymer chain dynamics with the introduction of CNCs. In addition, the fibre-matrix and fibre-fiber interactions can influence the formation of the physical network structure and at the same time progressive destruction of the structure with increasing shear rate. This in turn leads to the shear thinning behaviour in the terminal zone (Ten et al. 2013).

It has been reported that the complex viscosity of polylactic acid (PLA)-CNC composites was higher than that of pure PLA for fibre loading up to 2.5 wt%, indicating better dispersion at this concentration. However, the η* value was reduced with a further increase in loading, reaching the minimal value at 5 wt% (Mukherjee et al. 2012). The decrease in complex viscosity at higher loading could be caused by the decrease of polymer molecular entanglement density as a function of filler aggregates. The formation of aggregates could result in disruption in the polymer chain entanglement network (Hatzikiriakos et al. 2005). In another study, addition of CNCs appeared to increase the complex viscosity of PMMA/CNC nanocomposites at every concentration. However, most significant changes occurred between 1 and 5 wt% loading; otherwise the changes were moderate (Littunen et al. 2013). In a further study of poly (oxyethylene) (PEO) and cellulose whisker composites, the composite showed higher complex viscosity than their respective matrices. This phenomenon confirms that the mechanical strength is induced by the whiskers via interations of whiskers/PEO and whiskers/whiskers (Alloin et al. 2011). A similar behaviour of the saturation effect at higher fibre content was reported by Alvarez et al. (2004). Strong interactions existed between PEO chains and cellulose. This effect was attributed to the large cellulosic surface inherent to any nanoparticle. Wik et al. (2011) reported that the addition of 0.5 wt% CNCs in natural polyl matrix increased the complex viscosity by 400 times compared to unfilled polyl mainly in the low-frequency zone (Fig. 4). The authors suggested that the dispersions showed power law behaviour at low frequencies and consequently there was no low-frequency plateau. However, the neat matrix had constant viscosity in the whole range of investigated frequencies (Wik et al. 2011).

Other factors influencing the rheological behaviour of CNC-based nanocomposites

In addition to the fibre concentration and shear frequencies, the rheological behaviour of CNC-based nanocomposites depends on other factors such as the fibre shape and size, surface area, aspect ratio, flexibility, surface chemistry of the fibre, rheological

![](Fig_4_Complex_viscosity_versus_frequency_curves_of_the_nanocrystal-polyliquid_susensions.png)
properties of the matrix materials and temperature of the system. Studies associated with the influence of fibre morphology, surface chemistry and temperature on the rheological behaviour of various CNC-based composites are described below.

Effect of fibre shape and size

The fibre dimensions (i.e. the shape and size or aspect ratio) of CNCs influence the rheology of the resulting composites. It is well known that the fibre dimensions are the main factor governing the homogeneity of the reinforcement particle distribution in the composites. Smaller fibre diameters yielded higher overall relative bonded areas between fibres because of the increased surface area, better distribution of fibres and increased bonding density (Zoppe et al. 2009). Improved mechanical and rheological behaviours of the nanocomposites are related to the reinforcing contribution of CNCs with optimum fibre shape and size as well as the aspect ratio of the fillers. Zhou et al. reported that the $G'$ and $\tan \delta$ of the PAM-CNC composite can vary with different CNC aspect ratios. However, the $G'$ decreased and plateau $\tan \delta$ increased with decreases in the CNC dimensions. This character can be interpreted by the fact that the shortened rigid-rod cellulose nanocrystals reduced the effective network junction, also acting as multifunctional crosslinkers through physical adsorption and chemical bonding with the PAM network (Zhou et al. 2011a, b).

Effect of CNC surface modification

Surface properties of the polymer and filler have a significant impact on the rheological as well as mechanical properties of the final composites because of the formation of a filler network through interaction of the polymer-filler and filler-filler. Several researchers reported that modification of CNC surface properties by using various methods altered the rheological properties of the final materials.

CNCs are known to be hydrophilic in nature, so incompatibilities arise when CNCs are dispersed in nonpolar hydrophobic polymeric media (Rubenthaler et al. 2015b). A widely used CNC surface modification method is covalent adsorption of small molecules as well as polymers to decrease the polar character of the nanocrystals and have better dispersibility with hydrophobic polymers. A recent study reported that PMMA and PMMA-grafted CNC composites were more elastic, enabling improved contact between the fibrils and suspended PMMA compared to the ungrafted samples. The same amount of grafted CNCs also decreased the value of complex viscosity and $\tan \delta$ slightly compared to the unmodified composites (Litunen et al. 2013). The complex viscosity $\eta^*$ of the polyurethane (PU) and polyaniline-grafted cellulose nanofibril (PANI-CNC) composite increased with the PANI-CNC concentration; even a low concentration of PANI-CNC produced a non-Newtonian response (Auad et al. 2011). The modulus value increase was higher than that previously observed from the unmodified CNC-PU composite (Marcovich et al. 2006). This difference might be due to the gluing action of the PANI as it grew on the surface of the nanofibrils. PANI could link the nanofibrils and consequently behave as thicker fibres of lower aspect ratio compared to the unmodified counterparts (Auad et al. 2011). Another experiment conducted at low-frequency reported an increase in $G'$ values by one to two orders of magnitude with the addition of CNCs into either polycaprolactone (PCL) or polylactide (PLA) or P(CL-LA) diblock in binary blends of PCL and PLA copolymer with respect to the PCL/PLA blend loaded with unmodified CNCs (Goffin et al. 2012). The ‘solid-like’ behaviour of this composite might be due to the strong interactions and adhesion between grafted polyester chains and the components of the blend. In a previous study by the same authors, PCL-grafted CNC-based PCL/CNC nanocomposites displayed a greatly improved elastic response compared to the pristine PCL matrix and ungrafted PCL/CNC melt blends (Goffin et al. 2011). Solid-like behaviour and network-like structure were also observed in the PCL/8 wt% CNC-g-PCL system. Both of these studies observed that the elastic modulus effect was even more significant at higher grafted CNC content (Goffin et al. 2011, 2012). The formation of a polymer physical network was based on the entanglement of the surface-grafted polymer chains with the free PCL matrix chains. The formation of this network structure increased the resistance of material against the applied deformation over the low frequency range (Goffin et al. 2011).

Surface modification of CNCs by other chemical methods, for example, acetylation, is another important approach described in extensive studies. CNCs are hydrophilic, containing polar –OH groups that can facilitate intra- and promote intermolecular hydrogen
bonding between the cellulose chains. Thus CNCs and the hydrophobic polymer are not compatible and have a tendency to repel each other; therefore, CNCs tend to agglomerate among themselves (Goh et al. 2015). The formation of hydrophobic surfaces restricts the agglomeration and thus results in better dispersion of CNCs in the polymer matrix. It was observed that the elastic property \( G' \) of the PLA composite with surface-modified CNCs by acetylation increased compared to unmodified CNC-PLA composites and neat PLA (Mukherjee et al. 2013). However, an exponential drop in the \( G' \) value was observed at higher CNC loading (Mukherjee et al. 2012). The acetylated CNCs (Ac-CNCs) were more compatible with the PLA matrix and could be attached in the polymer chain constraints because of a weak van der Wals force. In a nanocomposite containing carboxilated cellulose nanocrystals and PVAc, the \( G' \) and \( \tan \delta \) values were considerably different from those of the neat CNC/PVAc nanocomposite. However, the nanocomposites having different nanofiller charge densities showed no significant difference in the \( G' \) and \( \tan \delta \) values (Dagnon et al. 2013).

Kargarzadeh et al. (2015) reported their work on cellulose nanocrystals (CNCs) isolated from kenaf bast fibre-reinforced unsaturated polyester resin (UPR) composites toughened with liquid natural rubber (LNR). The CNC surface was modified with silane, and the effects of this treatment on the viscoelastic properties were studied. The storage modulus of the reinforced composites increases with the filler (untreated CNC and silane-treated CNC) content of the samples. This phenomenon highlights the reinforcing effect of the CNCs in both the glassy and rubbery regions of the LNR-UPR matrix. Above the \( T_g \) of the matrix, the rubber particles become extremely soft, and the presence of rigid CNCs—which become harder at higher temperatures as moisture evaporates—restricts the motion of the polymer chains in the matrix. In this context, moreover, the formation of a rigid network of CNCs interconnected by hydrogen bonds is noteworthy. The surface-treated CNCs interact more weakly with one another, forming weaker networks; they adhere more strongly to the matrix, thereby hindering the segmental motions of the polymer chains and pushing the \( T_g \) to higher temperatures. The increase is less substantial than with untreated CNCs because the surface-treated CNCs are less crystalline and rigid. The addition of surface-treated CNCs to the matrix also leads to a more intense \( \tan \delta \) peak. This may be because the network surrounding the rubber particles is less rigid, allowing higher molecular mobility and increasing the intensity of the \( \tan \delta \) peak.

Modifications of surface properties of CNCs by physical methods have also been studied. Cao et al. (2013) investigated the effect of surface modification of CNCs by a mechanical method via vulcanisation on the rheological properties of CNC-nitrile rubber (NBR) composites. NBR latex was mixed with a CNC suspension at a specific ratio by strong mechanical stirring at room temperature before being compressed and vulcanised at 160 °C. In this case, cross-link density can be the result of the combination of chemical cross-links and physical adsorption such as chain entanglements. However, the physical adsorptions between the hydroxyl groups (–OH) on the surface of CNCs and nitrile groups (–CN) were more dominant in the presence of CNCs compared to the chemical cross-linking. This interaction acted as physical cross-linking points, and thus the cross-link density increased. They reported that the storage modulus, \( G' \) of the composites gradually increased with increasing CNC content for both unmodified and modified CNC-NBR composites. However, the treated composite had a higher \( G' \) value, mainly due to the cross-linked network restricting the mobility of rubber the chains (Cao et al. 2013). The increasing \( G' \) trend indicated that more rigid filler-filler structures were developed with increasing CNC loading. Besides, the interaction between the CNC and NBR molecules was enhanced by the addition of physical cross-linked points, which yielded higher \( G' \) values (Datta et al. 2010).

Effect of temperature

In general, the storage modulus of all composite materials decreased with increasing temperature. A recent study by Cao et al. (2009) reported that for all the waterborne polyurethane (WPU)/CNC nanocomposite films, the storage modulus curves displayed the typical semicrystalline polymer behaviour with three distinctive zones compared to the neat WPU, which is an amorphous polymer in nature. The modulus decreased slightly with temperature at lower temperature ranges; however, dynamic mechanical analysis measurements may not be possible at a higher
temperature range. At a particular temperature, a transition appeared where the storage modulus dropped because of the main relaxation process (Cao et al. 2009; Peresin et al. 2010; Zoppe et al. 2009).

A brief summary of the DMA results reported by Cao et al. (2009) for the storage modulus is described below and illustrated in Fig. 5. They analysed the storage and loss modulus of waterborne polyurethane (WPU)/CNC nanocomposite films at different CNC concentrations against temperature. At a very low temperature below $-40^\circ\text{C}$, the glassy state and molecular motions in the glassy state of neat WPU was restricted to a short range rotation and vibration. However, the storage modulus of the composite was only slightly decreased with increasing temperature. When the temperature was higher than $-35^\circ\text{C}$, a rapid decrease in the storage modulus was found due to the glass-rubber transition of WPU (Cao et al. 2009). This decrease in storage modulus was attributed to the irreversible polymeric chain flow that resulted from the elastomeric behaviour of the WPU. In contrast to the neat WPU, the storage modulus curves of WPU/CNC nanocomposite films normally displayed typical partially crystalline polymer behaviour with three distinctive zones compared to neat WPU. The modulus decreased slightly at the glassy state ($<-40^\circ\text{C}$). A sharp drop in the storage modulus reportedly occurred at approximately $-35^\circ\text{C}$ because of the main relaxation process. The amorphous, rubbery and crystalline domains coexisted at a temperature range between $-35$ and $50^\circ\text{C}$. The melting of the crystalline part of the matrix and progressive flow of amorphous WPU chains resulted in a decrease of the storage modulus. At temperatures above $50^\circ\text{C}$, the modulus decreased significantly. At this state, deformations were unrecoverable because the crystalline zones of the WPU matrix were completely melted. This significant difference proved that the crystalline structure was present within the WPU/CNC nanocomposite (Cao et al. 2009).

The main chemicals used in the formulation of WPU are polycaprolactone (PCL) diol and isophorone diisocyanate (IPDI). Subsequently, PCL-based-WPU/CNC nanocomposites were prepared via a one-pot synthesis reaction between the exposed hydroxyl (–OH) groups on the CNC surfaces and isocyanate group on the terminal ends of the WPU pre-polymer, followed by the casting-evaporation technique (Cao et al. 2009). The wide-angle X-ray diffraction (WAXD) analysis indicated the amorphous nature of the neat WPU as there was only a broad diffraction hump at $2\theta = 19^\circ$. Thus, it can be confirmed that polyurethane prepared with PCL, having soft segments with a molecular weight lower than 2000, shows no crystallinity. After the addition of CNCs into the WPU matrix, new diffraction peaks appeared. By comparison with the WPU and CNC patterns, two new peaks ($2\theta = 20.8^\circ$ and $2\theta = 22.8^\circ$) could be assigned to the crystalline phase of PCL soft segments in the WPU matrix because PCL is a type of partially crystalline thermoplastic polymer with three of its characteristic peaks (Cao et al. 2009). Besides, Cao et al. (2009) concluded the importance of the crystallinity regions in WPU/CNC nanocomposites prepared by transforming the nanocomposites from having an elastomer-like behaviour to a thermoplastic-like behaviour.

**Fig. 5** DMA results of the WPU/CNC nanocomposite films with different CN loading: (a) WPU, (b) WPU/CNC-2, (c) WPU/CNC-4, (d) WPU/CNC-6, (e) WPU/CNC-8 and (f) WPU/CNC-10 (Cao et al. 2009)

**Perspectives and challenges for the CNC industries**

CNCs can play an important role as new green materials with applications such as films, hydro-/aerogel structures, composite applications and formulations. The numerous value-added properties possessed by these materials can easily initiate a brand new area of research and development that ultimately develops into a commercialisation adventure. However, there are numerous obstacles before these materials can be unanimously accepted within industries, as was the case for other types of new...
There are limitations of CNCs that may pose some challenges before they can be commercialised. CNCs’ compatibility with hydrophobic matrices is relatively poor. It also has a highly complex extraction process and rather challenging dispersibility in hydrophobic media. In addition, the high production cost versus the current technology or products may be a major obstacle to its commercialisation (Chauve and Bras 2014).

Although CNCs have great potential for expanded use of the new composite materials, they still face some challenges, one of the major ones being to decrease the internal damage in CNCs as a result of the extraction process. The extraction of CNCs from a given source material has the inadvertent effect of altering the percent crystallinity and particle morphology, possibly introducing new defects within the CNCs. The challenge posed here is to minimise these defects in order to improve CNCs’ tensile, elastic and thermal properties. Application of pretreatments, such 2,2,6,6-tetramethyl-piperidinyl-1-oxyl radical (TEMPO), to facilitate the fibrillation of biomass fibres has led to lower amounts of mechanically induced damage to the CNCs. In order to capitalise on the remarkable intrinsic mechanical stiffness of CNCs, it is mandatory that the CNCs (1) are well dispersed within the dispersing medium and (2) present a chemical affinity with the matrix which, in most cases, requires modifying its surface chemistry. This chemical compatibilisation is a mandatory step to broaden the application field by making the CNCs available for every targeted use. Besides, CNCs may face the competition of other fillers such as nanoclays, CNTs, glass, etc.

Another important challenge is to develop an extraction process with tighter controls on particle size distributions (length, width, aspect ratio). This measure will provide more control in liquid suspensions, surface functionalisation and CNC-polymer blends and consequently in the design and processing of nanocomposites. Scaling up of CNC processing from laboratory size quantities to pilot plant quantities is a needed first step toward industrial-scale CN-composite processing. The availability of larger CNC quantities allows applied research to process larger sized CNC-composite samples (tens to hundreds of centimetres in dimensions), which are more realistic in terms of potential products compared to the much smaller laboratory scales (typically about 1 cm in size). Pilot plant facilities have been made or are in the design stage for CNC processing, e.g., FP Innovations Domtar, Bio Vision Technology, Inc. and the USDA Forest Service Forest Products Laboratory (Moon et al. 2011).

In addition, measuring the CNC nanomechanical properties remains a major scientific challenge nowadays. The characterisation of CNCs is lacking, in particular the percent crystallinity, location of amorphous regions (i.e. on the CN surface or throughout the core), Ia/Ib ratio, location of the Ia and Ib regions within the CNCs (i.e. at the surface or core) and identification of defects and the CNC surface chemistry. The development of standardised measurement methods and reporting for CN properties is needed. A SPM nanoindentation technique has been used to measure the transverse elastic modulus of an individual tunicate CNC at multiple locations. Quantitative mechanical property measurements are problematic for such small particles as measurement uncertainty is amplified because displacement measurements are near the SPM sensitivity limits and assumptions used in contact models for property extraction are extensive. Great care must be taken when reporting mechanical properties from such measurements as more work is needed to prevent the propagation of uncertainty (Postek et al. 2010). In addition, legislative, regulatory and policy aspects in relation to environmental and governmental agencies must also be taken into consideration before the commercialisation of products containing CNCs.

As for the long-term development of the nanocellulose world, the volume foreseen is rated exponentially. Currently, the world production capacity for CNC products is difficult to evaluate. However, the prediction from the beginning of 2012 indicated production close to 80 tons/year, which is way below the actual capacity for CNC production considering the CelluForce demonstration mill produced 1 ton/day. Additionally, this estimation surely underevaluates the non-officially advertised pilot units. The evolution of the world nanocellulose production capacity is anticipated to reach 800 tons by 2017 (Future Markets 2012).

**Conclusions**

In recent years, cellulose nanoparticles have been extensively used in a wide variety of applications because of their nanosized dimensions and other important properties. An increasing number of studies in the area of cellulose nanocomposites have also been...
reported during the last few years because of the enormous interest in their industrial applications. This review summarises the current studies and their findings on the rheological properties of polymer composites embedded with cellulose nanofibres extracted from different sources by various means. Various studies have shown that the viscoelastic properties of nanocomposites depend strongly on the CNC content. Even at low CNC loading, the storage modulus significantly increased compared to the neat polymer matrix. According to the literature, the viscoelastic components are independent of the shear frequency in most cases. However, the frequency dependency of \( G' \) and \( G'' \) was also observed in some reports, where a significant increase at low frequencies and non-significant increase at high frequencies were observed. In fact, the complex viscosity of all CNC-polymer nanocomposites increased with increasing CNC content compared to the virgin polymer. Moreover, the elastic component of these composites decreased with an increase in system temperature. In all cases, surface modification improves the viscoelastic behaviour of nanocomposites filled with modified compared to unmodified CNCs.

Acknowledgments  
The authors would like to acknowledge the financial support from High Impact Research MoE grant UM.C/625/1/HIR/MoE/52 from the Ministry of Education Malaysia, FP030-2013A, RU022A-2014, RP011A-13AET, RG031-15AET and FP053-2015A, which contributed to the success of this project.

References


Mukherjee T, Sani M, Kao N, Gupta RK, Quazi N, Bhattacharya S (2013) Improved dispersion of cellulose microcrystals in polylactic acid (PLA) based biopolymer. In: 36th annual condensed matter and materials meeting, February, Wagga, Australia, pp F003:01-04


