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Alumina nanoparticle modified phenol-formaldehyde resin as a wood adhesive

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ABSTRACT

Phenol-formaldehyde resin was synthesized and modified by alumina nanoparticles (ANPs). The crystal form of the ANPs was characterized by X-ray diffraction (XRD), and differential scanning calorimetry (DSC) was used for thermal analysis of the resin. In addition, the resin was applied in plywood manufacture, and the curing time as well as the bonding strength was measured. The results showed, with an appropriate doping amount of ANPs, both the curing rate and the bonding strength increased significantly. The modified resin showed extensive application prospects in the wood construction industry.

1. Introduction

Adhesives have played an important role in the wood construction industry during many decades. Among the various types of adhesives employed, phenol-formaldehyde (PF) resins have been widely used in plywood, oriented strandboard and particleboard panel manufacture due to the advantages of strong resistance to moisture, low initial viscosity and excellent temperature stability [1,2]. The most common PF resin used in the plywood industry is the "resol-type", which can be stabilized in solution by incorporating excess alkali and which can finally be changed to branched and cross-linked three-dimensional networks after hot-press treatment [3–5]. The energy consumption during the hot-press process is high and the curing efficiency needs to be improved, especially for large-size components [6,7]. So accelerating and optimizing the curing process is vital to cost reduction and quality improvement in plywood manufacture [8].

Recently, a considerable amount of research has focused on the curing process of the PF resin and some progress has been made. Fan et al. studied the cure properties of phenol-urea-formaldehyde and found that sodium carbonate, zinc oxide and magnesium oxide could increase the curing rate as a catalyst [9]. Other inorganic salts or inorganic oxides were also found to have an effect on the cure reactions of a PF resin, such as barium carbonate [10], silicon dioxide [11], magnesium oxide [12] and titanium dioxide [13]. Most of these inorganic salts or inorganic oxides have low solubility or dispersity in aqueous PF resin solutions, so the utilization ratio of the additives is relatively low. Researchers have also considered nanosize materials in an attempt to obtain a better reinforcement result and product performance [14,15]. Gao and Du studied the curing kinetics of a nano cupric oxide modified PF resin. Results showed that the addition of nano cupric oxide could effectively improve the shear strength of plywood [16]. In sisal fiber/PF resin composites, the incorporation of nano-silica was shown to improve the thermal stability of the composites and presented better wear resistance at different temperatures [17]. Lei and Pizzi et al. studied the influence of montmorillonite (MMT) nanoclay on PF and PUF resins for use as wood adhesives. Both dry and after boiling tensile strengths improved when the MMT with larger interlayer distance was introduced at a concentration of 5 wt% [18].

Alumina nanoparticles (ANPs) have been used as a reinforcement filler in polymer composites for many purposes [19], for example, dental resin composites [20] and epoxy electrical insulators [21,22]. With very small concentrations of ANPs, usually below 5 wt%, mechanical strength, abrasion resistance, thermal conductivity and electrical resistivity could be improved [23]. However, little research has been conducted on ANP reinforced PF resins as wood adhesives. Kumar et al. reported that ANPs could enhance the heat transfer rate of medium density fiberboard during hot-pressing, and could therefore improve mechanical properties [15]. ANPs have also been used to enhance the properties of PVA (polyvinyl acetate) polymers when used as wood adhesives. The bonding strength of PVAs under wet conditions and at elevated temperatures were increased by the addition of ANPs [24]. Recently, Dabbagh and Shahraki prepared mesoporous nanorod-like γ-alumina with a narrow pore size distribution using PF resin as a template [25]. Results showed there were strong interactions between ANPs and PF resins. Here, γ-ANPs were used to reinforce a PF resin for use as a potential wood adhesive with an attempt made to study the influence of ANPs on the curing process of a PF resin. Through mechanical tests and thermal analysis, reinforcement of a PF resin at

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different ANP contents revealed the existence of an acceleration effect on the curing process thus providing a good example of energy consumption control in plywood production.

2. Experimental

2.1. Materials and synthesis

Phenol (AR), formaldehyde (AR) and sodium hydroxide (AR) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd., China. Alumina nanoparticals (γ phase, 20 nm) were obtained from Suzhou Huaweite Powder Tech. Co., Ltd., China.

The aqueous PF resin (resol type) was synthesized via a common route: phenol and the first part of formaldehyde and sodium hydroxide aqueous solution were mixed at 40 °C in a three neck flask with a mechanical stirring bar and the mixture was slowly heated to 95 °C over a period of 1 h. After stirring at 95 °C for 30 min, the mixture was cooled to 75 °C, the second part of formaldehyde and, sodium hydroxide aqueous solution were added. Then the mixture was heated to 85 °C and the viscosity was continuously monitored. When the viscosity reached 500 mPa s, the mixture was quickly cooled to room temperature. The total molar ratio of formaldehyde to phenol was 1.76:1. The concentration of sodium hydroxide aqueous solution was 30 wt%. The mass ratio of the first and second parts of the formaldehyde and sodium hydroxide aqueous solution was 7:1 and 3:2 respectively. The viscosity of the final product was between 500 mPa s to 1000 mPa s, and the pH was about 11.

The ANPs were introduced into the PF resin with loading levels of from 0% to 4% (weight ratio to the PF resin solution). The samples were labeled as PF0, PF1, PF2, PF3 and PF4, according to the loading level of alumina. To prepare the samples, the nanoparticles were added into the resin with a precise amount, and then the mixture was stirred vigorously under ultrasonic conditions at room temperature for 1 h. For XRD and DSC characterization, the resin samples were vacuum freeze-dried for 72 h, and the residues were ground into a powder at room temperature.

2.2. Morphology characterization

The morphology of the ANPs was characterized by transmission electron microscopy (TEM, Tecnai G2 F20 U-TWIN, FEI Co., USA). The diameter of the nanoparticles was about 20 nm.

2.3. X-ray diffraction

The X-ray diffraction data of the powdered samples were collected using a Philips X'pert (PW3040/60) diffractometer with Cu Kα radiation of wavelength 1.5406 Å operated at a voltage of 40 kV, a current of 40 mA and a scanning rate of 10°/min (2θ range 30–90°), where θ is the diffraction angle.

2.4. Differential scanning calorimetry

The DSC measurements of the powdered resin samples were performed on DSC-Q100 from TA Instruments under a nitrogen atmosphere. The sample weight varied from 4 mg to 6 mg and the heating rate was 10 °C/min at a scanning temperature range from 40 to 200 °C.

2.5. Viscosity and curing time

According to Chinese national standard (GB/T 17657-2013), the viscosities of the PF resin with different amount of ANPs were measured using a Brookfield rotary viscometer at 25 ± 2 °C. The curing time of the resin was measured separately at 120 and 140 °C with no addition of other curing agent. Both the viscosity and the curing time were tested three times and the average result of each sample was recorded.

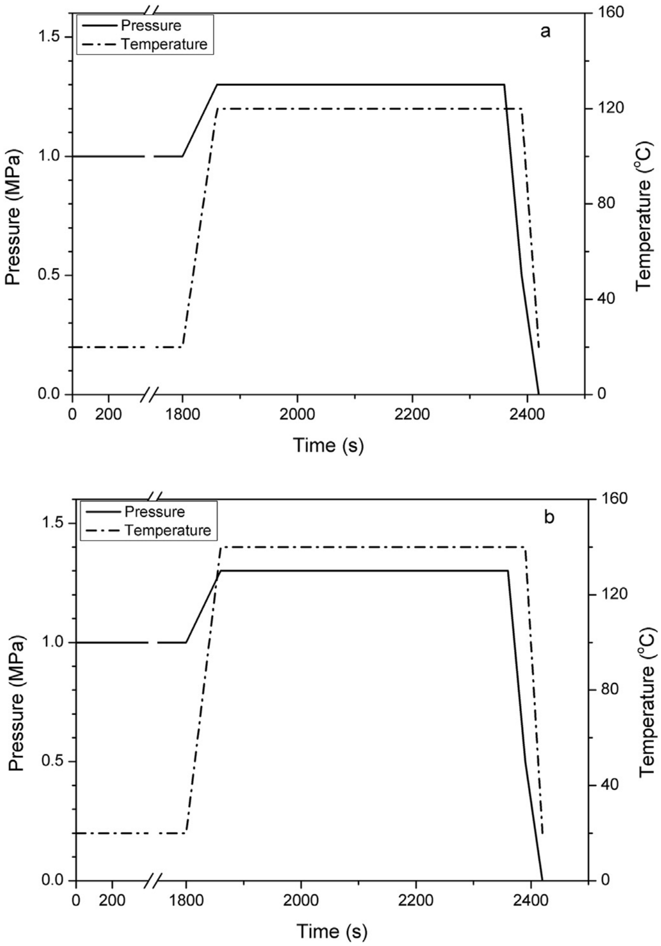

Fig. 1. Pressing condition of plywood production (a. 120 °C; b. 140 °C).

2.6. Bonding strength

Three-layer plywood panels were prepared for bonding strength tests. Each veneer with dimensions of 400 (Width) × 400 (Length) × 1.5 (Thickness) mm was prepared from Chinese white poplar (*Populus tomentosa*), and purchased from a local factory (Shandong Province) and dried to 8%-12% moisture content. Before glue spreading, 20% wheat flour was added to each adhesive sample by weight. The spreading amount was 300 to 360 g/m^2 double glue line. Then, the panel assembly was cold pressed for 30 min under 1 MPa at room temperature, as shown in Fig. 1. In this work, the hot press temperature was set at 120 and 140 °C, with a pressure of 1.3 MPa. After that, the pressure was released and the panel was cooled to room temperature in 60 s.

According to Chinese national standard (GB/T 17657-2013), the plywood panels were cut to dimensions of 100 mm × 25 mm and the bonding strength (wet shear strength) with twelve repetitions was tested using a rapid detection method: the specimens were soaked in boiling water for 3 h, and then cooled quickly to room temperature. Then the shear strength was tested in a wet state. According to the standard, a wet shear strength of more than 0.78 MPa is required for type I plywood [26]. Here, the shear strength was measured with an Instron 101 Universal Testing Machine under a crosshead speed of 5 mm/min.

3. Results and discussion

The viscosity and curing time of the PF resin samples varied with ANP content, as shown in Fig. 2. A TEM image of ANPs is shown in

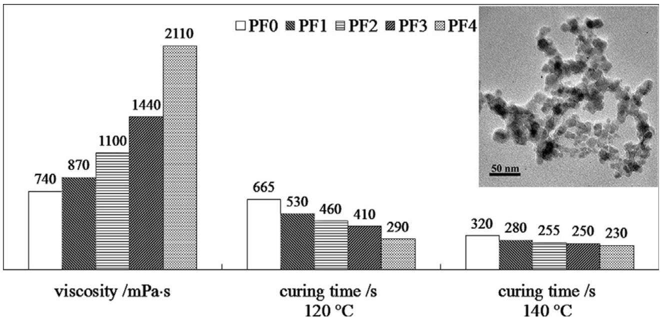

Fig. 2. Viscosity and curing time of PF resin samples with different ANP contents (Inset: TEM image of ANPs).

Fig. 2 as an illustration which shows the diameters of the ANPs to be approximately 10–30 nm. The viscosity rose with increasing ANP content in a multi-order relationship. When the weight ratio of ANPs reached 4%, the viscosity of the resin sample increased to 2110 mPa s, which was almost three times that of the original PF resin. Similarly, curing time correlated well with ANP content, with the correlation being of greater significance at 120 °C. The curing process of the PF resin was promoted by a condensation reaction between a hydroxymethyl group (or unreacted formaldehyde) and phenol. Therefore, the resol-type PF resin will become more viscous due to the formation of cross-linked three dimensional networks when the temperature increases. But in our study, the synthesized samples were kept at room temperature, so the increase of viscosity can probably be attributed to the presence of ANPs. On the one hand, the ANPs could increase the heat transfer rate of the PF resin during the ultrasonic treatment [15]; on the other, there would likely be some interaction between the surface of the ANPs and the PF resin through an “Al-O-phenol” bond [27]. We assumed that both factors accelerate the cross-linking of the resin even at room temperature. While at the higher temperature the curing rate also increased rapidly, so the acceleration effect caused by ANPs was not obvious at 140 °C. However, the curing time at 140 °C could be reduced by up to 70% of the original value, which could result in less energy consumption during the hot-press process.

XRD was used to characterize the crystal form of the ANPs in the resin. As shown in Fig. 3, the γ-ANPs had two intensive characteristic diffraction peaks at 2θ of 45.66° and 67.10° [28]. The pure PF resin (PF0) is an amorphous material and showed no responsive peak in the scanning area. The intensity of the diffraction peaks increased from samples PF0 to PF4. The surface of the ANPs would dissolve in alkaline PF resin solution during the ultrasonic treatment. When the ANP content increased, more ANPs could remain within their inner structure, and therefore a larger intensity in the XRD pattern.

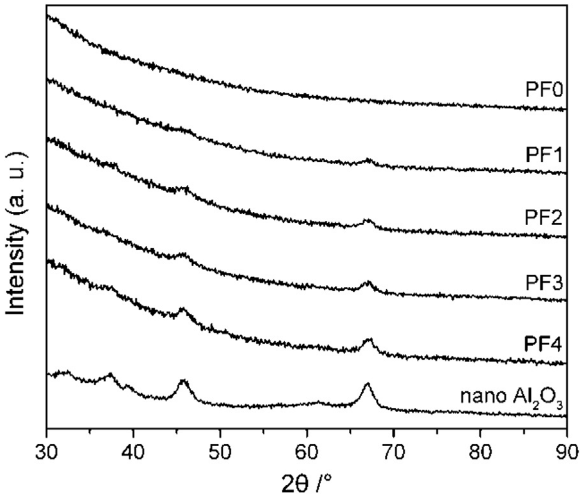

Fig. 3. XRD patterns of PF resin samples and pure ANPs.

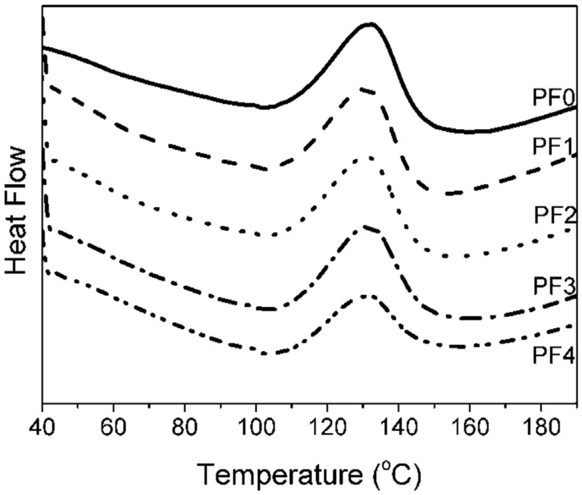

Fig. 4. DSC curves of PF resin samples.

The cure reaction rates of the PF resin samples were measured by DSC. The DSC curves of the freeze- dried PF resin powders are shown in Fig. 4, with the data listed in Table 1. T_{onset} and T_{peak} represented the initial and maximum exothermic temperatures, and ΔH was the reaction enthalpy measurement according to the exothermic peak of the DSC curve [16,29]. As shown in Table 1, the overall trend of the T_{onset} was lowered and ΔH was decreased, while the T_{peak} showed an inflection point for sample PF2. The peak temperature was approximately 140 °C, which was the common curing temperature during plywood manufacture.

As mentioned before, ANPs increased the viscosity of the resin and shortened the curing time. Due to the interaction between the ANPs and the PF resin and the increased heat transfer rate of the PF resin, parts of the cure reaction may start at room temperature. As a result, parts of the active groups of the PF resin were consumed. Consequently, the reaction enthalpy (ΔH) during the curing process was reduced. As shown in Table 1, T_{onset} was reduced with increasing ANP content, which would facilitate the curing reaction. The previous curing time measurement also showed the same result. According to a previous study on UF/ANPs, the reaction enthalpy (ΔH) of a UF resin containing ANPs showed increasing enthalpy values in comparison to pure UF [15], which means the increased heat transfer rate caused by the ANPs led to a high degree of cure in the UF resin. In contrast, the reaction enthalpy (ΔH) of the PF/ANPs studied here decreased with increasing ANP content. Considering that the increasing heat transfer rate could have similar results here which may increase the reaction enthalpy (ΔH), it is assumed that the interaction between ANPs and the resin could accelerate the curing process even at room temperature. Therefore a “pre-cured” resin could result having less active reaction groups and a lower reaction enthalpy. This speculation could also be supported by the test results from the viscosity and curing time assessments mentioned earlier.

For a wood adhesive, wet bonding strength is an important property. Thus the shear strength of a three-layer poplar plywood was measured after immersion in boiling water bath for 3 h. The results are

Table 1
Curing kinetics parameters of PF resin with different amount of the ANPs.

	PF0	PF1	PF2	PF3	PF4
T_{onset} (°C)	113.9	108.4	107.3	105.4	106.2
T_{peak} (°C)	139.7	137.0	129.3	133.6	135.3
ΔH (J/g)	25.26	24.74	18.25	15.20	13.06

Table 2
Wet shear strength of plywood with different resin or curing temperature.

	Wet shear strength (MPa)		Average deviation		Variation coefficient	
	120 °C	140 °C	120 °C	140 °C	120 °C	140 °C
PF0	0.26	1.01	0.161	0.078	0.799	0.099
PF1	0.57	1.11	0.146	0.087	0.321	0.095
PF2	0.68	1.23	0.117	0.074	0.223	0.084
PF3	0.72	1.21	0.109	0.057	0.198	0.056
PF4	0.98	1.20	0.087	0.144	0.115	0.143

shown in Table 2, where it is clear that the wet shear strength was closely related to the curing temperature. A positive correlation between ANP content and wet shear strength was observed, especially at a low curing temperature of 120 °C. The highest wet shear strength was 0.98 MPa (PF4 at 120 °C) and 1.23 MPa (PF2 at 140 °C). The shear strength of plywood was significantly increased after the addition of ANPs, which could reach a 277% increase at 120 °C and 22% increase at 140 °C.

According to the above DSC data, the onset and peak curing temperatures of the modified PF resins were about 105 °C and 135 °C respectively. In our five-minute hot press process, a temperature of 120 °C was not high enough for the resin to achieve full cure. As a result, the wet shear strength of the unmodified resin (PF0) was very low (0.26 MPa). The average deviation and the variation coefficient also indicated that the PF0 resin had a wide strength distribution. With the addition of ANPs (1% to 4%), the increase of strength was very significant and the strength distribution became uniform, which indicated that the addition of the ANPs could improve the performance of the plywood product. The peak value of the wet shear strength appeared in PF4 at 120 °C and PF2 at 140 °C. The variation coefficient decreased with increasing ANP content with the exception of the value of PF4 at 140 °C. Because the addition of ANPs also increased the viscosity of the resin this resulted in an uneven resin distribution on the veneer and a relatively higher variation coefficient. Moreover, the strength of plywood PF4 at 120 °C was very close to that of PF0 at 140 °C. This indicated that with an appropriate loading of ANPs, the strength of the plywood could reach a comparatively high value at a lower temperature, which could also meet the type I wood requirement of Chinese national standard (GB/T 17657-2013). As a result, the manufacturing process could be more energy efficient.

4. Conclusions

The ANPs were used as additives to enhance the performance of PF resin as wood adhesive. The ANPs could remain in their crystal form in the basic PF resin solution. With the addition of ANPs, the wet shear strength of plywood increased up to 20% at the normal hot press condition of 140 °C. With a doping content of 2% by weight, both the curing rate and the bonding strength of PF resin increased significantly. These results showed a way to accelerate and optimize the curing process using ANPs which could increase manufacturing efficiency and lower energy costs.

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References

[1] Pizzi A. Wood Adhesives: Chemistry and Technology. M. Dekker; 1989.

[2] Pizzi A. Synthetic Adhesives for Wood Panels: Chemistry and Technology. 2015.

[3] Park BD, Riedl B, Kim YS, So WT. Effect of synthesis parameters on thermal behavior of phenol-formaldehyde resol resin. J Appl Polym Sci 2002;83:1415–24.

[4] Holopainen T, Alvila L, Savolainen P, Pakkanen TT. Effect of F/P and OH/P molar ratios and condensation viscosity on the structure of phenol-formaldehyde resol resins for overlays - A statistical study. J Appl Polym Sci 2004;91:2942–8.

[5] Katović Z. Curing of resole-type phenol–formaldehyde resin. J Appl Polym Sci 1967;11:85–93.

[6] Conner AH, Lorenz LF, Hirth KC. Accelerated cure of phenol-formaldehyde resins: studies with model compounds. J Appl Polym Sci 2002;86:3256–63.

[7] Pizzi A, Stephanou A. Completion of alkaline cure acceleration of phenol–formaldehyde resins: acceleration by organic anhydrides. J Appl Polym Sci 1994;51:1351–2.

[8] Park B-D, Riedl B, Hsu E, Shields J. Application of cure-accelerated phenol-formaldehyde (PF) adhesives for three-layer medium density fiberboard (MDF) manufacture. Wood Sci Technol 2001;35:311–23.

[9] Fan D-B, Chang J-M, Li J-Z, Xia B-H, Sang Z-T. Cure properties and adhesive performances of cure-accelerated phenol-urea-formaldehyde resins. Eur J Wood Prod 2011;69:213–20.

[10] Zhang X, Ma Q-z, Zhang Z-f, Peng W-x, Zhang M-l. Effect of Nano BaCO3 on Pyrolytic Reaction of Phenol-Formaldehyde Resin, In: Leng J, Asundi AK, Ecke W. (Eds.), In: Proceedings of the Second International Conference on Smart Materials and Nanotechnology in Engineering, 2009.

[11] Peng W-x, Wu Y-q, Zhang Z-f, Qi H-c, Ma Q-z. Effect of Nano SiO(2) on Pyrolytic Reaction of Phenol-Formaldehyde Resin, IEEE, 2009.

[12] Zhang Y, Zhang Y, He L, Zhou Z. Cure rate of Phenol–Formaldehyde (PF) resol resins catalyzed with MgO. J Adhes Sci Technol 2007;21:833–9.

[13] Ma Q-z, Peng W-x, Zhang D-q, Liu Q-m, Chen H., Effect of nano TiO_2 on state of cure and pyrolytic reaction of phenol-formaldehyde resin, In: Proceedings of the 3rd IEEE International Conference on Nano/Micro Engineered and Molecular Systems p. 574–77,2008.

[14] Veigel S, Müller U, Keckes J, Obersriebnig M, Gindl-Altmutter W. Cellulose nanofibrils as filler for adhesives: effect on specific fracture energy of solid wood-adhesive bonds. Cellulose 2011;18:1227.

[15] Kumar A, Gupta A, Sharma K, Nasir M. Use of aluminum oxide nanoparticles in wood composites to enhance the heat transfer during hot-pressing. Eur J Wood Prod 2013;71:193–8.

[16] Gao W, Du GB. Curing kinetics of nano cupric oxide (CuO)-modified PF resin as wood adhesive: effect of surfactant. J Adhes Sci Technol 2013;27:2421–32.

[17] Wei C, Zeng M, Xiong X, Liu H, Luo K, Liu T. Friction properties of sisal fiber/nano-silica reinforced phenol formaldehyde composites. Polym Compos 2015;36:433–8.

[18] Lei H, Du G, Pizzi A, Celzard A, Fang Q. Influence of nanoclay on phenol-formaldehyde and phenol-urea-formaldehyde resins for wood adhesives. J Adhes Sci Technol 2010;24:1567–76.

[19] Mallakpour S, Khadem E. Recent development in the synthesis of polymer nanocomposites based on nano-alumina. Prog Polym Sci 2015;51:74–93.

[20] Alsharif SO, Akil HBM, El-Aziz NAA, Ahmad ZAB. Effect of alumina particles loading on the mechanical properties of light-cured dental resin composites. Mater Des 2014;54:430–5.

[21] Fang L, Wu C, Qian R, Xie L, Yang K, Jiang P. Nano–micro structure of functionalized boron nitride and aluminum oxide for epoxy composites with enhanced thermal conductivity and breakdown strength. RSC Adv 2014;4:21010–7.

[22] Vaisakh SS, Mohammed P, Azeez A, Hassanzadeh M, Tortorici JF, Metz R, et al. Effect of nano-modified SiO2/Al2O3 mixed-matrix micro-composite fillers on thermal, mechanical, and tribological properties of epoxy polymers. Polym Adv Technol 2016;27:905–14.

[23] Koli DK, Agnihotri G, Purohit R. A review on properties, behaviour and processing methods for Al-nano Al 2 O 3 composites. Procedia Mater Sci 2014;6:567–89.

[24] Kaboorani A, Riedl B. Nano-aluminum oxide as a reinforcing material for thermoplastic adhesives. J Ind Eng Chem 2012;18:1076–81.

[25] Dabbagh HA, Shahraki M. Mesoporous nano rod-like γ-alumina synthesis using phenol–formaldehyde resin as a template. Microporous Mesoporous Mater 2013;175:8–15.

[26] Lei H, Du G, Wu Z, Xi X, Dong Z. Cross-linked soy-based wood adhesives for plywood. Int J Adhes Adhes 2014;50:199–203.

[27] Dabbagh HA, Shahraki M. Mesoporous nano rod-like γ-alumina synthesis using phenol–formaldehyde resin as a template. Microporous Mesoporous Mater 2013;175:8–15.

[28] Farag HK, Endres F. Studies on the synthesis of nano-alumina in air and water stable ionic liquids. J Mater Chem 2008;18:442–9.

[29] Lei Y, Wu Q, Lian K. Cure kinetics of aqueous phenol–formaldehyde resins used for oriented strandboard manufacturing: analytical technique. J Appl Polym Sci 2006;100:1642–50.