

EVALUATION OF TWO ULTRASONIC METHODS FOR PREPARING UREA-FORMALDEHYDE ADHESIVES WITH NANO-SiO₂

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Abstract:

This paper evaluates two methods for ultrasonic mixing of nano-SiO₂ into urea-formaldehyde (UF) adhesives. Nano-silica (SiO₂) was used in the form of 30% colloidal suspension, with the nanoparticles having a diameter of 7 nm. Its addition into the UF adhesive was 15%, based on the dry weight. The mixing of these components was performed with a probe-type ultrasonic homogenizer and with an ultrasonic bath, during 25 minutes of mixing time. The effects of each method were evaluated by SEM microscopy, and the results showed that the ultrasonic probe achieved much higher and almost complete homogenization of the UF / nano-SiO₂ mixture, in contrast to the ultrasonic bath method. Therefore, the ultrasonic probe was subsequently used to test the influence of the mixing time on the homogenization level and on the curing kinetics of the UF adhesive with nano-SiO₂. The homogenization level was not significantly altered when decreasing the mixing time from 25 to 5 minutes. For the same time range, the differential scanning calorimetry analysis also showed no significant influence of the mixing time on the curing behavior of the UF adhesive with nano-SiO₂. The results of this research provide the basis for a more effective and efficient mixing procedure when using similar nanomaterials with UF adhesives, without significantly decreasing its performances.

Key words: UF adhesives; nano-SiO₂; ultrasonic mixing; homogenization level; curing kinetics.

INTRODUCTION

Nanotechnology brings a number of possibilities to the wood industry sector, one of which concerns the modification of wood adhesives in order to improve the properties of the final wood-based products. Since urea-formaldehyde (UF) adhesives are still very much present in the production of interior use grade wood-based panels, some of the studies in recent years have been focused on modifying this type of adhesives with inorganic nanomaterials of silica (SiO₂), aluminum oxide (Al₂O₃) and zinc oxide (ZnO). It was found that relatively low addition (1% based on dry weight) of these nano-particles into UF adhesives lowers the free formaldehyde content in the particleboards (Candan and Akbulut 2013), while the addition of nano-SiO₂ and nano-Al₂O₃ particles into melamine-urea-formaldehyde (MUF) adhesives improves the mechanical properties and dimensional stability of plywood (Candan and Akbulut 2014).

Dudkin et al. (2006) reported that nano-Al₂O₃ effectively sorb free formaldehyde in UF resins, thus reducing their toxicity. Another study showed that the addition of nano-Al₂O₃ particles into UF adhesives

improves heat transfer during hot pressing of medium density fiberboards (MDF). This further results in an increased internal bond and modulus of elasticity of the MDF, but with no improvement of the bending strength and thickness swelling (Kumar et al. 2013). Dukarska (2013) found that the addition of nano-SiO₂ into UF adhesives showed positive effects in the production of rape straw boards, significantly increasing their internal bond and to a lesser extent their bending properties, while decreasing the formaldehyde content of the boards. On the negative side, the water resistance of the boards showed a tendency to decrease with the increase in the level of nano-SiO₂ particles. Salari et al. (2013) also used UF adhesives modified with nano-SiO₂ particles to produce experimental oriented strand boards (OSB). They found that the addition of nano-SiO₂ improved the mechanical properties and water resistance, and reduced the formaldehyde emission of the OSB.

These studies also showed that relatively low amounts of inorganic nanomaterials are needed to modify the UF adhesive in order to improve the properties of wood composites. Depending on the type of nanoparticles and the actual application, the optimal addition was usually in the range of 0.5 - 3%, based on the dry weight of the UF adhesive. This apparent effectiveness of nanomaterials comes from their nano-scale size. However, higher addition levels of the applied nanoparticles tend to diminish their positive effect and even to reverse it. Due to their high surface energy, they have a tendency to agglomerate (Jiang et al. 2013; Qiao et al. 2016). For instance, nano-SiO₂ particles with the average size of 12 nm form larger aggregates with the size between 50 and 350 nm, when mechanically mixed into the UF resin (Roumeli et al. 2012). Therefore, beside the type and the amount of nanoparticles used to modify the adhesives, it is very important to consider the proper mixing procedure. An earlier study showed that the application of ultrasounds provides a simple and effective method for good dispersion of nano-SiO₂ particles into the UF adhesive (Jiang et al. 2013). Hence, this investigation was aimed at finding a suitable ultrasound technique for mixing the nano-SiO₂ particles into commercial UF adhesives. Another goal was to determine the sufficient duration of the selected mixing procedure, at which the appropriate homogeneity of the dispersion is achieved.

MATERIALS

In this research, Ludox SM-30 colloidal silica (W. R. Grace & Co. USA) was used, with the following characteristics: concentration in water of 30%, density of 1.216g/cm³, pH value of 9.9, average particle size of 7nm, and the specific surface of 337m²/g. Since nano-silica particles have very high surface energy, the colloidal suspension was used in order to facilitate better dispersion into the UF adhesive.

For the purpose of this study, commercial UF resin was obtained in the form of stabilized polymer emulsion with the following characteristics: solid content - 65.4% (EN 827); pH value - 8.05 (EN 1245); density - 1.27g/cm³ (areometer method) and viscosity - 415 (EN 12092).

Ammonium sulfate p.a. ((NH₄)₂SO₄) produced by Sigma Aldrich (Germany) was used as a hardener for the UF adhesive systems in differential scanning calorimetry experiments.

METHODS

Ultrasonic preparation of UF resin with nano-SiO₂

Two ultrasonic devices, the ultrasonic bath (Bandelin Sonorex) and the ultrasonic probe (Bandelin Sonopuls HD 2070), were compared in order to obtain the most homogeneous dispersion of nano-SiO₂ particles into the UF resin. The mixing time was 25 minutes for both methods, and the addition of colloidal nano-silica into the UF resin was 15wt%, based on the dry resin. The hardener, ammonium sulfate, was added in the amount of 1 and 3wt%, based on the dry resin, for the DSC and SEM experiments, respectively. UF mixtures with and without SiO₂ particles for the SEM investigation were prepared by addition of distilled water, in order to obtain 45% concentration.

Evaluation of UF adhesive / nano-SiO₂ mixtures by SEM

A scanning electron microscope (SEM, Tescan Vega TS 5130MM) with 20-keV accelerating voltage was used to evaluate the homogeneity of the UF/nano-silica mixtures, obtained from both ultrasonic mixing methods. The relevant mixtures were dried inside the molds and cut into tablets to create the solid samples for the SEM scans. Drying was performed in the laboratory oven at a temperature of 103±2°C, for 6h. The surface of the samples was vacuum-coated by evaporation with gold before the measurements. Secondary electrons (SE) were used for analysis of SEM-samples.

The same SEM technique was used to evaluate the influence of the mixing time on the curing reaction of UF/nano-silica mixtures. The samples were dried in the molds at ambient temperature for two days, and then cut into tablets for the SEM scans. After that, the samples were prepared for the SEM scans as in the previous procedure.

DSC analysis of UF adhesive / nano-SiO₂ mixtures

Differential scanning calorimetry (DSC) was another method used to evaluate the influence of the mixing time on the curing reaction of UF/nano-silica mixtures. The DSC measurements were carried out in isothermal regime in the range of 30°C to 200°C, using DSC Q20 (TA Instruments, USA). Each sample series, representing the UF adhesive system with nano-silica, was obtained under discrete periods of ultrasonic probe mixing: 5, 15 or 25min. The isothermal scans of these samples, together with the pure UF adhesive, were obtained using three constant heating rates (β): 5, 10 and 20°C/min. The application of multiple scans with different heating rates allows the calculation of activation energy of the curing reaction, based on the Kissinger equation and the assumption that the peak temperature (T_p) on the thermograph presents the temperature at the maximum rate of reaction (Kissinger 1957). In such case, the activation energy can be derived from the slope of the straight line of $\ln(\beta/T_p^2)$ in relation to $1/T_p$.

RESULTS AND DISCUSSION

Figs. 1a and 1b represent the SEM micrographs (magnification of 30,000x) that show the results of the ultrasonic mixing of nano-SiO₂ colloidal suspension into the UF resin. The use of ultrasonic bath produced the mixture in which the agglomerates of nano-silica can be clearly noticed (Fig. 1a). These agglomerates range in size from 50 to 250nm, and are not evenly distributed in the resin matrix.

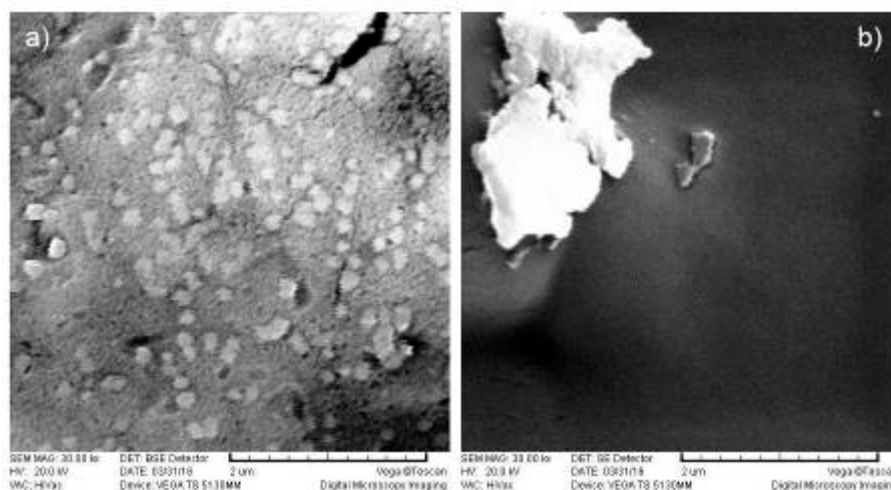


Fig. 1.

SEM micrographs of the UF resin with 15wt% of nano-silica particles (a) mixed with ultrasonic bath and (b) mixed with ultrasonic probe (mixing time was 25 minutes; bright spots on the Fig. 2b are impurities that were used to focus the image of resin).

Contrary to the mixing with ultrasonic bath, the ultrasonic probe produced a quite satisfactory homogenization of nano-silica into the UF resin (Fig. 1b). The micrograph shows no apparent agglomeration of nano-silica particles; hence, the size of the nano-silica agglomerates should be less than 20nm (Fig. 1b also depicts the impurities used to obtain clear focus).

Since the ultrasonic probe produced better homogenization of nano-silica in UF resin, this technique was also used to evaluate the effects of different mixing time. The SEM micrographs in Figs. 2a, 2b and 2c show the results of ultrasonic mixing after 5, 15 and 25 minutes, respectively. However, there are no apparent differences between the UF/nano-SiO₂ mixtures, and all micrographs show satisfactory homogenization of nano-silica particles inside the UF resin matrix.

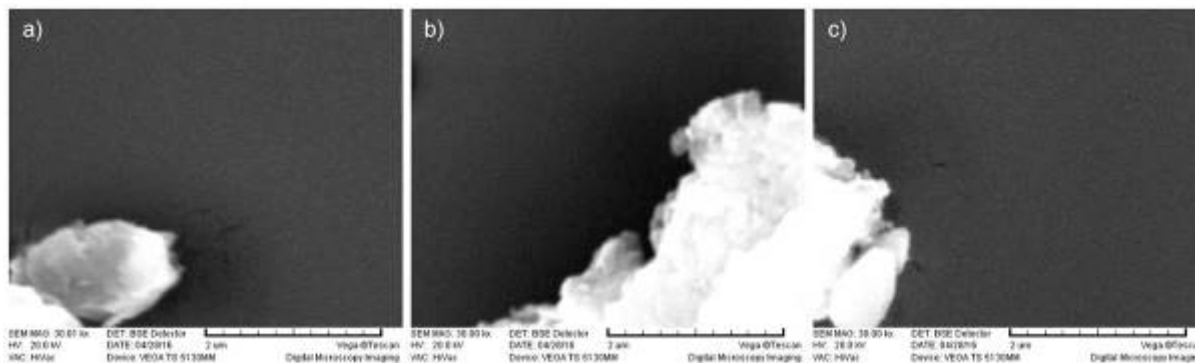


Fig. 2.

SEM micrographs of the UF resin with 15wt% of nano-silica particles mixed with ultrasonic probe during (a) 5 minutes, (b) 15 minutes and (c) 25 minutes (bright spots on the micrographs present the impurities that were used to focus the image).

DSC method was yet another way to study the effects of nano-silica addition to UF resin, and the influence of the mixing time on the characteristics of UF/nano-silica adhesive mixtures. Fig. 3 shows the DSC thermographs of the pure UF adhesive and the UF/nano-silica samples obtained with the shortest (5min) and the longest (25min) mixing time by the ultrasonic probe.

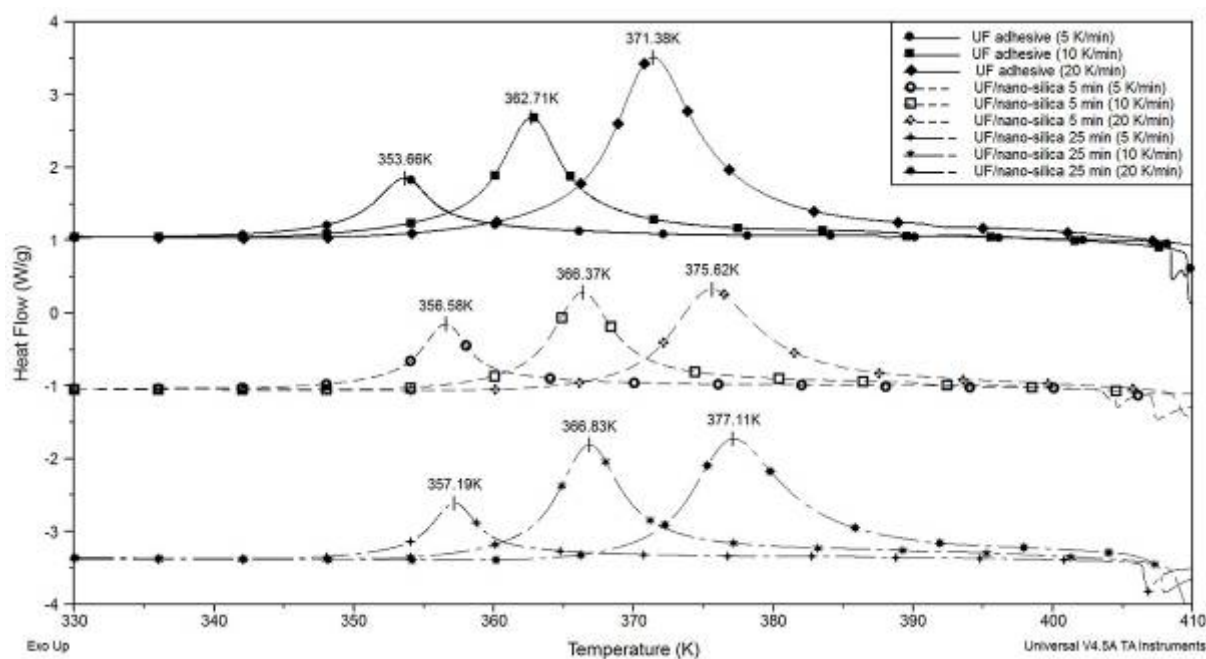


Fig. 3.

DSC thermographs of the curing reaction of the pure UF adhesive and the UF/nano-SiO₂ adhesives prepared with the ultrasonic probe with different mixing times: 5 and 25 minutes (each sample series was tested with three different heating rates: 5, 10 and 20°C/min; the addition of nano-SiO₂ was 15% per dry weight of UF resin).

The exothermic peak presents the polycondensation reaction of primary amino groups of unreacted urea with hydroxymethyl groups of the UF resin systems (Siimer et al. 2003). It can be noticed that the addition of colloidal nano-SiO₂ increases the peak temperature of the UF adhesive curing reaction. This retarding effect of the nano-SiO₂ particles possibly arises from their interaction with the UF polymer chain through the bond formation or from their participation in the condensation reactions (Roumeli et al. 2012). On the other hand, the influence of the mixing time on the curing behavior of the UF/nano-SiO₂ system was quite negligible. The increase of the mixing time only slightly shifts the peak temperatures to a higher level, which suggests that the longer application of ultrasonic probe could have promoted further interactions between the UF resin and the nano-SiO₂ particles. However, this finding is interesting in the sense that the shortest applied mixing time (5 minutes) proves the effectiveness of the ultrasonic probe method, and its efficiency in the possible industrial scale applications.

Table 1

Enthalpy (ΔH) and activation energy (E_a) of the curing reaction of pure UF adhesive and the UF/nano-SiO₂ adhesives prepared with the ultrasonic probe (mixing time: 5, 15 and 25 minutes)

Sample	Peak temperature (°C)			ΔH (J/g)	E_a (kJ/mol)	R^2
	β °C/min	β °C/min	β °C/min			
UF adhesive	80.51	89.56	98.23	63.36 ± 7.37	79.34	0.9992
UF / nano- SiO ₂ (5 min)	83.43	93.22	102.47	47.70 ± 9.47	74.92	0.9989
UF / nano- SiO ₂ (15 min)	83.96	93.47	103.49	49.57 ± 3.29	73.28	1
UF / nano- SiO ₂ (25 min)	84.04	93.68	103.96	50.16 ± 7.69	71.83	1

Table 1 presents the results for the enthalpy and activation energy of the curing reaction of different UF adhesive systems. The reaction enthalpy decreased with the addition of nano-silica, but there was no significant influence of the mixing time. These results suggest that less heat is emitted during the curing of the UF adhesive in presence of nano-silica in general, which may further imply that less crosslinking occurred, probably due to earlier reactions of the adhesive with nano-silica during mixing. This trend is in compliance with the results of peak temperatures that also showed slightly retarding effects of the nano-silica addition (Fig. 3).

Similar to the results of enthalpy, the activation energy of the curing reaction decreased for the systems with nano-silica. However, this trend of the results of the activation energy suggests the faster promotion of the curing reaction for the UF adhesive in presence of nano-silica systems, which is contrary to the assumptions based on the results of peak temperatures and the reaction enthalpy values. This is probably due to the change of the adhesive phase with the addition of nano-silica.

It can also be noticed that the results of the activation energy decrease with the increase of the mixing time. This effect could result from the influence of the ultrasonic treatment, which probably caused the ultrasonic-induced catalytic actions on polymerization reactions, due to the cavitations' energy release in that process.

CONSLUSIONS

The ultrasonic methods are suitable for mixing the colloidal nano-SiO₂ into UF adhesives. However, the use of the ultrasonic probe enabled significantly better dispersion of nano-SiO₂ particles in the adhesive matrix in comparison to the ultrasonic bath.

Decrease of the mixing time from 25 to 5 minutes did not affect the dispersion of nano-SiO₂ into the UF adhesive, i.e. the same level of homogenization was achieved with all of the applied mixing times.

In addition, different mixing times also showed negligible effects on the curing reaction of the UF/nano-SiO₂ adhesive, as observed on the DSC thermographs. However, the activation energy tended to decrease with the increase of the mixing time.

The addition of nano-silica itself slightly increased the peak temperature of the curing reaction and decreased the reaction enthalpy.

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