CELLULOSE CHEMISTRY AND TECHNOLOGY

NANOPARTICLES BASED ON MODIFIED LIGNINS WITH BIOCIDE PROPERTIES

VALENTIN I. POPA, ADINA-MIRELA CĂPRARU, SILVIA GRAMA
and TEODOR MĂLUŢAN

"Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and
Environmental Protection, Department of Pulp and Paper;
Department of Environmental Engineering and Management,
71, D. Mangeron Blvd., 700050 Iasi, Romania

Received November 9, 2010

The paper discusses the obtaining and characterization of nanoparticles based on hydroxymethyl and epoxy lignin, which were tested in terms of their biocidal properties. Lignins from annual plants (wheat straw and Sarkanda grass) and commercial products (Protobind 1000, 2000, 3000), offered by Granit Recherche Developement SA Lausanne – Switzerland, were used for the reactions. Under suitable synthesis conditions, nanoparticles used for the treatment of birch veneer samples were obtained. The samples were immersed successively in 5% concentrated solutions containing copper ions and unmodified and modified lignins, dissolved in 0.1N ammonia solutions, which led to *in situ* complexes between the two partners. The biostability of the thus treated veneer samples was assessed by their burial in soil for 6 months, and by their characterization as to mass loss and contact angle values. The obtained results show that the treatment of birch veneer with complexes of nanoparticles with copper assures a high stability of the substrate timber products, comparatively with the unmodified products used for the same purpose.

Keywords: lignin, hydroxymethylation, nanoparticles, bioprotection, biocides, birch veneer

INTRODUCTION

Lignin is a macromolecular compound more chemically active than cellulose or other natural polymers, due to the functional groups contained in its macromolecule, being considered the main aromatic component of plant tissues – representing 20-40% of the higher plants' mass – located in the cellular wall and in intercellular spaces. Globally, lignin is regarded as a raw material with a high recovery potential, accessible from renewable sources, with low costs and a negligible pollution degree.[1-7]

Large-scale development of lignin-based products is not as achievable as it is accessible, but research in this area is being done by advanced research institutes rather than by producers.[4,8-11] Obtaining of natural polymer nanoparticles constitutes a major concern for many research teams, due to their accessibility and environmental compatibility. Information on the synthesis of lignin-based nanoparticles is relatively limited and covered by patents.[9]

Nanoparticles' applicative impact is especially important, if considering the wide range of fields identified so far: in medicine – to provide drugs, new smart nano-sized coatings, already applied at an industrial scale, and also in IT, auto, cosmetics, chemicals and packaging industries. This paper presents results on the synthesis of nanoparticles based on modified lignin, on the possible obtaining of their copper ion complexes, and on biocide potential evaluation with respect to wood protection.

EXPERIMENTAL

Materials

Two types of lignin isolated through alkaline delignification on annual plants were used: wheat straw (L1) and Sarkanda grass (L2). Three commercial products – Protobind (Pb1000, Pb2000, Pb3000) – offered by Granite Company, Switzerland, were also used.

Cellulose Chem. Technol., ***45*** *(3-4), 221-226 (2011)*

Method

1. Synthesis of nanoparticles by hydroxymetylation of lignins

10 g lignin were suspended in 47 mL distilled water, under stirring for 2 h, at room temperature. After obtaining the lignin suspension, 1.29 g of a 50% NaOH solution and 3.14 g of a 25% NH_4OH solution as a catalyst, were added, and the mixture was shaken for 2 h. Further on, 6.7 g of 37% formaldehyde were introduced in the system and the reaction was performed at 85 ºC for 4 h in a water bath. The resulted product was recovered by precipitation at pH 2 with a 1N HCl solution, then separated by centrifugation. The solid phase was washed twice with distilled water and then dried and weighed.[9] The resulting product was subjected to nanoparticles dimensional distribution analysis using Multi Seiser.

2. Synthesis of nanoparticles by epoxydation reaction of lignins

In this case, the nanoparticles were obtained after performing the epoxydation reaction of the commercial products Protobind (Pb1000, Pb2000 and Pb3000), when the nanoparticles resulted from the supernatant separated after the reaction.[4-6] The products obtained were analyzed for determining the size distribution of the nanoparticles present in the supernatant.

3. Treatment of birch veneer samples with unmodified lignin, lignin-based nanoparticles and cupric solutions

Birch veneer samples (size 1x10 cm) were used for the treatment with lignin-based nanoparticles dissolved in 0.1N ammonia solution at a concentration of 5%, as follows:

- the birch veneer samples were immersed in solutions containing copper ions (copper chloride or copper ammonia solutions) for 5 min, followed by drying at room temperature (laboratory conditions);
- the samples were immersed in unmodified and modified lignin solutions for 5 min and dried under mild conditions. The treated birch veneer samples were previously weighed to determine the quantity of material retained on the sample surface, after which they were buried in soil under laboratory conditions for 6 months, with regular watering, to maintain the specific soil moisture. The biodegradation degree was evaluated by determining the mass loss and the contact angle measured on the surface of the birch veneer treated with lignin derivatives and copper solutions.

Determination of nanoparticle dimensional distribution

A SALD-7001 device, equipped with three key technological possibilities for the characterization of super fine particles, was used. Using an ultraviolet laser light source combined with a single optical system, the 15-500 mm sized particles were determined by the diffraction method. With a view to their characterization, the samples were suspended in distilled water and then subjected to dimensional analysis.

Determination of mass loss

The biocide treated and untreated veneer samples were weighed on an analytical balance before and after they were kept in soil for 6 months, to assess the mass loss, expressed in percentages.

Determination of contact angle

Contact angle measurements were made with a Kruss Model FM40 Easy Drop Goniometry. The assay and image processing were consistent with the SR.EN.828/2001–L73 standard. The software of the device allows surface energy assessment, video recording and experimental data storage. The contact angle was measured on the veneer surface using distilled water as a solvent, with 5 μL droplets.

RESULTS AND DISCUSSION

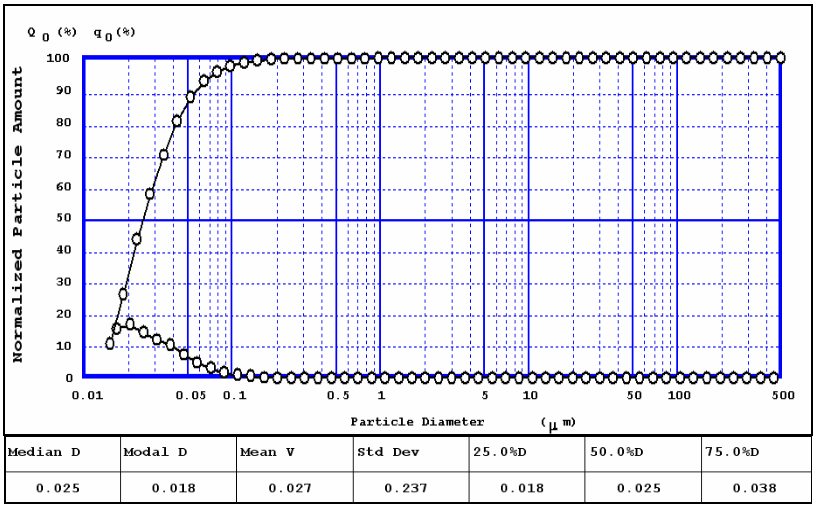
In the study, the formation and identification of lignin nanoparticles was observed, as well as their utilization in the treatment of birch veneer. First, obtaining of nanoparticles based on hydroxymethylated lignin was studied by a patented procedure.[9] The dimensional distribution results for the studied lignins are presented in Figures 1-5.

As seen from the size distribution curves of grass lignin (L2), there is a unimodal curve, while nanoparticles obtained from Pb1000 lignin are characterized by bimodal distribution and larger size nanoparticles. The particle size distribution range is between 0.01-0.1 mm. Figures 3-5 present the size distribution curves for nanoparticles synthesized from wheat straw lignin (L1) and commercial Protobind (Pb2000 and Pb3000) lignins.

The nanoparticles resulted from the other three types of commercial lignin are characterized by a more uniform distribution, while the dimensional range is different, as depending on the substrate nature. A great similarity may be observed for Protobind samples, when nanoparticle distribution shares the same dimensional range, between 0.1~0.8 μm.

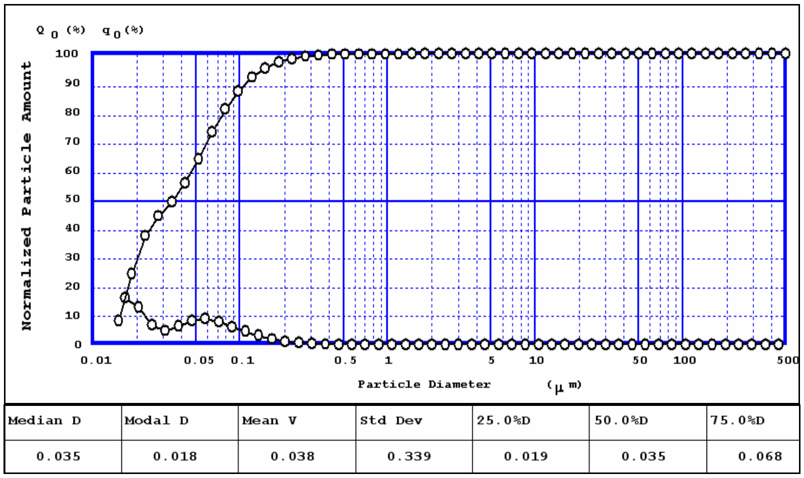
The nanoparticle distribution domain for wheat straw lignin is between 0.05-0.5 μm. The above figures confirm the presence of nanoparticles in hydroxymethylated lignins. Therefore, medium-sized nanoparticles with a more even distribution may be observed for hydroxymethylated grass lignin (L2 nano).

The synthesized products were initially used for birch veneer biostability determination. Also, nanoparticles were identified in the supernatants resulted from lignin epoxydation.[3-6]



Median D	Modal D	Mean V	Std Dev	25.0%D	50.0%D	75.0%D
0.025	0.018	0.027	0.237	0.018	0.025	0.038

Figure 1: Dimensional distribution curve for nanoparticles synthesized from hydroxymethylated grass lignin (L2)



Median D	Modal D	Mean V	Std Dev	25.0%D	50.0%D	75.0%D
0.035	0.018	0.038	0.339	0.019	0.035	0.068

Figure 2: Dimensional distribution curve of nanoparticles synthesized from hydroxymethylated Protobind 1000 (Pb1000) lignin

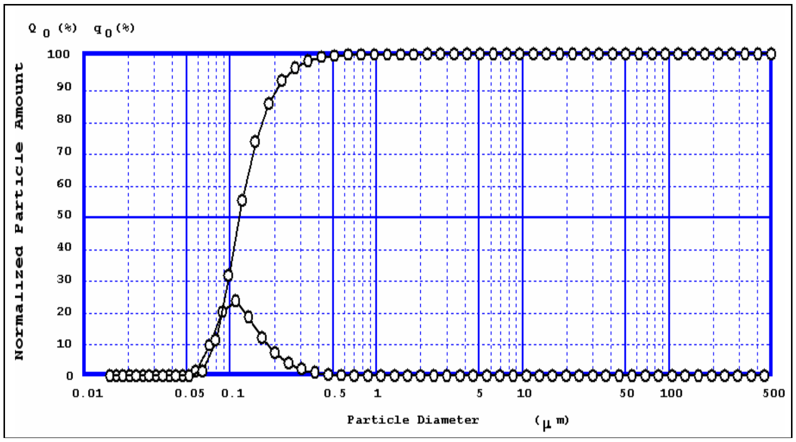


Figure 3: Dimensional distribution curve of nanoparticles synthesized from hydroxymethylated wheat straw lignin (L1)

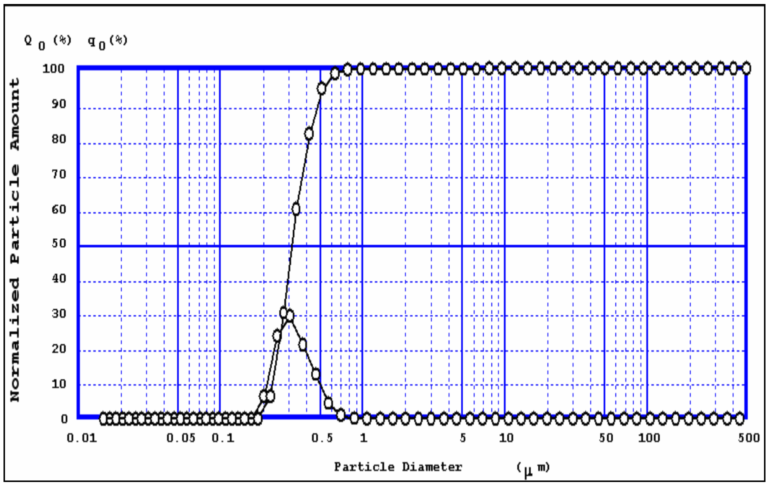


Figure 4: Dimensional distribution curve of nanoparticles synthesized from hydroxymethylated Protobind 2000 (Pb2000) lignin

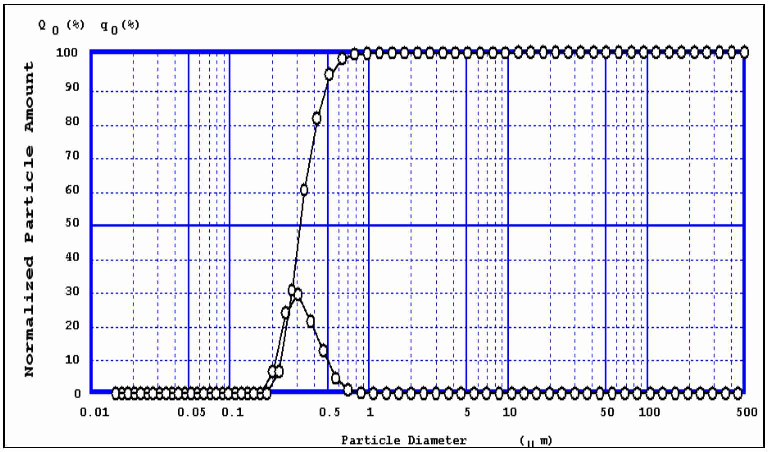


Figure 5: Dimensional distribution curve of nanoparticles synthesized from hydroxymethylated Protobind 3000 (Pb3000) lignin

Figure 6 plots particle size distribution in the case of nanoparticles identified in epoxydation supernatants separated after each lignin substrate. It was found out that the supernatants of lignin epoxydation (L1 and L2) do not contain nanoparticles in suspension. At the same time, it is noted that nanoparticles were separated only from the supernatants resulted after modification of commercial lignins by epoxydation. Suspensions of nanoparticles were characterized in terms of dimensional distribution.

The recorded data show a nanoparticle uniform distribution, comparable for all three types of studied lignin. The average particle size was of about 0.246-0.248 μm. Some of the observed features seemed similar to those reported for nanoparticles synthesized through hydroxymetylation of the same commercial lignin products, for which the distribution range was broader, between 0.05 and 0.5 μm. In a series of preliminary experiments, the nanoparticles could be recovered through centrifugation. From this perspective, the ascertainment of other characteristics and the recognition of other opportunities might entail further research directions.

Mass loss determination recorded for birch veneer samples treated with nanoparticles based on hydroxymetylated lignin

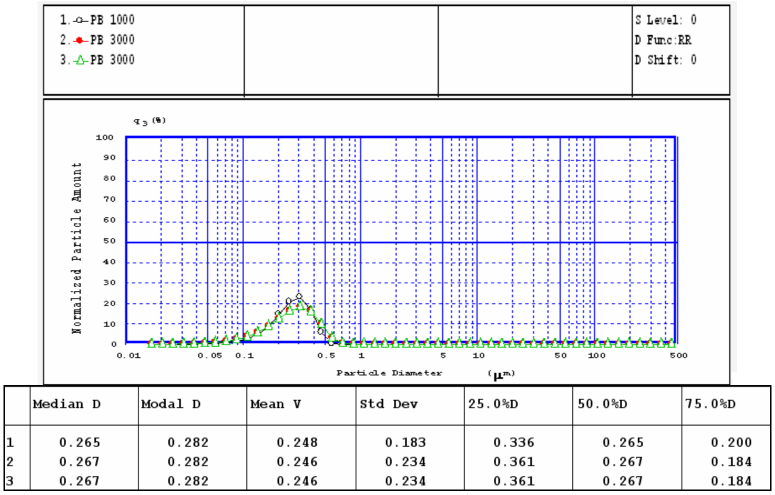
The veneer samples were treated with nanoparticles based on hydroxymethylated lignin, with their copper complexes and with copper solutions ($CuCl_2$ and Cuam). The biodegradation degree of the thus obtained samples was determined by mass loss after burial in soil for 6 months. Figures 7-8 show the mass loss variations recorded in birch veneer samples.

The data obtained for samples treated with lignin-based nanoparticles and copper compounds show that the mass loss is lower, compared to the untreated samples. The lower mass loss was caused by the toxic effects of copper, the lignin derivatives and the two components' complexes, which limit and inhibit the microorganism attack. Wood surface treatment with copper-containing solutions, especially when provided by the chloride derivative and lignin nanoparticles, proved to be more efficient. Lignin-copper complex derivatives fall in the following order: Pb2000nano > Pb3000nano > Pb1000nano > L2nano > L1nano, in terms of assurance of wood biological stability. This situation may be correlated with their various functionalities, induced through hydroxymetylation, different degrees of copper complex forming and wood surface interaction thus resulting.

Contact angle determinations recorded for birch veneer samples treated with nanoparticles based on modified lignin

After having been buried in soil for 6 months, the birch veneer samples were recovered and then used to determine the contact angle, to track the effectiveness of the applied treatment and also to establish a direct correlation between its values and mass loss (Figs. 9-10).

The data show that the contact angle reaches higher values (94-116^o) for the samples treated with copper lignin derivative complexes, compared to the reference or to the samples exposed to copper ion solutions. Therefore, such treatments provide biological stability and hydrophobicity to wood surfaces.



	Median D	Modal D	Mean V	Std Dev	25.0%D	50.0%D	75.0%D
1	0.265	0.282	0.248	0.183	0.336	0.265	0.200
2	0.267	0.282	0.246	0.234	0.361	0.267	0.184
3	0.267	0.282	0.246	0.234	0.361	0.267	0.184

Figure 6: Dimensional distribution curve of nanoparticles in supernatant resulted from Pb1000, Pb200 and Pb3000 lignin epoxydation

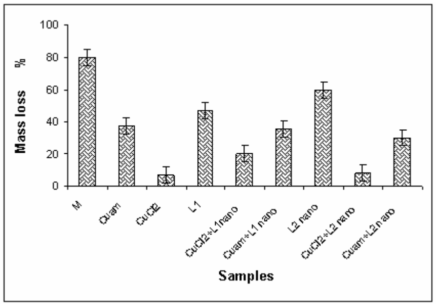


Figure 7: Variation of mass loss for birch veneer samples non-treated (M) and treated with $CuCl_2$, Cuam, L1nano, $CuCl_2$L1nano, CuamL1nano, L2nano, $CuCl_2$L2nano, CuamL2nano

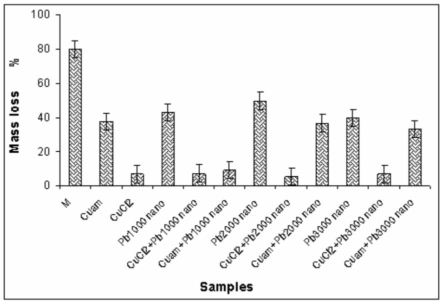


Figure 8: Variation of mass loss for birch veneer samples non-treated (M) and treated with $CuCl_2$, Cuam, Pb1000nano, $CuCl_2$Pb1000nano, CuamPb1000nano, Pb2000nano, $CuCl_2$Pb2000nano, CuamPb2000nano, Pb3000nano, $CuCl_2$Pb3000nano, CuamPb3000nano

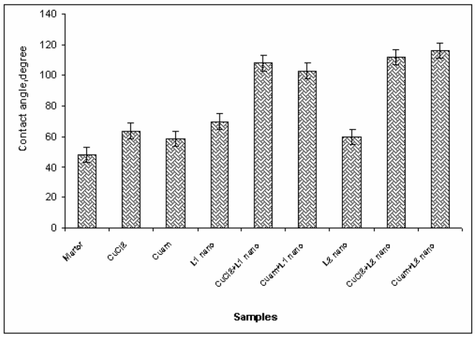


Figure 9: Variation of contact angle for veneer samples non-treated (M) and treated with Cuam, $CuCl_2$, L1nano, $CuCl_2$L1nano, CuamL1nano, L2nano, $CuCl_2$L2nano, CuamL2nano

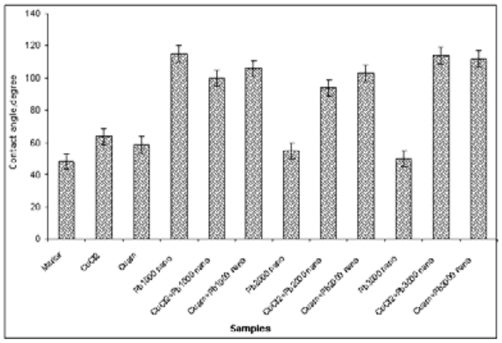


Figure 10: Variation of contact angle for veneer samples non-treated (M) and treated with Cuam, $CuCl_2$, Pb1000nano, $CuCl_2$Pb1000nano, CuamPb1000nano, Pb2000nano, $CuCl_2$Pb2000nano, CuamPb2000 nano, Pb3000nano, $CuCl_2$Pb3000nano, CuamPb3000 nano

These results are determined by a more efficient action of lignin nanoparticles in the presence of copper, fixing itself on the wood substrate, and thus assuring an optimal protection against microbiological attack. During contact angle measurements, a very low level of surface hydrophilicity could be observed, as in some cases, a drop of water would not penetrate the wood surface. One may therefore assume that the synthesized lignin products provide a high wood surface stability when submitted to the action of soil microorganisms.

CONCLUSIONS

Lignin hydroxymetylation under special conditions, as well as the amendment of commercial products through epoxydation led to the obtaining of nanoparticles.

The hydroxymethylated lignin-based nanoparticles were characterized by dimensional distribution.

The nanoparticles obtained through epoxydation of the Protobind commercial type lignin were identified in the separated supernatants and characterized in terms of dimensional distribution.

Birch veneer treatment tests with lignin-based nanoparticles modified in the presence of copper ions proved their ability to ensure a high biological wood stability, as assessed by mass loss and contact angle determinations.

The veneer samples analyzed after burial in soil for 6 months were featured by low mass loss values and high contact angle values determined for long periods of time, as a result of a high hydrophobicity.

ACKNOWLEDGEMENTS: The authors would like to thank Granit Recherche Developement S.A., Trans Furans Chemicals bvba, for supplying the lignin and the furan resin samples, and ECOBINDERS (SIXTH FRAMEWORK PROGRAMME, NMP2-CT-2005-011734), as well as CEEX-CNCSIS, LIGNOMAT, 4153/2006 for their financial support.

REFERENCES

[1] A. M. Căpraru, E. Ungureanu and V. I. Popa, *15th International Symposium on Wood*, *Fibre and Pulping Chemistry*, Oslo, Norway, 2009, pp. 50-55.

[2] A. M. Căpraru, E. Ungureanu and V. I. Popa, *EEMJ*, **7**, 525 (2008).

[3] M. I. Totolin and G. Cazacu, "Adezivi, materiale compozite şi alte aplicaţii pe bază de lignină" (in Romanian), Pim Publishing House, Iaşi, 2010, pp. 195-197.

[4] Th. Măluţan and V. I. Popa, "Protecţia lemnului prin metode specifice" (in Romanian), Cermi Publishing House, Iaşi, 2007, pp. 141-153.

[5] Th. Măluţan, R. Nicu and V. I. Popa, *Bio/Resources*, **3**, 13 (2008).

[6] A. M. Căpraru, V. I. Popa, G. Lisa and Th. Măluţan, *Buletinul Institutului Politehnic din Iaşi*, Tome LV (LIX), fasc. 4, 59 (2009).

[7] Y. Matsushita, S. Wada, K. Fukushima and S. Yasuda, *Ind. Crop. Prod.*, **23**, 115 (2006).

[8] V. I. Popa, in "Tehnologii de valorificare a ligninei" (in Romanian), Polytechnic Institute of Iaşi, 1983, pp. 11-13.

[9] P. Schilling, US Patent no. 5,192,361, March 9, 1993.

[10] E. Ungureanu, A. M. Căpraru and V. I. Popa, *COST 50/ILI joint meeting*, October 27-29, 2008, Switzerland, p. 40.

[11] H. Yamaguchi and K. Yaoshino, *Holzforschung*, **55**, 4644 (2001).