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SHORT COMMUNICATION

Mechanical property of lignin-modified phenolic foam enhanced by nano-SiO$_2$ via a novel method

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Abstract Recently, the application of nano-SiO$_2$ in composite materials has received wide attention. In this work, a new method was explored to prepare nano-SiO$_2$ using phenol instead of other organic alcohols. The obtained nano-SiO$_2$ was characterized by Fourier transform infrared spectroscopy (FT-IR) and by the zeta potential method. The phenol dispersant containing the prepared nano-SiO$_2$ exhibited much higher reactivity toward formaldehyde than pure phenol. The preparation parameters of phenolic resin (PR) involved by nano-SiO$_2$ were mild. This novel phenolic resin was successfully applied to fabricate a phenolic foam (PF) with a 153% increase in compressive strength.

Keywords Nano-SiO$_2$ · Lignin · Free formaldehyde · Phenolic foam

Introduction

PF exhibits low flammability, a low peak heat release rate, low smoke density, lack of dripping during combustion and nontoxicity compared with polystyrene and polyurethane foams, which produce toxic gases and melt when exposed to combustion (Hirano and Asami 2013). These characteristics of PF have attracted increasing attention, especially in applications where fire resistance is necessary. However, the most notable drawback of PF is that it has a low mechanical strength, which limits its wider usage (Saz-Orozco et al. 2015). To date, many efforts have been made to solve the issue with some success (Nordberg et al. 2010; Li et al. 2011). Meanwhile, worldwide industrial development increases the worldwide consumption of petroleum and petro-chemicals and strains chemical feedstocks. Thus, an urgent issue for researchers is searching for new raw material resources. Dorrestijn et al. (2000) proposed to use biomass as an alternative resource for chemicals, and Lora and Glasser (2002) suggested that lignin could be used as a sustainable alternative to nonrenewable materials.

When PF was modified to replace 20 wt% of its phenol with oxidatively degraded lignosulfonate, there was almost no pulverization, and its compressive strength increased by 54.5% over that of pure PF (Hu 2012). Saz-Orozco et al. (2014) used wood flour (1.5 wt% incorporation) to reinforce PF, and found that the compressive modulus and strength increased by 30 and 54%, respectively, compared with pure PF. Liang et al. (2016) used polyhydroxylated cardanol (20 wt% incorporation) in the presence of H$_2$O$_2$ and HCOOH to replace phenol to fabricate foaming resin with a 57% increase in compressive strength and a 56% increase in flexural strength compared to pure PF. Recently, many researchers have reported that nano-SiO$_2$ can reinforce polymeric materials and improve their properties. Li et al. (2015) used silica sol (with an average particle size of 25 nm) to enhance the mechanical properties of PF via in situ polymerization with phenol and formaldehyde, the compressive strength, compressive modulus and tensile strength of the modified PF increased by 47.37, 38.55 and 57.14%, respectively, compared with those of pure PF.

To date, almost all reported nano-SiO$_2$ has been obtained in alkaline ethanol/H$_2$O solution, using tetraethyl orthosilicate (TEOS) or tetrapropyl orthosilicate (TPOS) as

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a silicon source (Rodríguez et al. 2016; Long et al. 2016; Ye et al. 2017). However, the process is complicated and time consuming, and a large amount of organic solvent is needed. Based on our previous work (Jing et al. 2015), phenol has dual functions in the preparation of nano-SiO_2: one as a new dispersant (Hu et al. 2011) and another one as one of the main reactants in the following reaction. In this paper, a novel method of SiO_2 nanoparticles' preparation was for the first time reported. Also, as-prepared SiO_2 was applied to reinforce phenolic foam (PF) which is simple and labor saving showing higher compressive strength.

Methods

General

TEOS and ammonia, purchased from China National Pharmaceutical Group, were of analytical grade. Lignosulfonate was purchased from Feihuang Chemical Company ($M_w = 19605$, $M_n = 17774$, 16.3% ash) and used without further purification. Other materials used were of analytical grade. FT-IR spectroscopy of the nano-SiO_2 (after freeze drying) was performed on a Nicolet iS 10 IR spectrometer (Nicolet Co., USA), equipped with a deuterated triglycine sulfate detector. Crystallinity data were obtained via X-ray diffraction (XRD) with a D8 Focus(-Bruker, Germany) operated at 45 kV and 40 mA, using Cu Kα radiation with a graphite-diffracted beam monochromatic. Data were acquired in a 2-theta scale from 10° to 80°. A small amount of nano-SiO_2 was put into approximately 50 mL of purified water in a beaker and dispersed with an FS-450 N Ultrasonic Homogenizer (Shanghai, China). Some of this aqueous solution was put into a cuvette in a Nano-ZS ZEN3600 Dynamic Light Scattering System (Malvin, UK) and detected for nanoparticle size and distribution using the zeta potential method. The amount of free formaldehyde was determined by the GB/T 14074-2006 method, and the apparent density of the modified foam was calculated according to ASTM D 1622-08. The compressive strength of the foams was determined according to ISO 844:2004.

Description of the experiment apparatus

Preparation of nano-SiO_2

A 500-mL flask was outfitted with a reflux condenser and a mechanical stirrer. The flask was charged with 6.3 g of TEOS and 40 g of melted phenol and stirred in a 40 °C water bath for 0.5 h. Then, a mixture of 6 g ammonia and 10 g water was dropwise added into the flask through

50-ml constant pressure-equalizing dropping funnel. The system was stirred at 40 °C for 1 h to produce nano-SiO_2.

Reactivity determination toward formaldehyde

A 100-mL flask was equipped with a reflux condenser and a mechanical stirrer and put in a 50 °C water bath, and was charged with 2 g of the phenol dispersant containing the prepared nano-SiO_2 and 30 g of water. The pH was increased to 12 by adding an aqueous solution of 4 mol/L NaOH (Vázquez et al. 1997). Then, 2 g of formaldehyde (37% aqueous solution) was added. After stirring for 0.5, 1, 2, 3 or 4 h, the amount of free formaldehyde was analysed. A control experiment was performed using pure phenol.

Preparation of PR

After oxidatively degraded lignosulfonate was prepared, a dose of alkaline catalyst was put into the black homogeneous liquid and stirred for 5 min at 60 °C. Then, melted phenol and paraformaldehyde were added three times with a pause of 10 min, with a 1:1.7 molar ratio between phenol and paraformaldehyde. After the paraformaldehyde was totally dissolved, the phenol dispersant containing the prepared nano-SiO_2 (0.1 wt% in PR) was added to the above paraformaldehyde solution, and the temperature was maintained at 85 °C for 1 h. Then urea was added to react with any free formaldehyde and the mixture was then cooled to 50 °C, thus LSPR was obtained as a black and viscous liquid. As a reference, nano-SiO_2 phenolic resin (SPR) was prepared using the same method but without oxidatively degraded lignosulfonate. Pure phenolic resin (PR) and lignin phenolic resin (LPR) were prepared referring to the articles (Alonso et al. 2005; Hu et al. 2013) as well.

Preparation of PF

LSPR, n-pentane (acting as a foaming agent) and Tween-80 (acting as a surfactant) were thoroughly mixed at room temperature using an overhead mechanical stirrer. Vigorous stirring of the mixture was continued for several seconds after adding the curing agent (a solution of phosphoric acid, toluene-p-sulfonic acid, sulfocarbolic acid and water, 3:2:1:2, w/w) until the mixture was homogeneous and became warm. Then, the mixture was quickly poured into a square paper box (15 × 15 × 15 cm) in a pre-heated oven at 75 °C. The foam formed in 10–15 min and cured completely after 20 min. After cooling, the foam was removed from the mold for characterization. Three other kinds of foams were fabricated in the same way.

## Results and discussion

Analysis of nano-SiO₂

Sample of the phenol dispersant containing the prepared nano-SiO_2 was washed by alcohol three times, followed by centrifugation and high-temperature calcination, and a white nano-SiO_2 was achieved. The chemical structure was confirmed by FT-IR. spectroscopy. Figure 1 shows that the peak at 3443 cm^{-1} was attributed to the O–H stretching vibration of water, and the weak band at 1637 cm^{-1} was due to the O–H flexural vibration of water. These two peaks were possibly caused by physically adsorbed water (Sarawade et al. 2010; Gu et al. 2013). The strong and broad absorption peak at 1060 cm^{-1}, corresponding to the asymmetric stretching vibration and shear bands of Si–O–Si, is the characteristic absorption peak of nano-SiO_2 (Shi et al. 2007) and 791 cm^{-1} was identified as the symmetric stretching vibration of Si–O–Si. In addition, 940 cm^{-1} was attributed to the flexural vibration of Si–OH. From the above FT-IR data, it was obvious that the structure of the nano-SiO_2 obtained in this way was consistent with the literature reports (Lin et al. 2015). From the DLS result, it is clear that the particle size of as-prepared SiO_2 is about 120 nm with a very narrow size distribution, shown in Fig. 2. The crystallization phase of the SiO_2 powder was detected by XRD spectrum. As shown in Fig. 3, a broad peak at about 25° was observed, which indicated an essentially amorphous form of SiO_2 (Gu et al. 2013).
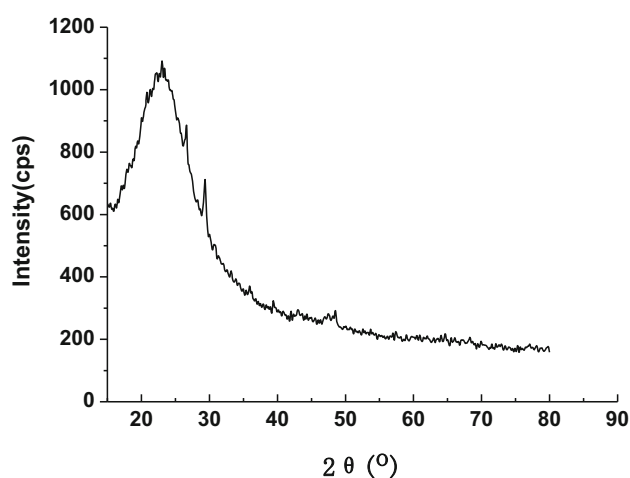
Reactivity toward formaldehyde

The reactivity of the phenol dispersant containing the prepared nano-SiO_2 toward formaldehyde is shown in Fig. 4. Interestingly, the phenol dispersant containing the
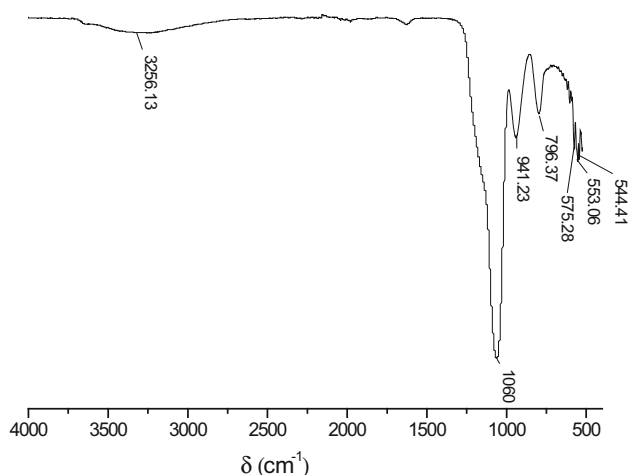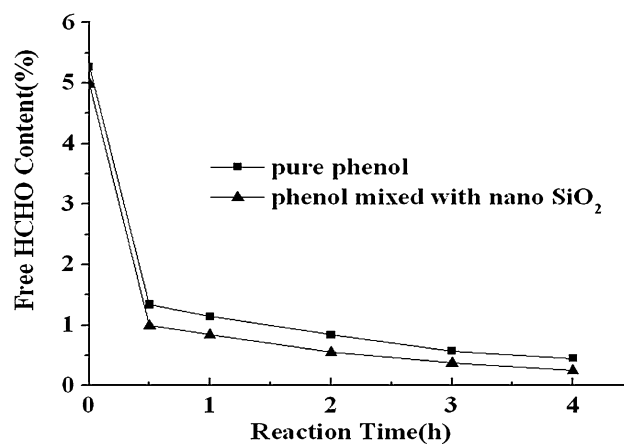
Fig. 1 FT-IR spectrum of nano-SiO₂
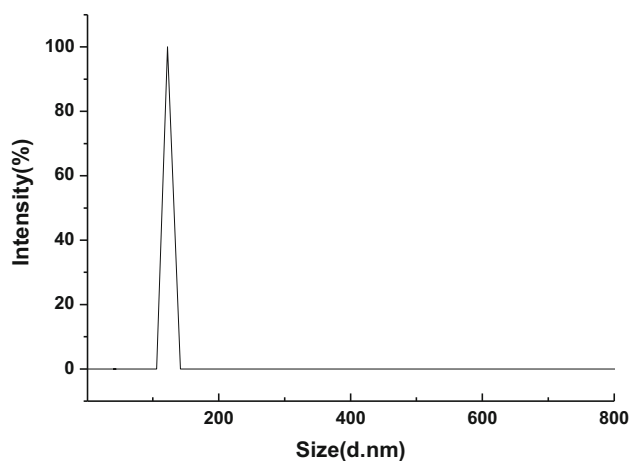
Fig. 2 Size and distribution of nano-SiO₂

Fig. 3 X-ray diffraction patterns of nano-SiO₂

Fig. 4 Free formaldehyde percent and free formaldehyde content curves

prepared nano-SiO_2 had a much higher reactivity than pure phenol. For the sample prepared by hydrolyzing TOES and reacted with formaldehyde for 0.5 h and 1 h, the content of

free formaldehyde dramatically decreased from 4.99% (2 g) to 0.99% (0.31 g) and 0.84% (0.12 g), respectively, for the control experiments using pure phenol reactant, the content of the formaldehyde decreased from 5.27% (2 g) to 1.34% (0.51 g) and 1.14% (0.41 g), respectively. When the reaction was carried out for 2 h, the content of the formaldehyde decreased to 0.55% (0.10 g) versus 0.85% (0.29 g) in the control. It was worth noting that the content of the phenol dispersant containing the prepared nano-SiO$_2$ was only 64.2 wt%, while for the control experiments, the phenol reactants had 100 wt% content. This encouraging discovery may stem from the interactions between nano-SiO$_2$ and phenol, which could then react with more formaldehyde despite the lower phenol content in the preparation of nano-SiO$_2$ mixture. This will be further discussed in a forthcoming paper.

Reaction parameters of PR

To further investigate reactivity of the phenol dispersant containing the prepared nano-SiO$_2$ toward formaldehyde, the following products were prepared: PR, LPR, SPR and LSPR. It was found that there was a big difference among the preparation conditions. For example, PR and LPR required approximately 2 h for addition and polycondensation at 83–85 °C and further polycondensation for 0.5–1 h at 95 °C, but SPR and LSPR preparation required only approximately 1 h at 85 °C, indicating that the phenol dispersant containing the prepared nano-SiO$_2$ has higher reactivity than pure phenol. This may be attributed to the fact that conjugative effect between OH groups located on the surface of SiO$_2$ and Ph-OH, which reduces the activation energy of the subsequent reaction with paraformaldehyde (Bu et al. 2014). In this case, the phenol dispersant containing the prepared nano-SiO$_2$ enhanced phenol reactivity toward formaldehyde.

Mechanical property of PF

To reveal the effect of nano-SiO$_2$ on the mechanical property of PF, four types of phenolic foams were successfully fabricated: PF1 (derived from PR), PF2 (derived from SPR), PF3 (derived from LSPR) and PF4 (derived from LPR). PF1 and PF4 had comparable compressive strength (0.12 and 0.15 MPa, respectively), but the compressive strength of PF2 increased to 0.35 MPa, an improvement of 192%. PF3 had the same enhancement in strength as PF2, increasing 153% to 0.38 Mpa, which is higher than that in the literature (Lei et al. 2010). Here, only 0.1% nano-SiO$_2$ was required and much lower than other reports, due to the interaction among SiO$_2$, lignin and PR. Nano-SiO$_2$ acts as an reinforcement, linking each part of the matrix like a bridge, ultimately, forming a stable cross-linked network structure (Meikleham et al. 1994). It was reported that lignin–SiO$_2$ hybrid was prepared via chemical method, and phenolic binders with lignin–SiO$_2$ fillers had better thermo-mechanical properties than systems with lignin or SiO$_2$ alone, confirmed by inverse gas chromatography (IGC) method (Strzemiecka et al. 2016).

Conclusions

In summary, relative homogeneous nano-SiO$_2$ with diameters of approximately 120 nm, was prepared in a simple way using phenol instead of methanol, ethanol or isopropyl alcohol. The phenol dispersant containing the prepared nano-SiO$_2$ was more reactive toward formaldehyde than pure phenol reactant. Furthermore, both the reaction temperature and reaction time of PR preparation decreased. Moreover, adding just 0.1 wt% of nano-SiO$_2$ to PR enhances the compressive strength of PF-modified lignin by 153%.

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