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**Reduction of formaldehyde emission from plywood using composite resin composed of
resorcinol-formaldehyde and urea-modified scallop shell nanoparticles**

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Abstract: More than 200,000 tons of scallop shells are disposed annually alone in Japan. Nanoparticles derived from scallop shells have the potential to adsorb gaseous formaldehyde; therefore such discarded shells have now been tested as additive filler in plywood adhesive by mixing high specific surface area, urea-modified shell nanoparticles with a resorcinol–formaldehyde resin; with this procedure it was found that the emission of formaldehyde from the resulting plywood could be substantially reduced. The urea-modified scallop shell nanoparticles were prepared by two different methods: (i) by a dry method in which the shells were treated with planetary ball-grinding under ambient conditions — a completely dried powder was obtained after addition of the surface-modifying urea solution; (ii) by a moist method by treating dry-ground shell particles in a wet grinding process with the urea solution, followed by the use of centrifugation to obtain a paste. The specific surface area of the nanoparticles obtained by both treatments was $42 \pm 3 \text{ m}^2/\text{g}$. Measurement of the subsequent formaldehyde emission showed that the addition of the modified scallop shell nanoparticles substantially reduced the formaldehyde emission from plywood; the reduction depends from the specific mass uptake of urea on the nanoparticles which especially was the case when resins containing nanoparticles processed by the moist method were used.

Keywords: Nanosized scallop shell, Formaldehyde, Resorcinol-formaldehyde resin, Plywood, Specific surface area.

1. Introduction

Resorcinol–formaldehyde resins (RF) are used in laminated veneer lumber and laminated wood, yielding excellent durability and thermo-stability. However, all formaldehyde-based adhesives are known to emit formaldehyde, which was reclassified in 2004 as a Group 1 human carcinogen by the International Agency for Research on Cancer (IARC); as a consequence it is extensively regulated in indoor environments (IARC 2006). Several plywood adhesives emit formaldehyde due to hydrolysis of weak chemical bonds both during the production of wood-based materials and during long-term use. Therefore, standards for regulation of the formaldehyde emission have been implemented, such as in Europe (EN 13986: 2005), Australia and New Zealand (AS/NZS 1859.1&2: 2004), USA (ANSI A 208.1&2: 2009), or Japan (JIS A 5905&5908: 2003). In order to reduce the formaldehyde emission from wood-based materials, scavengers such as natural compounds (Kim 2009; Kim et al. 2006), bisulfite salt (Costa et al. 2012; Costa et al. 2013), amine compounds (Boran et al. 2011), and urea (Park et al. 2008) have been proposed. Among these scavengers, urea is the most adaptable compound due to its high reactivity with formaldehyde and its low price; however, addition of urea can decrease the reactivity of the resins and considerably reduce the adhesive strength.

Scallop shells are a waste product from the seafood industry; Japan annually produces *ca.* 200,000 tons of scallop shell waste per year. Many applications for this material have been proposed, such as desulfurization (Kim et al. 2002), skin protection (Liu et al. 2002), phosphate removal (Yeom and Jung 2009), heavy metal adsorption (Abdallah and Gagnon 2009; Ghimire et al. 2008), nutrition supplements (Liu and Hasegawa 2006), and antibacterial agents (Sawai et al. 2001; Sawai and Shiga 2006; Jeong et al. 2007; Xing et al.

2013). With these research efforts high added value could be achieved for a traditional waste product, hence contributing to a shift towards more sustainable social and economic development. In a previous paper, it was demonstrated that scallop shells have potential to adsorb gaseous formaldehyde (Yamanaka et al. 2013). A simple nano-grinding method had been described, in which nano-sized scallop shell particles with high specific surface area ($\sim 50 \text{ m}^2/\text{g}$) are prepared by planetary ball milling under dry conditions, followed by water addition in order to exceed the limitations of dry grinding.

The aim of the work reported here was the effective use of discarded scallop shells as a filler of plywood adhesive; a new composite RF based adhesive system had to be developed which exhibits both, low formaldehyde emission and high adhesive strength; this aim should be achieved by mixing urea-modified shell nanoparticles with their high specific surface area into a standard RF resin. Formaldehyde emission and adhesive strength of plywood bonded by means of this adhesive system were tested, followed by discussion of the effects of urea absorption and dispersibility of the shell particles within the RF resin on the emission of formaldehyde.

2. Experimental procedure

2.1 Materials

Curing agent (TD-473, main component is paraformaldehyde) and RF resin (non-volatile content *ca.* 58 mass%) were provided by DIC Kitanihon Polymer, Japan. According to the manufacturer, the gel time of this RF resin is 35-50 min at 30°C. The apparent viscosity of the RF resin measured using a viscometer (DV-1 Prime RV, Eko instruments, Japan) was 0.6 Pa·s at 25°C. Scallop shell powder was purchased from

1 Tokoro-cho Industry Promotion Public Corporation (Kitami, Japan). The feed shell powder
2 was mainly composed of the calcite phase of calcium carbonate. The median particle size
3 and the specific surface area of the powder were 20 μm (corresponding to a 50 mass%
4 diameter) and 1.5 m^2/g , respectively. The specific surface area was determined by nitrogen
5 gas adsorption based on the BET method (AdsotracDN-04, Nikkiso, Japan).

6 7 *2.2 Mechanical grinding*

8 To prepare a nano-sized powder with high specific surface area, a nano-grinding
9 procedure was followed as described in detail elsewhere (Yamanaka et al. 2013). Briefly,
10 92.7 g of the dried feed shell powder was sealed in an yttria-stabilized zirconia pot with a
11 volume of 500 cm^3 , filled with 669 g of commercially available yttria stabilized zirconia
12 beads (Nikkato Corporation, Japan) with diameters of 3.0 mm as grinding media. Dry
13 grinding was performed under atmospheric conditions using a planetary ball mill (P-6,
14 Fritsch, Germany). The rotation of the pot was set to 400 rpm for 8 hours dry grinding, 100
15 ml of distilled water or of an aqueous urea solution were added into the milling pot.

16 In this study, surface-modified shell powders were prepared following two methods
17 (**Table 1**). In the so-called dry method, 100 ml of an aqueous urea solution with
18 concentrations 1.0 and 15.0 w%, resp., was added to the ground shell, with pure water as
19 control. The suspension was immediately removed from the milling pot, centrifuged at
20 1095 G (Type 5800, Kubota, Japan), and dried at 60°C in an oven to yield the modified,
21 high-surface area shell powder. For the so-called moist technique again 100 ml of the same
22 aqueous urea solutions and again with pure water as control were added to the ground shell,
23 and further wet grinding was carried out for 1 hour in order to crack the agglomerated shell

particles. The suspension was then centrifuged at 1095 G in order to get a paste like material. The water content of the moist sample was measured using thermogravimetric-differential thermal analysis (TG-DTA, Exstar 6200N, Seiko Instruments, Japan), yielding a weight loss of 46.3 mass% at 100 °C. TG-DTA measurements were conducted under atmospheric conditions at a ramp of 2 K/min. It should be noted that modified-shells from the moist method could be uniformly distributed in the RF resin, whereas the dry modified-shells (dry method) showed difficulties in redispersing the dried and agglomerated shell particles into the RF resin: the effects of the preparation method on dispersibility of the shell particles into the RF resin and on formaldehyde emission are discussed in Section 3.2. The specific surface area of these samples is summarized in **Table 1**.

To estimate the urea adsorption on the shell particles, FTIR spectra (FT/IR-460PlusK, JASCO, Japan) were acquired using a KBr pellet technique with a scan range from 600 to 2000 cm⁻¹. The KBr pellets contained 1–2 mass% of shell particles.

2.3 Plywood preparation and analysis

120 g RF resin (nonvolatile content weight was 69.6 g), 58.3 g shell nanoparticles (as dry weight), 18.0 g curing agent (manufacturer's recommended value), and water (added to produce a total weight of 246.0 g) was stirred using a propeller-type impeller at 1,200 rpm for 10 min. The proportion of the shell nanoparticles was 46% based on the sum of RF resin solid plus the shell nanoparticles. The apparent viscosity of the resulting composite resin were 0.7-2.1 Pa·s at 25°C. 34.5 ± 0.8 g of the resulting composite resin were spread on a 320×320×2.0 mm³ piece of veneer (*Abies sachalinensis*; grown in Hokkaido, Japan). 2-ply

boards were prepared by hot pressing for the formaldehyde emission test, and 3-ply boards for bonding quality tests. The pressing temperature, specific pressure, and time were set to 60°C, 0.8 MPa, and 10 min, respectively, independently of the type of the plywood.

The formaldehyde emission was measured by the desiccator method (JIS A 1460: 2001); the absorbance was measured with the acetylacetone method at 415 nm using a UV-Vis spectrophotometer (UV-2400PC, Simadzu, Japan). The emission tests were performed 6 times for the control RF resin and 3 times for the scallop shell–RF composite resins, respectively.

The bonding quality of the prepared plywood was measured by the cyclic steaming test (JAS 233: 2003). In each test, bonding strength was assessed for 10 pieces under wet conditions by measuring the maximum load.

We also tested the bonding quality and the formaldehyde emission using control RF resin without the shell powder in order to demonstrate the effect of the shell particles within the RF resin on the bonding strength and the formaldehyde emission.

3. Results and discussion

3.1 Characterization of modified-scallop shell particles

Figure 1 depicts typical scanning electron microscope (SEM) images of the shell particles according to the dry procedure and the moist procedure, resp. As mentioned above, the dry shell particles were obtained after dry grinding for 8 hours followed by water recovery; the moist shell particles were prepared by wet grinding for 1 hour in addition to 8 hours dry grinding (see Section 2.2). Both types of shell particles were found to possess specific surface areas of $42 \pm 3 \text{ m}^2/\text{g}$ (see Table 1), and particle sizes of 50 to 100 nm. This

primary particle size was in good agreement with the calculated equivalent diameter $d_{SSA}=60$ nm according to the equation $d_{SSA}=6/(\rho_p \times SSA)$, with ρ_p density of the feed scallop shell (2440 kg/m³ measured using a pycnometer) and SSA specific surface area. Without the solution (distilled water or aqueous urea) recovery process, the specific surface area of the ground product was measured to be only 6.5 m²/g, which is a usual value for dry grinding of calcite crystal (Tsai et al. 2008). The specific surface area increased to the above mentioned 42 m²/g on addition of either distilled water or the aqueous urea solution to the dried product, independent if there was additional wet grinding after dry grinding and addition of the solutions or not. In contrast, when the shells were processed solely by wet grinding for 1 hour, the specific surface area was as low as *ca.* 10 m²/g, which is good agreement with reported values for the wet grinding of calcium carbonate (He et al. 2006). As shown in the SEM micrographs in Fig. 1, the dry ground shells partially form aggregates (10 µm or more in size, Fig. 1a). The particle size distribution was measured using a laser-diffraction analyzer (MicroTrac MT3000EX, Nikkiso, Japan); these results were in agreement with the SEM observation; the samples exhibit a broad particle size distribution ranging from sub-micron to values of several tens of microns with the 50 mass% diameter at 14.3 µm. Particles according to the wet grinding method had sizes from sub-micron to a few microns in size as shown in Fig. 1b, with the 50 mass% diameter of *ca.* 1.5 µm. Although both types of shell particles form aggregates, we expected that the coarse aggregates as observed in the dry ground shells could be disintegrated by the wet grinding. The coarse aggregates were cracked during the wet grinding process as expected. It should be noted that although these distributions reflect the material's dispersibility within the RF resin, there is only small influence either on the overall formaldehyde emission or on the

1 adhesive strength of the composite resin (see Section 3.2).

2 FTIR spectra of the sample powders (**Figure 2**) show the internal modes of the
3 carbonate ion in calcite ($710, 875\text{ cm}^{-1}$) and the combinations (1795 cm^{-1}) of symmetric CO
4 stretching and OCO bending mode (Andersen and Brečević 1991). The absorption peak at
5 1668 cm^{-1} (CO stretching, Barlow and Corish 1959), and 1627 cm^{-1} (NH vibrations, Piasek
6 and Urbański 1962) is due to urea adsorption, with increasing intensity of these peaks with
7 higher concentration of the urea solution. Additionally, the intensities of these urea peaks
8 were seen to be much higher for the particles processed by the moist method (with the 15.0
9 w/v% urea solution) compared with those obtained by dry method.

10 Urea undergoes multi-stage decomposition to carbon dioxide and ammonia at
11 temperatures between 100 and 400°C (Chen and Isa 1998; Schabera et al. 2004); therefore,
12 the amount of adsorbed urea was estimated using TG-DTA from the powder weight loss in
13 the range 100 to 500°C (at a ramp of 2 K/min) under atmospheric conditions. From these
14 results, the mass ratio of urea to total weight was calculated: for the urea solution
15 concentration of 1.0 w/v\% , the mass ratios for the dry and the moist method were 0.37 and
16 0.81 w/w\% , resp.; for the 15.0 w/v\% solution the ratios were 3.9 and 10.3), resp. These data
17 suggest that urea adsorbed on the shell surfaces during urea treatment, and that the
18 additional wet grinding step is the more efficient method for modification of the shell
19 particle surfaces.

21 **3.2 Formaldehyde emission from plywood**

22 The specific surface area of the various powders, the adsorbed amount of urea, and the
23 formaldehyde emission from the tested plywood are summarized in **Table 1. Figure 3**

shows the formaldehyde emission as a function of urea solution concentration: the emission from the boards with the control RF resin was 11.4 ± 3.0 mg/L, whereas the resin with unmodified shell particles gave 9.5 ± 1.1 mg/L as result, showing that the high surface-area, nano-sized shell particles scavenge 17% of the formaldehyde emitted by the control RF resin.

When the dry method particles treated with 1.0 and 15.0 w/v% urea solution, resp., were incorporated into the RF resin, the emission decreased slightly to 8.7 ± 0.2 and 7.5 ± 0.1 mg/L, resp. For the moist method particles treated by wet grinding in 1.0 w/v% urea solution the emission was 9.2 ± 1.8 mg/L; for the 15.0 w/v% urea solution the emission was significantly reduced to 3.9 ± 0.4 mg/L (**Fig. 3b**); this means an overall emission reduction of around 60% compared with the control samples with unmodified powder (9.5 ± 1.1 mg/L); the upper limit of F** class is 1.5 mg/L according to JIS A 5905&5908: 2003.

The question arises, if these results might be explained by both, the dispersibility of the particles within the RF resin as indicated in Fig. 1, and by the adsorbed amount of urea on the shell surface. **Figure 4** depicts typical Ca intensity distribution within the RF resin as measured by SEM-EDS (SEM-energy dispersive x-ray spectroscopy). The Ca intensity of the RF resin obtained via dry and moist method treated with 15.0 w/v% urea solution (calculated from each 10 measurements) were 381 ± 331 and 433 ± 193 cp, respectively, and their coefficients of variation were 0.87 and 0.45. The judgment for dispersibility of shell particles was based on coefficients of variation because average values are proportional to scanning time, Ca concentration within the RF resin, and so on. The value of coefficient of variation for moist method was only half compared to that for dry method. These data reveal that scallop shell nanoparticles prepared by the moist method were better

1 uniformly distributed for modified particles. As mentioned above, the particle processing
2 methods had a pronounced effect on the adsorbed amount of urea: from this point of view,
3 formaldehyde emission was positively correlated with the surface urea adsorption as shown
4 in **Fig. 5**.

5 For the dry and moist method particles using 1.0 w/v% urea solution the amount of
6 adsorbed urea were 0.37 and 0.81 w/w%, respectively (see Table 1). Although these two
7 samples **may differ** in the dispersibility of the particles within the RF resin **as expected**
8 **above SEM-EDS measurement**, the formaldehyde emission amount of both samples ($8.7 \pm$
9 0.2 mg/L for the dry method, and 9.2 ± 1.8 mg/L for the moist method) was almost same.
10 Compared to the control (unmodified powder) this is only a small decrease of 8% and 3%,
11 resp. This is linked with the only small absorbed amount of urea. On contrary, with the
12 much higher amounts of absorbed urea (based on the treatment with the 15% urea solution)
13 and especially the highest absorption on the moist method powder, the emission decreases
14 by 21% and 59%. Based on these results it looks like that the main influence on the
15 formaldehyde emission is based on the amount of urea absorbed on the powder surface.
16 **Because particle surface characteristics have significant impact on the dispersion behavior, the**
17 **effects of a wet grinding time on the adsorbed amount of urea and the dispersibility of the shell**
18 **particles within the RF resin will be investigated in the near future.**

19 Urea is an excellent formaldehyde scavenger **(see Table 2)**. However, the adhesive
20 strength of the resin decreased with increasing urea content. As shown in Table 2, plywood
21 treated with RF resins containing more than 1.0 w/w% urea failed the strength test, whereas
22 the presence of either the dry or moist scallop shell particles exceeded the level required by
23 the standard of adhesive force (0.7 MPa, JAS 233: 2003).

1 In RF resins the bond between the resorcinol monomers and formaldehyde is very
2 strong; however RF cannot cure unless additional formaldehyde is added. This
3 formaldehyde originating from the added paraformaldehyde reacts with the resorcinol end
4 groups in the RF and perform the cross linking during curing. If urea is mixed directly into
5 the liquid RF resin, this urea competes with the resorcinol moieties in the reaction with the
6 added formaldehyde. Although quite a high addition of curing agent took place (15 w/w%
7 based on liquid RF resin), this competing reaction of the mixed urea can slow down the
8 curing reaction and, hence, decrease the bond strength in the cycling steaming test.

9 According to the manufacturer of the RF resin (DIC Kitanihon Polymer, Japan), the
10 curing reaction proceeds at room temperature and can be almost completed by hot-pressing
11 treatment for around 10 minutes at 60°C.

12 However, due to the big proportion of added paraformaldehyde, residual formaldehyde
13 will remain in the boards as subsequent formaldehyde emission. For resins containing urea,
14 formaldehyde emission is reduced as the urea is an effective scavenger; however, this is an
15 extremely fast reaction which also inhibits the curing reaction, hence the non-shell,
16 urea-containing RF resins possess poor adhesive properties. In contrast, the urea adsorbed
17 on the shell particles cannot react so easily with the RF resin, because it is not entirely
18 mixed with the resin; therefore the adhesive strength of resins containing these particles is
19 not compromised as the curing reaction is not inhibited to the same degree. However, after
20 the press process and the hardening of the resin, gaseous formaldehyde remaining from the
21 addition of paraformaldehyde and having not reacted during the curing reaction of the RF
22 resin might react with the urea absorbed on the shell particles.

4. Conclusion

It was shown that the modification of a RF resin with urea-coated scallop shell nanoparticles reduces the formaldehyde emission from plywood. The lowest formaldehyde emission was 3.9 ± 0.4 mg/L, which, however, is still above the emission limit of the F** class. The urea-modified scallop shells could prevent a decrease in adhesion strength, which usually is the main drawback of the use of urea as formaldehyde scavenger. In addition, the overall formaldehyde emission was observed to depend strongly on the amount urea adsorbed on the shell nanoparticle surface.

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Figure captions

Fig. 1. SEM images of scallop shell particles processed by (a) dry method, and (b) moist method. Both types of shell particles were found to possess specific surface areas of 42 ± 3 m²/g (see Table 1), and particle sizes of 50 to 100 nm. The median particle size of both aggregates measured using a laser-diffraction analyzer was 14.3 μ m for the dry method, and 1.5 μ m for the moist method.

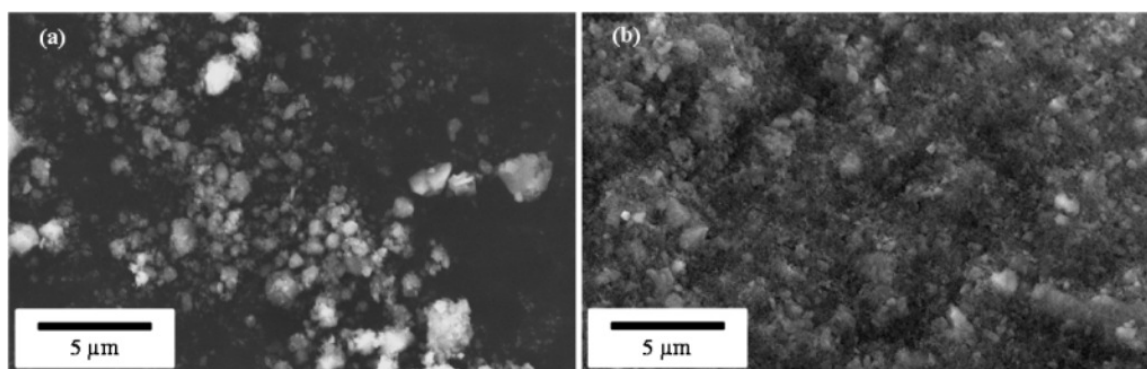
Fig. 2. FTIR spectra of (a) dry method, and (b) moist method scallop shell powder.

Fig. 3. Formaldehyde emission as a function of urea solution concentration: (a) dry method, and (b) moist method shell particles. Black filled circle, and triangle denote the control RF resin without any addition of powder, and with unmodified shell sample obtained by dry method, respectively.

Fig. 4. SEM-EDS measurement of Ca intensity distribution in the RF resin. (a) dry method, and (b) moist method shell particles.

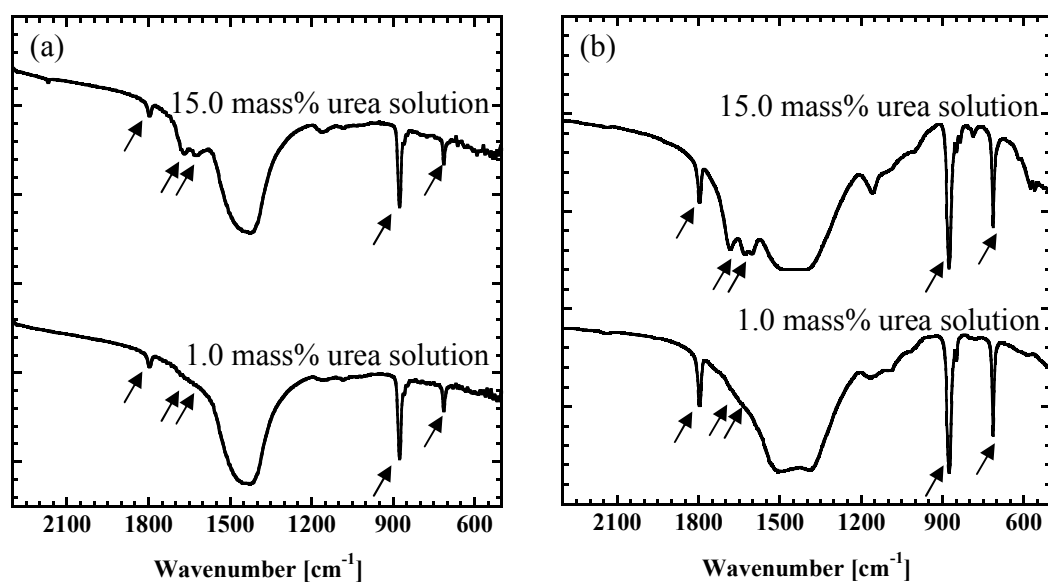
Fig. 5. Relation between formaldehyde emission and adsorbed amount of urea. The adsorption amount was the ratio of urea to the shell particles. Black filled triangle denotes unmodified shell sample obtained by dry method.

Fig. 1



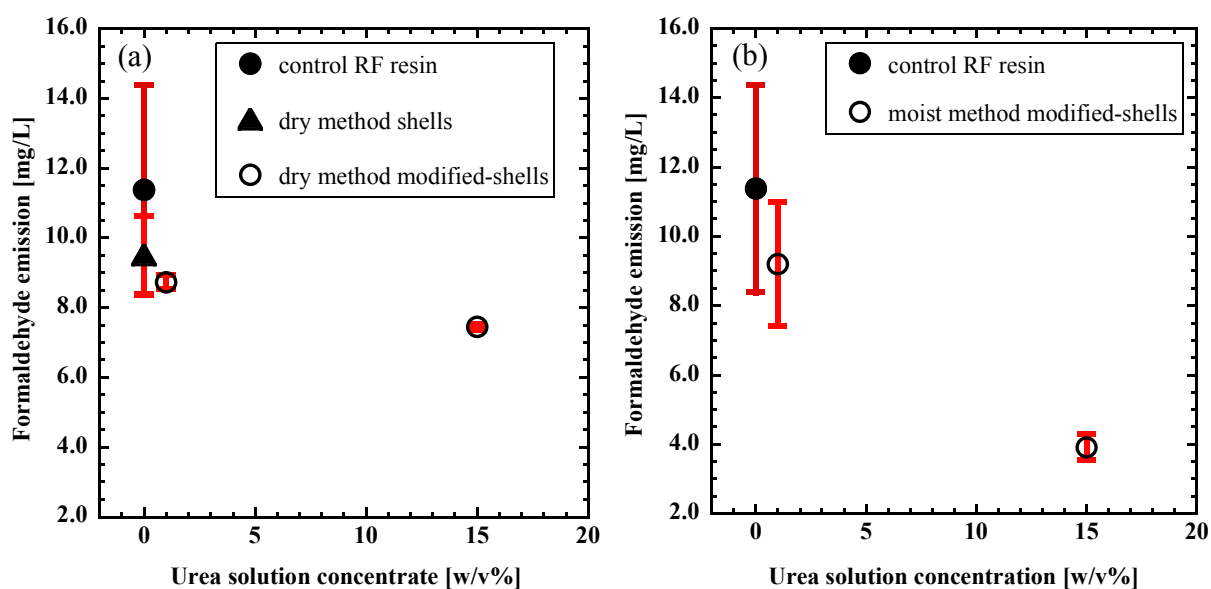
SEM images of scallop shell particles processed by (a) dry method, and (b) moist method. Both types of shell particles were found to possess specific surface areas of $42 \pm 3 \text{ m}^2/\text{g}$ (see Table 1), and particle sizes of 50 to 100 nm. The median particle size of both aggregates measured using a laser-diffraction analyzer was 14.3 μm for the dry method, and 1.5 μm for the moist method, respectively.

Fig. 2



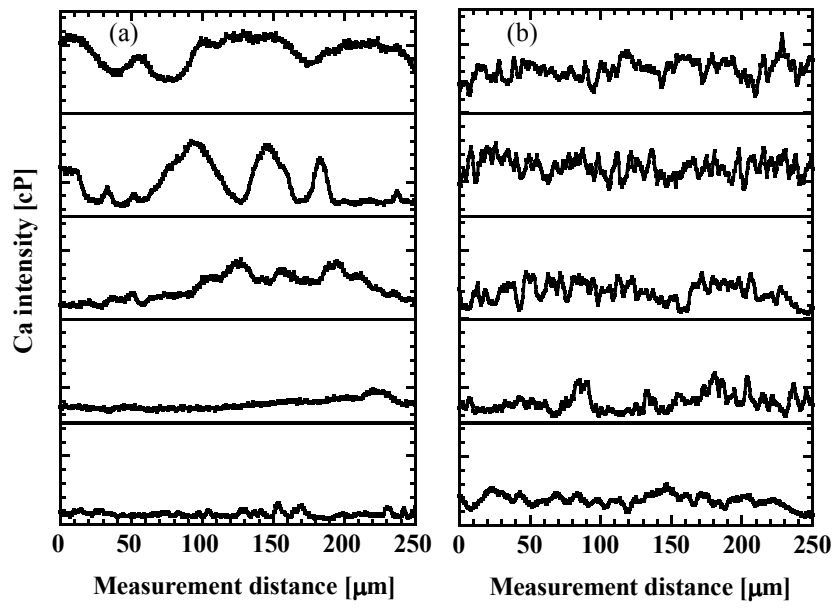
FTIR spectra of (a) dry method, and (b) moist method scallop shell powder.

Fig. 3



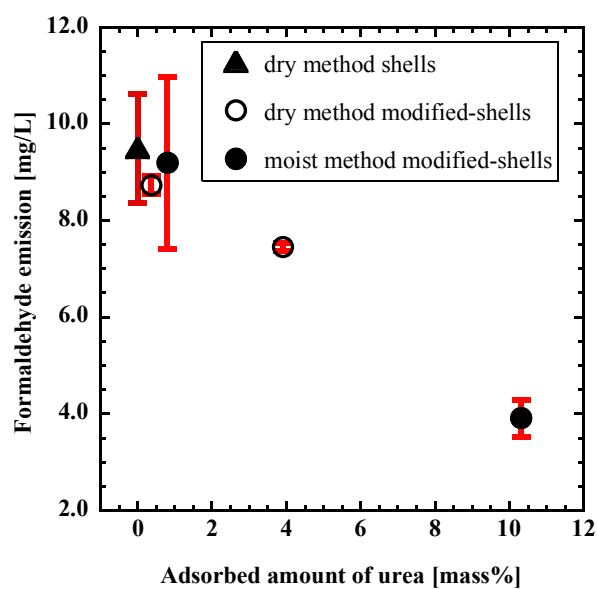
Formaldehyde emission as a function of the urea solution concentration. (a) dry method samples, and (b) moist method samples. Black filled circle, and triangle denote the control RF resin without any addition of powder, and with unmodified shell sample obtained by dry method, respectively.

Fig. 4



SEM-EDS measurement of Ca intensity distribution into the RF resin. (a) dry method samples, and (b) moist method samples.

Fig. 5



Relation between formaldehyde emission and adsorbed amount of urea. The adsorption amount was the ratio of urea to the shell particles. Black filled triangle denotes unmodified shell sample obtained by dry method.

Table 1 Particle features of shell powder prepared by dry and moist method

Sample	Dry	Wet	Conc. of urea	Specific surface	Adsorbed amount	Formaldehyde
	grinding	grinding	sol.	area	of urea	emission
	[h]	[h]	[w/v%]	[m ² /g]	[w/w%]**	[mg/L]
	8	0	0	47	0 (0.0)	9.5 ± 1.1
Dry collection	8	0	1.0	41	0.37 (0.18)	8.7 ± 0.2
	8	0	15.0	42	3.91 (1.90)	7.5 ± 0.1
Moist	8	1	1.0	42	0.81 (0.39)	9.2 ± 1.8
collection	8	1	15.0	38	10.32 (5.01)	3.9 ± 0.4
Control RF	—	—	0	—	—	11.4 ± 3.0
resin	—	—	1.0*	—	—	5.1 ₉ ± 0.0 ₂
	—	—	5.0*	—	—	5.2 ± 0.1

* denotes the weight ratio [w/w%] of urea to the RF resin.

** the number in parentheses denotes the weight ratio [w/w%] of urea to the RF resin.

Table 2 Adhesive strength test results

Sample	Dry	Wet	Conc. of urea sol.	Shear strength	Minimum shear	Percent wood
	grinding	grinding	[w/v%]	[MPa]	strength	failure[%]
	[h]	[h]			[MPa]	
Dry collection	8	0	0	1.63 ± 0.19	1.37	55 ± 26
	8	0	1.0	1.50 ± 0.17	1.23	57 ± 25
	8	0	15.0	1.33 ± 0.22	1.05	76 ± 16
Moist collection	8	1	1.0	1.24 ± 0.08	1.08	85 ± 11
	8	1	15.0	1.36 ± 0.21	1.07	45 ± 23
Control RF resin	—	—	0	1.00 ± 0.24	0.37	57 ± 24
	—	—	1.0*	0.96 ± 0.15	0.71	76 ± 23
	—	—	5.0*	Fail	—	—

* denotes the weight ratio [w/w%] of urea to the RF resin.