FUNGAL RESISTANCE OF PLYWOOD PRODUCED FROM BEECH VENEERS TREATED WITH N-METHYLOL MELAMINE COMPOUNDS AND ALKYL KETENE DIMER

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ABSTRACT

Rotary cut Beech (Fagus sylvatica. L) veneers with dimension of 1.5 × 400 × 400 mm³ (rad × tang × long) were impregnated with three chemicals: N-methylol melamine (NMM-1 - 10% solid content), fatty acid modified N-methylol melamine/paraffin compound (mNMM-2 - 5% solid content), alkyl ketene dimer (AKD - 1% solid content). The impregnated veneers were pre-dried in a drying-oven at 40°C, 24 h to a moisture content of 3-8% before glue spreading. An amount of 160 g m^{-2} PF glue was applied per veneer. Afterwards, 5-layer-plywood was produced in a hot press (130°C) at 1.5 MPa (10 min pressing time). The resistance against white rot fungus (Pleurotus ostreatus) and brown rot fungus (Coniophora puteana) of the plywood was performed according to the ENV 12038. The plywood treated with 10% solid content of NMM-1 solution disclosed high protection to the brown rot fungus C. puteana and the white rot fungus P. ostreatus. While the treatment of veneers with 5% mNMM-2 and catalyst RB (an aluminium salt) imparted medium resistance to plywood against P. ostreatus and no resistance to C. puteana. The veneer treatment with 1% solid content of AKD totally failed to protect plywood from the brown rot fungus C. puteana and the white rot fungus P. ostreatus after 16 weeks of incubation.

Keywords: *alkyl ketene dimer, beech veneer, fungal resistance, N-methylol melamine.*

TÓM TẮT

Ván mỏng bóc từ gỗ Dẻ gai (Fagus sylvatica. L) với kích thước 1,5 × 400 × 400 mm³ (XT × TT × DT) được ngâm tẩm với 3 loại hóa chất: N-methylol melamine (NMM-1-sử dụng ở hàm lượng rắn 10%), fatty acid modified N-methylol melamine/paraffin (mNMM-2-sử dụng ở hàm lượng rắn 5%), alkyl ketene dimer (AKD - sử dụng ở hàm lượng rắn 1%). Ván mỏng sau khi ngâm tẩm được sấy trong lò sấy ở nhiệt độ 40°C, thời gian 24 h tới độ ẩm 3-8%. Tiếp theo, ván mỏng được tráng keo phenol formaldehyt (PF) với lượng keo 160 g/m² rồi sản xuất ván dán 5 lớp ở chế độ ép: 130°C, áp suất 1,5 MPa, thời gian ép: 10 phút. Khả năng kháng nấm mục trắng (Pleurotus ostreatus) và nấm mục nâu (Coniophora puteana) của ván dán được đánh giá theo tiêu chuẩn ENV 12038. Kết quả nghiên cứu cho thấy: ván dán biến tính với dung dịch NMM- ở hàm lượng rắn 10% có khả năng chống nấm mục nâu C. puteana và nấm mục trắng P. ostreatus rất tốt. Trong khi đó, ván dán sản xuất từ ván mỏng biến tính với mNMM-2 (hàm lượng rắn 5%) và chất xúc tác RB (muối nhôm) có khả năng kháng nấm mục trắng P. ostreatus ở mức độ trung bình và ít có khả năng kháng nấm mục nâu C. puteana. Ván mỏng xử lý với 1% hàm lượng rắn của AKD không đem lại hiệu quả chống nấm mục nâu C. puteana và nấm mục trắng P. ostreatus cho ván dán biến tính sau 16 tuần ủ trong các loại nấm này.

Từ khóa: *alkyl ketene dimer, beech, khả năng kháng nấm, N-methylol melamine.*

INTRODUCTION

Wood decay fungi and wood staining fungi cause considerably economical damage for wood in service. Decay fungi induce significant mass and strength loss of wood due to serious degradation of cell wall constituents (hemicellulose, cellulose and lignin). The most important conditions for fungal growth in wood are: the wood substrate can be metabolized by the fungi, and the moisture content of the

substrate must be above a certain threshold (above 20% moisture content); in addition, there are requirements about temperature, oxygen and pH value of the environment (Eaton and Hale, 1993; Haygreen and Bowyer, 2003).

Over a long time, several methods have been applied to wood in order to increase the fungal degradation resistance. In addition to the conventional treatment of wood with biocidal preservatives, it is well established that chemical modification of wood is able to provide protection against fungal attack (Hill, 2002; Rowell, 1983). The protection against decay of chemically modified wood is considered to be explained by three mechanisms: (a) the moisture content of wood cell wall is not sufficiently high for fungal growth; (b) changes of the cell wall polymers (due to substitution of hydroxyl groups) become unrecognizable for enzymes; (c) physical blockage of the cell wall pores inhibits the accessibility of enzymes (Hill, 2002; Militz et al., 1997; Rowell, 2005). There have been several studies on the decay protection mechanisms of modified wood such as: anhydride modified wood (Hill and Hale, 2004; Hill et al., 2006; Hill and Kwon, 2009), acetylated wood (Mohebby, 2003; Rowell et al., 2009), DMDHEU modified wood (Trinh Hien Mai et al., 2009; Verma et al., 2009), N-methylol melamine modified veneer (Trinh Hien Mai, 2013). In all cases, the decay resistance is mostly related to the degree of cell wall bulking which lowers the moisture content of the cell wall which becoming too low to support the fungal attack.

The plywood produced from beech veneers treated with two N-methylol melamine formulations and AKD dispersions at different solid contents exhibited bonding quality above the requirements of plywood used in non-covered exterior conditions (Trinh Hien Mai et al, 2012a). Both N-methylol melamine formulations resulted in high water repellence and dimensional stability of plywood specimens during cyclic water submersion and drying-procedure (Trinh Hien Mai et al, 2012b). In this study, decay resistance of plywood produced from beech veneers treated with 2 types of N-methylol melamine compounds and alkyl ketene dimer was evaluated with white rot fungus *Trametes versicolor* and brown rot fungus *Coniophora puteana* according to the ENV 12038.

MATERIAL AND METHODS

Chemicals for veneer modification

Methylated N-methylol-melamine (NMM-1*)* is Madurit MW 840/75 WA (produced by Ineos Melamines company, Frankfurt/ Main, Germany). It is supplied as an aqueous stock solution with a solid content of approx. 75% (determined by evaporation of water at 120°C for 1 h). The dynamic viscosity of the formulation is 430 mPa s, the density 1,256 g ml^{1} and the pH-value 9.3 (all values at 25°C). NMM-1 is partly methylolated (with residual amino groups of the melamine) and partly methylated; the behaviour of NMM-1, hence, is rather hydrophobic, but still with possibility of hardening.

The fatty acid modified Nmethylolmelamine formulation containing paraffin (mNMM-2) is Phobotex VFN (produced by Ciba company, Basel, Switzerland). It is a white, slightly cationic emulsion with a pH-value of 5.3 and a specific gravity of 0.991 g ml^{1} at 25°C. Due to the modification with fatty acid and the addition of paraffin the substance shows predominately hydrophobic character. An aluminium salt catalyst solution (Catalyst RB, produced by Ciba company, Basel, Switzerland) is used for the curing of Phobotex VFN.

Alkyl ketene dimer (AKD) is Basoplast AKD delivered by BASF company. It is a fatty acid in form of a white dispersion with average pH value from 3.5 - 4.5. AKD is hydrophobization of paper, especially when made under alkaline conditions. AKD is widely used for liquid containers, ink-jet printing paper, and many other grades of paper and paperboard. AKD is especially favored for products that need to resist water over a long period.

Plywood production

Rotary cut beech (*Fagus sylvatica* L.) veneers with thickness of 1.5 mm were cut in sizes of 1.5 × 400 × 400 mm^3 (rad × tang × long).

Then, the beech veneers were impregnated in an autoclave under vacuum (60mbar) for 30 min and subsequently under pressure (12 bar) for 2 h with the prepared solutions as described in Table 1. Water impregnated veneers were used to produce control plywood.

Table 1. Chemical concentrations for impregnation of beech veneers to produce plywood

No	Chemical	Solid content (%)	Catalyst	Concentration (%)
1	NMM-1	10	-	-
2	mNMM-2	5	RB	1.9% (15% of mNMM-2 stock solution)
3	AKD	1	-	-

The impregnated veneers were pre-dried in a drying-oven at 40°C, 24 h to a moisture content of 3-8% before glue spreading. An amount of 160 g m^{-2} PF glue (Prefere 4976, delivered by Dynea, Norway) was applied per veneer using a roller. Afterwards, 5-layer-plywood was produced in a hot press (130°C) at 1.5 MPa (10 min pressing time). The prepared plywood was stored in a room condition for 3 days before cutting into different sizes as required for the tests.

Specimen preparation for fungal degradation test

The resistance against white rot fungus (*Pleurotus ostreatus*) and brown rot fungus (*Coniophora puteana*) of the plywood was performed according to the ENV 12038.

The plywood specimens were cut in sizes of 50 × 50 × t (mm^3) with the quantity as in Table 2.

Table 2. Number of plywood specimens for the fungal test according to the ENV 12038

Type of fungi	Plywood specimens	Replicates/ treatment
Coniophora puteana	Test plywood specimens	10
Pleurotus ostreatus	Test plywood specimens	10
	Mass plywood specimens	6
	Wetting plywood specimens	2
	Moisture content plywood specimens	5
	Total	33

As recommended from the previous works (Dieste et al., 2008; Van Acker et al., 2001), modified plywood glued with PF resin should be pre-leached before fungal test to remove unfixed chemicals and to reduce fungi inhibiting factors from the resin. Hence, the plywood specimens were submersed in water for 2 weeks with 9 water changes according to the EN 84 (weight loss 2-2.7%); then conditioned in a climate chamber 20°C and 65% RH until constant weight (about 4-5 weeks). At least 5 plywood specimens from each treatment were oven-dried to determine the moisture content at 20°C and 65% relative humidity (RH). From the weight of the specimens at 20°C and 65% relative humidity (RH) and their moisture content, the oven-dry weight of each plywood specimens before the fungal tests was calculated.

Besides test plywood specimens for each type of fungi and moisture content plywood specimens, the mass plywood specimens (specimens on agar for 16 weeks) and conditioned plywood specimens (specimens in a 20°C and 65% RH climate chamber for 16 weeks) were prepared to check the moisture content after the tests.

According to the ENV 12038, solid wood specimens from scots pine sapwood and beech were used as size control specimens and virulence specimens. They were conditioned in the climate chamber 20°C and 65% RH for 2 weeks before the tests. Their dimension and quantity are listed in Table 3.

Table 3. Dimension and quantity of wood specimens

Type of fungi	Wood species	Wood specimens	Dimension l x t x r (mm^3)	Replicates
Coniophora puteana	Scots pine sapwood	Virulence control specimens	50 × 25 × 15	12
		Size control specimens	50 × 50 × 7.5	10
Pleurotus ostreatus	Beech wood	Virulence control specimens	50 × 25 × 15	12
		Size control specimens	50 × 50 × 7.5	10

Procedure of the tests

The plywood and wood specimens were stored in plastic bags and sealed carefully before sterilization by gamma radiation (25 kGy, Gammaster, Netherlands). Under antiseptic condition, one or two specimens were placed into a culture vessel in which the white rot fungus *P. ostreatus* (FPRL 40C) or the brown rot fungus *C. puteana* (BAM Ebw. 15) were inoculated in malt-agar for 2-3 weeks. Moreover, the specimens were surrounded by previously sterilized vermiculite to maintain high moisture content environment in the vessels of the white rot fungus *P. ostreatus* test. These culture vessels were incubated in a culture room at 22 ± 1°C and 70 ± 5% RH for 16 weeks, after that mycelia were removed from surface of the specimens. To determine the moisture content of the specimens after the tests, the specimens were weighted as soon as they were cleaned, then oven-dried and weighted again. The weight loss caused by fungal attack was calculated from the oven-dry weight of the specimens before and after the tests as in Equation 1.

$$WL\ (\%) = \frac{(W_b - W_a)}{W_b} \times 100 \quad \text{(Equation 1)}$$

Where:

WL: Weight loss of veneer after the fungal incubation

W_b: Oven-dry weight of veneer at the beginning of the test

W_a: Oven-dry weight of veneer after the fungal incubation

RESULTS AND DISCUSSION

Resistance against the brown rot fungus *C. puteana*

After 16 weeks of incubation with *C. puteana*, the size control and virulence specimens from Scots pine wood presented high weight loss of 62.8% and 52.6%. While the control beech plywood specimens also got quite high weight loss of 44.1% (Figure 2A); these weight losses surpassed the minimum weight loss requirement according to the ENV 12038. Therefore, the results of the fungi test with *C. puteana* are to be seen as valid.

The size control and virulence Scots pine wood specimens were more easily attacked by *C. puteana* than the control beech plywood due to the differences in structure between the Scots pine solid wood specimens and beech plywood specimens; the softwood is more susceptible to *C. puteana* than the hardwood (Eaton and Hale, 1993). In addition, the PF resin, which is a relevant part of the weight of the plywood specimens (approx. 8%), is not attacked by fungi (Dieste et al., 2008).

The plywood treated with 10% solid content of NMM-1 solution imparted high resistance against *C. puteana* fungus, reflecting by a low weight loss after 16 weeks (only 4.2%). These results were in accordance with the outcome of fungi test for NMM-1 treated veneers (Trinh Hien Mai, 2013).

The weight losses of the plywood specimens treated with mNMM-2 (5% solid content, catalyst RB 1.9%) and AKD (1% solid content) were contrary to the weight loss of NMM-1 treatments; even they were a little bit higher

than those of control plywood (Figure 2A). The mNMM-2 and AKD treatments failed to protect plywood from *C. puteana,* whereas the veneers treated with mNMM-2 and AKD (at the same solid contents as in the treated plywood) brought about medium resistance against *C. puteana* (Trinh Hien Mai, 2013). These results might be attributed to the difference in the curing process of the veneers (2 h, 140°C in a drying-oven) and the combination of curing and pressing (130°C, 10 min, 1.5 MPa in a hot press) of the treated plywood.

Moisture contents of the specimens in all cases were almost similar with the exception of NMM-1 treated plywood (Figure 2B). In agreement with the *C. puteana* fungus test for veneers, NMM-1 treated veneers always displayed lower moisture contents than the untreated veneers while mNMM-2 and AKD treated veneers showed the similar moisture contents compared to the untreated veneers (after incubation).

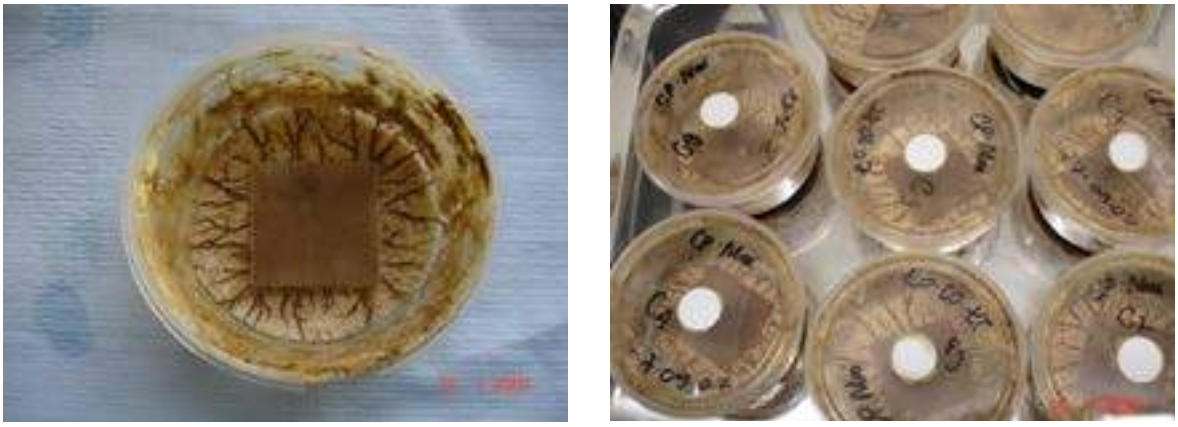

Figure 1. Plywood specimens after 16 weeks of incubation with *C. puteana*

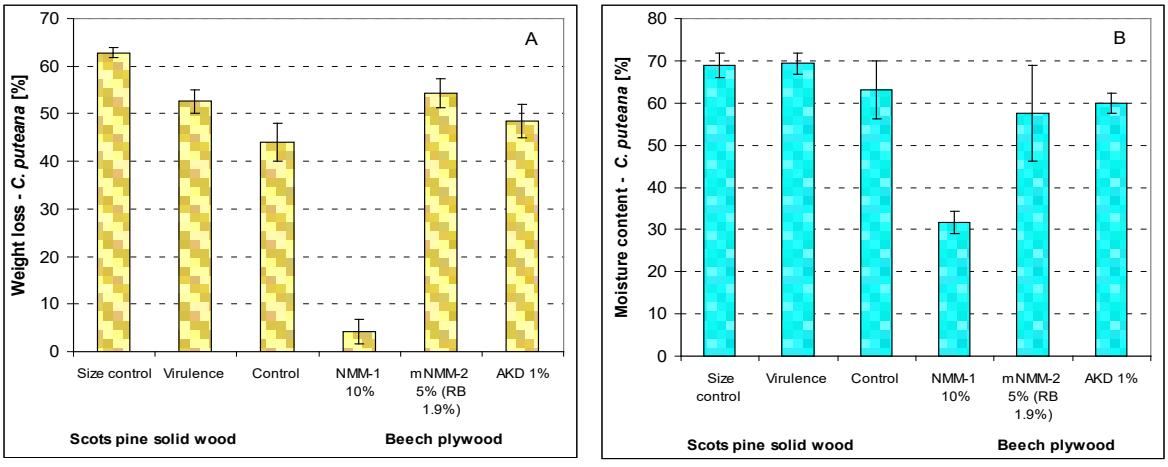

Figure 2. Weight loss (A) and moisture content (B) of the specimens after 16 weeks of incubation with *C. puteana*

Resistance against the white rot fungus *P. ostreatus*

As shown in Figure 4A, the size control and virulence specimens from beech wood in *P. ostreatus* fungus test revealed weight losses of 16.3% and 15.1 % which were much lower than those from Scots pine sap wood with *C. puteana*. The control plywood specimens incubated with *P. ostreatus* presented a weight loss of 24.1% which was lower than with *C. puteana*. The weight loss of virulence beech wood did not really reach the requirement of weight loss of 20% according to the EN 12038 but the results could be accepted because the weight loss of the control plywood was higher than 20%. On the other hand, the requirements

regarding the minimal weight loss of virulence specimens in the ENV 12038 are recommended to alter in case of *P. ostreatus* fungus test due to low decay rates observed in many experiments with this fungus (Van Acker et al., 2001).

In contrary to the *C. puteana* test, the control beech plywood exhibited higher weight loss than the size controls and virulence solid beech wood. This can be explained with the differences in structure of solid wood and plywood specimens. Moreover, *P. ostreatus* is the least affected by the PF glue volatiles emission in comparison to the other types of fungi (Van Acker et al., 2001).

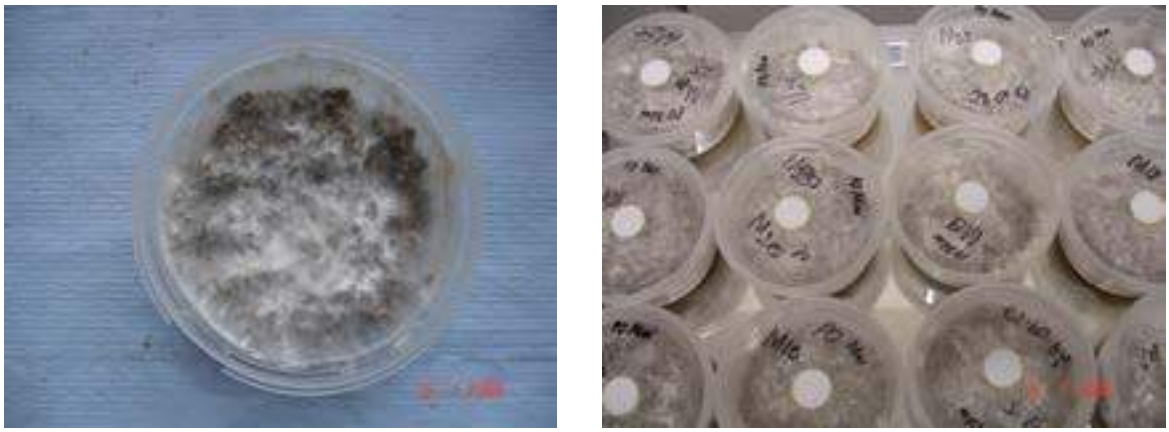

Figure 3. Plywood specimens after 16 weeks of incubation with *P. ostreatus*

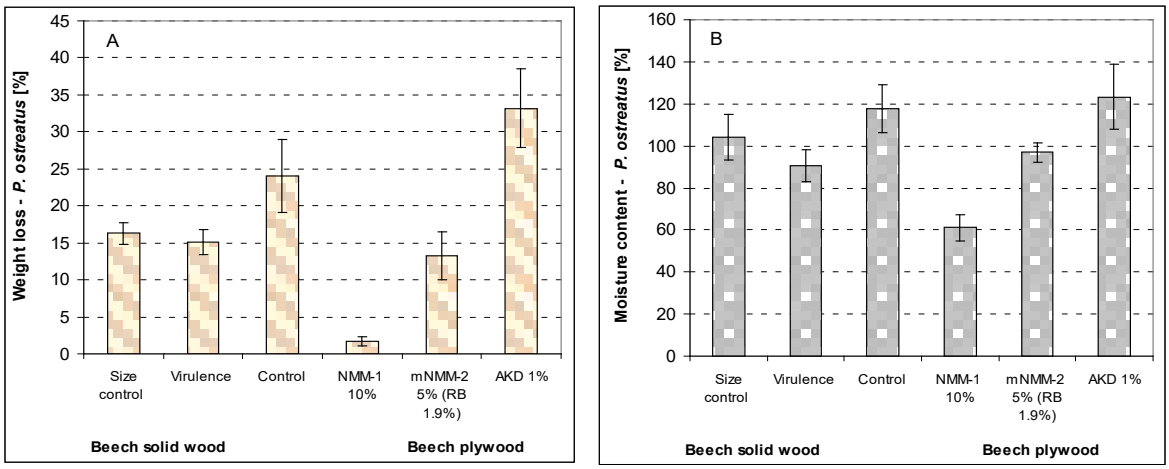

Figure 4. Weight loss (A) and moisture content (B) of the specimens after 16 weeks of incubation with *P. ostreatus*

NMM-1 treated plywood imparted very high fungi resistance reflected by low weight loss (1.7%) after 16 weeks of incubation with *P. ostreatus*. This result was in accordance with basidiomycetes of the NMM-1 treated veneers (Trinh, 2013).

Weight loss of mNMM-2 treated plywood specimens was lower than that of the control plywood specimens. Thus, 5% solid content mNMM-2 treated plywood (with catalyst RB) resulted in medium resistance against *P. ostreatus*. In contrast to NMM-1 and mNMM-2 treated plywood, AKD treated plywood induced even higher weight loss than the control plywood in *P. ostreatus* fungus test. Hence, AKD treated plywood did not bring about any protection against both fungi.

In general, the moisture contents of the specimens in *P. ostreatus* fungus test (Figure 4B) were higher than those with *C. puteana* due to moisture from vermiculite addition which was used to enhance the ability of *P. ostreatus* to maintain the virulence throughout the test. The moisture content of NMM-1 treated plywood

was the lowest, followed by mNMM-2 and AKD treated plywood. This shows the similar tendency to the weight losses of the treated plywood after incubation with *P. ostreatus*.

CONCLUSIONS

A pre-leaching of plywood before the fungal tests is necessary to remove unfixed chemicals which may lead to misunderstanding about weight loss caused by fungal decay. Furthermore, pre-leaching helps to overcome the impact of glue components in decay testing of plywood.

The plywood treated with 10% solid content of NMM-1 solution disclosed high protection to the brown rot fungus *C. puteana* and the white rot fungus *P. ostreatus* after 16 weeks of incubation following the ENV 12038. The results were in line with the basidiomycetes inhibition of the NMM-1 treated veneers.

The treatment with 5% mNMM-2 (with catalyst RB) showed medium resistance to plywood against *P. ostreatus* and no resistance to *C. puteana*. This showed different results from the veneer treatments and can be probably explained with differences in curing processes of the veneers and plywood.

The treatments with 1% solid content of AKD totally failed to protect plywood from the brown rot fungus *C. puteana* and the white rot fungus *P. ostreatus* after 16 weeks of incubation. This outcome was in agreement with the decay inhibition of the veneers treated with 1% solid content of AKD.

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