In Situ Cure of Cellulose Whiskers Reinforced Thermosetting Phenolic Resins: Impact on Resin Morphology, Cure and Performance

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Abstract

In the past decade, much research has been devoted to reinforcing polymers with nanoscale cellulose whiskers (CNW) mainly with thermoplastic polymers. Polycondensation resins such as phenolics are high-modulus thermosets that are widely used in wood-based composites. Due to their reactivity towards cellulose, resoles are ideal candidates for in situ cure together with CNWs, potentially leading to superior nanocomposite adhesives thanks to strong interfiller and interfacial adhesion. In this study, we report the preparation of well-dispersed thermosetting nanocomposites with CNWs. As expected, CNWs reinforce high modulus phenolic resins. Besides, CNW addition to phenolic prepolymer prior to cure is found to significantly alter cure properties and thermal stability of the phenolic resin. Overall, CNWs are found to be valuable nanoscale fillers for the development of high performance thermosetting adhesives for composite applications.

Keywords: Cellulose Whiskers, In situ Cure, Nanocomposite, Phenolic Adhesive, Thermosetting
Introduction

Much work has recently been devoted to the reinforcement of thermoplastic polymers with nanoscale cellulose such as cellulose whiskers (CNWs) (Azizi-Samir, 2005). A few studies have also reported the reinforcement potential of cellulose nanoparticles on thermosetting adhesives. For example, tunicate cellulose whiskers were reported to reinforce flexible, low T_g epoxy resins (Matos Ruiz et al., 2000, 2001). In relatively higher T_g epoxies (ca. 160°C) a reinforcing effect was also reported with CNWs especially above the resin glass transition temperature (Tang and Weder, 2010). Besides when used in large amount (>15wt%) microfibrillated cellulose (MFC) has been shown to enhance the performance of phenolic resins (Nakagaito and Yano, 2008). In this study we report on the preparation of cellulosic nanocomposites based on CNWs and resole prepolymer. The challenges and questions that are particularly addressed in this work are: i) a method of preparation to produce well dispersed nanocomposites, ii) the impact of CNWs on the cure properties of phenolic resins and iii) the impact of CNWs on the performance of the cured adhesive.

Experimental

Materials

A liquid phenol-formaldehyde (PF) resole (grade Durite SC-830A; abbreviated as “PF”) was kindly provided by Hexion Specialty Chemical Co. It had a solid content of 69%, a Brookfield viscosity of 275cPs at 25°C and a pH of around 7.9-8.3. Cellulose nanowhiskers were prepared by acid hydrolysis of microcrystalline cellulose following the method reported by Bondeson and Oksman (2005). In order to produce homogeneous and stable dispersions of CNWs in the phenolic liquid prepolymer, the CNWs suspension was first condensed and then mixed in controlled amount with the liquid phenolic resin after which the mixture was solvent-exchanged to dimethyl formamide. A stable and transparent dispersion of CNWs and resole was thus obtained. Films with 1.2~1.5 mm in thickness, were prepared by pre-curing the above mixture in DMF at 80°C for 38 hours in an oven, then curing at 140°C for 2 hours under vacuum, and finally post-curing at 185°C for 1 hour under vacuum.

Characterization methods

The morphology of the cured CNW/phenolic materials was evaluated with scanning electron microscopy (FE-SEM, FEI Quanta 200F) at an accelerating voltage of 15kV. To evaluate the cure properties of the CNW loaded phenolic resin, differential scanning calorimetry (DSC2620 apparatus from TA Instruments) was performed on fresh CNW/resole mixtures using four heating rates, i.e. 2.0, 5.0, 10.0, and 20.0°C/min. Finally dynamic mechanical analysis (DMA Q800 from TA Instruments) was performed in a single-cantilever mode on the fully cured samples from 35°C to 300°C at a heating rate of 2°C/min and 1Hz.
Results and Discussions

Both the pure phenolic resin and the CNW reinforced cured resin appeared transparent suggesting that no micrometer scale or larger scale agglomeration of the cellulose nanoparticles occurred in the samples. Examination with SEM also did not evidence any micrometer scale agglomerates of the CNWs (Figure 1).

Figure 1. SEM micrograph (×50,000) of pure PF (a) and PF-based nanocomposite comprising 5 wt% CNW (b) post-cured at 185°C for 1hour under vacuum.

Unfortunately a finer observation of the CNW reinforced phenolic resin was not successful despite our attempts to image the nanocomposites with atomic force microscopy and transmission electron microscopy. Overall these observations suggested that well-dispersed CNW/phenolic nanocomposites had likely been produced during the cure of the prepolymer mixture. The curing behavior was further examined in order to understand the impact of the CNWs on the cure properties of the thermosetting resin. DSC thermograms for the pure resole and for the resole modified with CNWs do not exhibit striking differences (Figure 2).
In particular the peak temperature appears unchanged upon addition of CNWs. However upon closer evaluation, we note that in presence of CNWs, the total heat of reaction underlying the cure exotherm increases significantly. For example the heat of cure measured at 5°C/min increased from 380 J/g for the pure resin up to 536 J/g for the resin modified with 5wt% CNWs. This increase in heat of reaction or degree of conversion suggests that additional reactions might take place during the cure of the resole in contact with cellulose whiskers. Perhaps, interactions between cellulose and the phenolic prepolymer occur.

The impact of the CNWs on selected mechanical properties was examined in flexural mode using DMA (figure 3). The reinforcing effect of CNWs on the phenolic resin is clearly seen over the entire temperature range (Figure 3a). We note however that the magnitude of the modulus increase above Tg is small (ca 110% at 275°C) at least compared to what has been observed with thermoplastic polymers. Such relatively modest modulus increase in the case of phenolic resins likely stems from the already high stiffness of the pure resin, in comparison to a thermoplastic or elastomeric polymer. Indeed, the glass transition temperature of the phenolic resin is quite high (over 250°C) and does not exhibit consistent increase upon addition of CNWs (Figure 3b). Therefore the potential for reinforcement of CNWS in a high modulus and high Tg is here also demonstrated with a phenolic adhesive.
Conclusions

In this work resoles were modified with cellulose nanowhiskers and cured under high temperature conditions to yield well dispersed cellulosic nanocomposites. The addition of cellulose whiskers affected several properties of the phenolic resin. For example the cure properties appeared to be altered in presence of CNWs. Additionally, and as expected a moderate increase in the flexural storage modulus was observed as the phenolic resin was loaded with CNWs. No clear effect of the resin glass transition was noted.

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References


