COMPOSITE MATERIAL OF PARTICLES OF PLANT ORIGIN

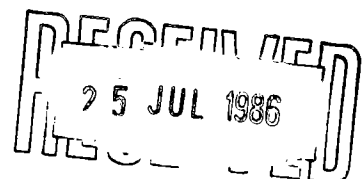R. A. Bareš [x] , A. Vašíček [xx]

SUMMARY

Composite materials of particles of plant origin are produced at present by the bonding of disintegrated phytomass particles by thermosetting binders on the basis of urea-form-aldehyde, phenol-formaldehyde or melamine-formaldehyde substances. The production and use of composite materials based on the afore mentioned binders are accompanied by a long-term release of formaldehyde and its oligomers which have an unfavourable effect on human organism. The adhesive bond of the individual composite particles is effected by the continuous phase of the thermosetting binder, the phytomass acting as inert filler. In this type of composite materials the chemical compounds contained in the particles of the lignocellulose filler are not utilized.

The disadvantages of classical composites of particles of plant origin are eliminated by the "binderfree" composite material described in the paper. The principle of its production lies in the provision of the surface of the particles with an acid activating hydrolyzing agent which, at a higher temperature, produces a partial fission of the polymer lignocellulose substances present into their individual components /e.g. lignine/ and the conversion of other substances present /e.g. poly-saccharides, tanning matters, volatile oils, tannin, etc./ into monomers or oligomers capable of polymerization, and ensures, in the further synergic process, the origin of a firm polymer structure between and on the surface of the individual particles.

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[x] Richard A. Bareš, Eng., Ph.D., D.Sc., Research Professor, Department of Mechanics of Composite Materials and Systems, Institute of Theoretical and Applied Mechanics, Czecho-slovak Academy of Sciences, Prague 2, Vyšehradská 49

[xx] Alois Vašíček, Eng. Ph.D., Research Fellow, Chemical Technical University, Prague, Department of Technical Physics and Electrical Engineering, Prague 6, Suchbátarova 5

INTRODUCTION

Increasing need of plant-based agglomerated materials /particularly for construction purposes/ and the necessity of ensuring locally acceptable ecological conditions requires a reduction or, preferably, complete elimination of the release of the products of fission of the resin binder usually bonding the particles of the phytomass.

Composite materials of particles of plant origin are produced at present by bonding the disintegrated plant particles with thermosetting binders, generally on the basis of phenol-formaldehyde, urea-formaldehyde and melamine-formaldehyde resins. The plant particles are used as filler without using in any way the chemical compounds contained in the plant mass. Moreover, there arise difficult problems with the release of certain binder components both in the process of production and, in the long run, during the use of the material. This concerns particularly formaldehyde or the urea and formaldehyde oligomer, phenols, whose carcinogeneous, mutageneous or otherwise harmful effect on human organism has been proved beyond doubt. For this reason the presence of formaldehyde and its compounds in environment is extremely undesirable and the use of materials containing formaldehyde has been banned already in a number of countries.

The harmful effect of the product of fission of urea-formaldehyde substances and, simultaneously, the endeavour to comply with the requirements of higher quality class initiated various measures on the part of the producers to reduce the emission of harmful matters.

The first method is based on the replacement of the urea-formaldehyde binders with phenol-formaldehyde binders, guaranteeing a higher conversion in the proceeding polycondensation. The second method reduces the emission of formaldehyde by means of admixtures capable of binding free formaldehyde into chemically stable compounds, such as hexamethylenetetramine. Another method increases the conversion of the polycondensation reaction by an overstoichiometric addition of urea to the water dispersion of the urea-formaldehyde pre-condensate. Most

effective is the first method; the efficiency of other methods
is limited and is connected with the capacity of the added aub-
stance; it does not practically influence the hydrolytic emis-
sion of formaldehyde and its oligomers with urea, which is a
long-term process.

The principal idea of the formulation of the binderfree
composite material of particles of plant origin is the integral
utilization of the phytomass by a single-stage method of pro-
duction, i.e. particularly the utilization of the majority of
chemical substances contained in plant particles for the
"in situ" generation of a suitable binder during the moulding
of an agglomerated element and, consequently, the elimination
of unfavourable ecological as well as economic aspects of
classical and modified technologies. The aim was to find an
optimum method of controlled depolymerization of the mass into
substances which could be repolymerized in the next phase with-
out the permanent degradation of the remaining cellular wood
structure.

PHYTOMASS AS A RAW MATERIAL

From the chemical viewpoint the lignocellulose can be
considered as a polymer compound consisting of several basic
polymers /4/.

Highest representation is that of the cellulose, the
basic component of which is the D-glucopyranose, the units
of which are mutually linked by the β -glycosidic bond:
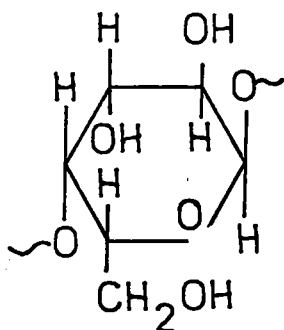
The degree of polymerization is
of the order of hundreds to
thousands of these units.

The other basic component of the
phytomass is lignine, the basic
structural unit of which is the
derived benzene group:

H OH
H
OH H
H
O
O H
CH₂OH

3

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     |
   — C —
   — C —
   — C —
      |
  ~O —⬡— O~
      |
      O
      ?
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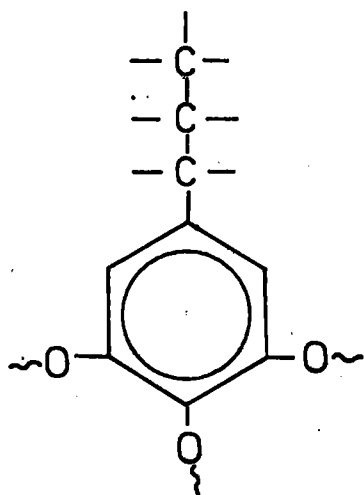
In contradistiction to the ideas about the constitution of cellulose the opinion about the structure of lignine is not yet uniform. The ideas about its structure are influenced by a number of factors the most significant of which is the difficulty of a structural analysis of polymers.

The other components contained in plant particles are usually summed into a group of the so-called hemicellulose. This group contains polysaccharides of the lower polymerization degree or another constitution. This group comprizes also saccharides other than hexosans, e.g. pentosans, whose presence in plants has been proved.

A closer view of the phytomass structure shows that the individual cellulose chains are mutually interconnected with lignine. The hemicellulose forms the fill in the cell irregularities and in the voids between the individual cell walls.

The strength of the chemical bonds between the individual components is lower than the strength of intermolecular bonds of the individual components. For this reason the effect of some agents, such as acids and lyes, results primarily in the break-up of the phytomass into the individual components. Secondarily the components are broken up into macromolecules of lower polymerization degree and/or into the very basic structural units. The limiting factor of the individual reactions of the hydrolytic fission of the phytomass is the choice of agent which influences also the yield of the individual fission products. Similar effect can be achieved also by the thermal decomposition of the phytomass.

It is known from the history of chemistry that the phytomass has been the primary source of such raw materials as methanole, furfural, phenol derivatives, sugars, etc. Some of these substances can join polycondensation reactions and enable the origin of polymers.

The utilization of compounds contained in the phytomass for the generation of a binder and, using the latter, for the generation of a composite material, is not a new idea /1, 2, 3/. The authors dealing with these problems used the acid hydrolysis of wood particles in the majority of cases so conducted as to primarily produce lignine. The aqueous solution of the products of fission was then applied as binder in the production of composite. However, the mechanical properties of the materials thus obtained did not achieve sufficient magnitude and the methods, therefore, have not found practical application.

PREPARATION OF A BINDERFREE COMPOSITE

On the basis of a thorough analysis of the possibilities of utilization of the phytomass substances capable of polymerization and using our experimental achievements and phased proofs· of the feasibility of this method we have devised a method of production of a composite material in a single-phase, integral process.

The principle of the proposed original "binderfree" method of production of a composite material of plant particles consists in the provision of the particle surface with an acid activation hydrolyzing agent which, at a higher temperature, causes a partial fission of the polymer lignocellulose substances present into their individual components /e.g. lignine/, and the conversion of other present substances /e.g. polysac-charides, particularly hexosans and pentosans, tanning agents, volatile oils, tannin, etc./ into monomers or oligomers capable of polymerization and ensures, in the further synergic process, the generation of a firm polymer structure between and on the surface of the individual particles. ·

Structural Characteristics

The structure of the new material differs substantially from the structure of standard particle materials with added binder, in which the cross-linked thermosetting polymer fills the voids between plant particles and thus forms a continuous spatial skeleton connected with the particles by adhesion

/Fig. 1/. Those are abviously composites of the IInd type and their mechanical properties are generally determined by the properties of the above mentioned skeleton.

In the new material the originating polymer cannot fill the voids among the individual particles under currently used pressing pressures, as the substances capable of polymerization are generated only from the thin surface layer of particles /in an ideal case of a perfect application of the activating agent to the whole particle surface/ or from the discrete areas of the surface layer of the particles, which have come into contact with the activating agent /in case of imperfect application/. In the places of contact of particles this layer generates cohesive bonds by means of which the individual particles are mutually bonded. It is the composite of the IIIrd type, in which the particles are aggeregated and bonded in the points of contact by the polymer. The polymer does not form its own geometrically and phase connected infrastructure. The only continuous infrastructure in the system is the gaseous phase in the voids between the particles /Fig. 2/.
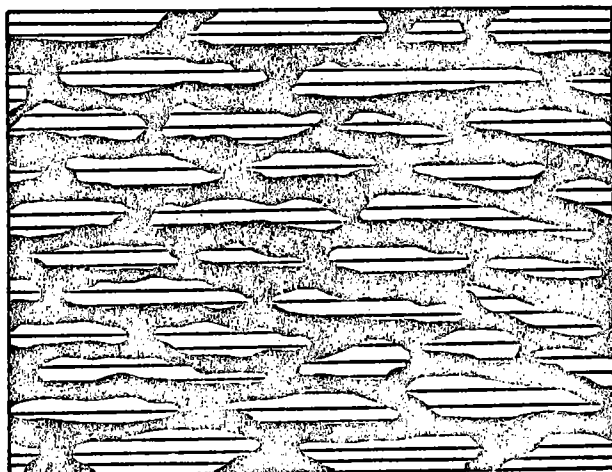
Fig. 1   Model idea of the structure of a composite material bonded by thermo-setting binders
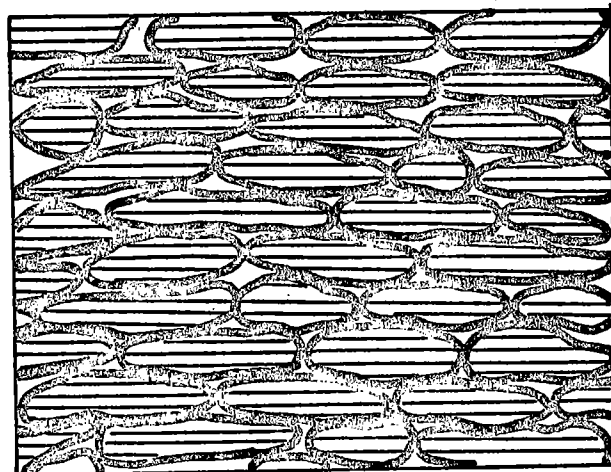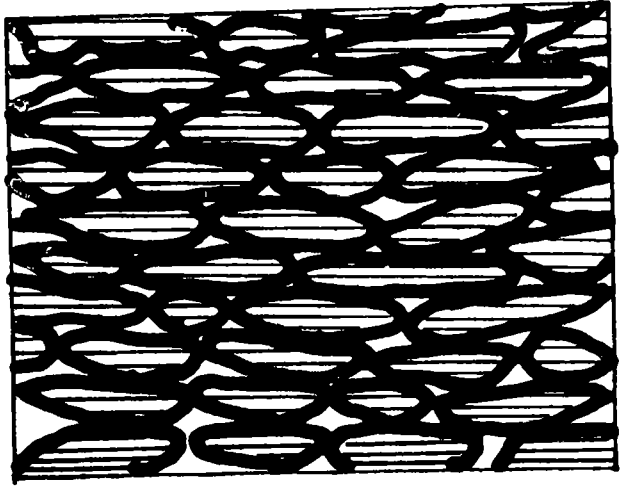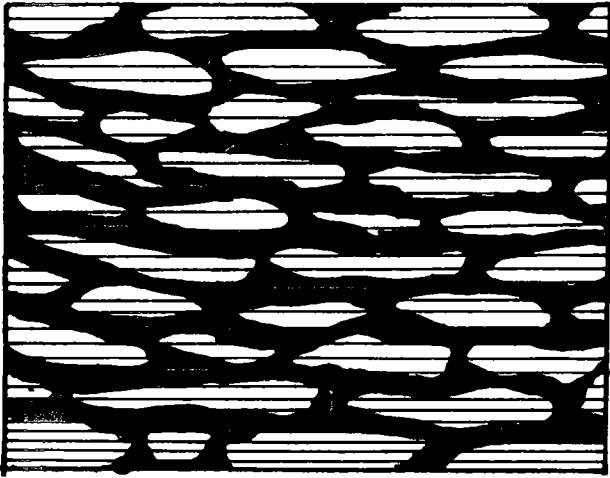
Fig. 2   Model idea of the structure of a composite material generated by the binderfree method

In contradistinction to the classical particle materials, in which the plant particles are used merely as a filler to the polymer, the particles in the new material represent a direct part of the bonding network /the binder bridge being bound with the natural polymer of the particles/. Particularly this fact affords the highest promise of high mechanical properties of the material.

The reaction kinetics of polymer generation requires that the maximum number of contact surfaces, capable of generating cohesive bond among the particles, be guaranteed at the time of heating during pressing. The reactions taking place in other parts of the particles will not influence practically the mechanical properties of the composite, as the surface layer will be disactivated again by the generation of the new polymer. The originated composite material has a similar chemical composition as the composition of the initical wood mass, but the density of bonds in the system is lower by several orders than the density of the bonds within the plant particles.

The necessary prerequisite for the achievement of higher mechanical properties, therefore, is obviously an increase of the number of bonding contacts. This can be achieved, on the one hand, by an increase of the pressing pressure, on the other hand by a higher filling of the space with the wood mass. The first method is only partly effective, as the practically applicable pressures /approx. 3.5 MPa/ enable maximally the doubling of the number of contacts, which results in the density of the material markedly rising in comparison with the materials produced by classical methods. The other method can be applied by the use of a well granulated particle mix comprizing also the particles of the minimum dimensions. Apart from a better filling of the space also the specific surface of the particles and, consequently, also the potential number of possible contacts will increase, which will result in an increase of the density of bonding points. The larger specific surface of the particles, however, brings about also the potential possibility of generation of a higher overall

7

binder quantity in the system. Another unfavourable consequence
is also an increase of the density of the resulting material,
particularly if hardwood particles are used.

Application Parameters

For the manufacture of the composite material a number
of activating agents was tested and an optimum method of their
application to the particles was sought. Practical application
however was made only of sulphuric acid, as other acids - due
to their weak dehydration effect or water contents - were
unable of catalyting the depolymerization and particularly
the subsequent repolymerization of the physomass into a poly-
mer with sufficient cohesive properties. To ensure a slower
acid diffusion into the particle depth and to prevent un-
necessary disturbance of the original polymer within the part-
icles the sulphuric acid was replaced with salts on the basis
of urea sulphate, urea acid sulphate and ammonium acid sulphate.
Active sulphate acid originates in this case only after the
thermal dissociation of sulphates, which results in an improve-
ment of mechanical properties. It has been ascertained that
the best results can be obtained, if the activating agent
/concentrated acid or sulphate/ is applied to the particles
in such a way as would ensure its covering maximum of their
surface in a layer of minimum thickness. This can be achieved
by the application of the activating agent in a fine aerosol
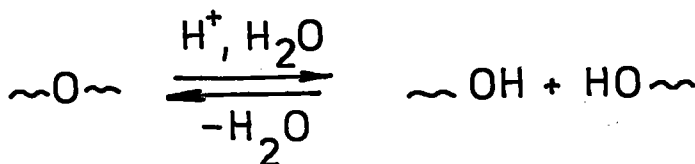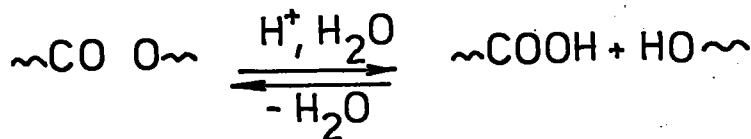to the suspended particles.

CONDITIONS OF COMPOSITE MATERIAL ORIGIN

The mechanism of the effect of the activating agent on
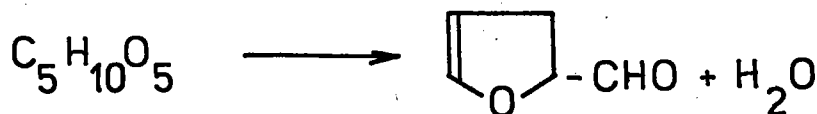the phytomass can be seen in the following reactions:
1. Fission of bonds between lignine and cellulose
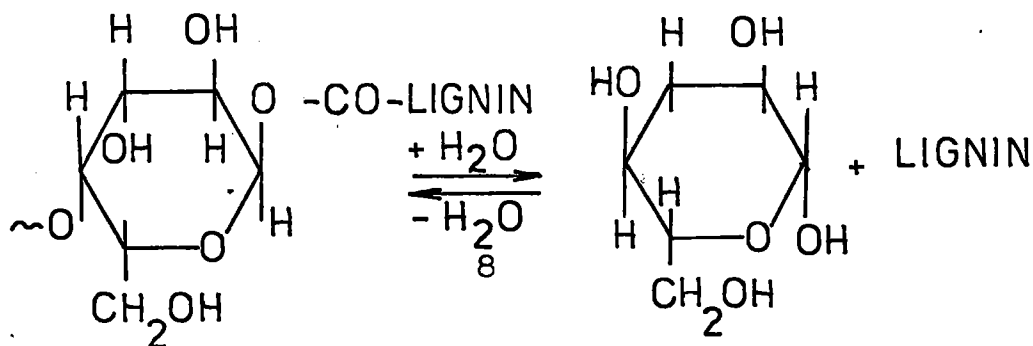
2. Fission of internal bonds within the cellulose and lignine components

$$\sim CO\ O\sim\ \underset{-H_2O}{\overset{H^+,\ H_2O}{\rightleftarrows}}\ \sim COOH + HO \sim$$

$$\sim O \sim\ \underset{-H_2O}{\overset{H^+,\ H_2O}{\rightleftarrows}}\ \sim OH + HO \sim$$

3. Sugar dehydration

$$C_5H_{10}O_5\ \longrightarrow\ \underset{O}{\square}-CHO + H_2O$$

     The origin of the repolymerized phytomass can be explained, on the basis of the assumed chemical reactions, by means of the following hypotheses: the activating agent causes hydrolysis of ester and ether bonds in the surface layers of particles, which results in the generation of minor molecules of higher mobility. Pressure transports the originating thermoplastic mass into the vicinity of other particles, where an opposite reaction, i.e. condensation, takes place, which produces a polymer of similar composition with that of the initial material. It cannot be excluded, however, that the originating polymer will be of a lower polymerization degree than the initial phytomass polymer, as the reactions in heterogeneous system do not ensure sufficiently the approach of the individual functional groups capable of reaction to within the bonding distance.

     Further idea about the progress of the reaction can be obtained from the fact that repolymerization takes place even in the absence of water. In this case the origin of radicals or ions, the transmission of the charge and the transmission of the chain can be assumed. The action of radicals or ions after their approach to the bonding distance of the functional

phytomass groups results in the connection of the chain. The more mobile radical or ion or low-molecular substances will link to another place of the phytomass molecule.

The mechanism of the repolymerization reactions, however, depends also on the type of activating agent used. When concentrated sulphuric acid us used, the dehydration reactions take place primarily, which result in the origin of furfural and dehydrated hexosans. This reaction manifests itself by the higher degree of blackening of the generated polymer. The hydrolytic reaction proceeds less intensively in the places, where the diluted acid was transported by water vapours. In these places the recombined lignine-cellulose or lignine-lignine bonds appear primarily. The incorporation of furaldehyde into polymerization reaction and its positive influence on the mechanical properties of the composite were proved by experiments.

The use of concentrated sulphuric acid as activating agent, however, brings about also some negative consequences due to insufficient homogeneity of its application to the particles. The use of water-diluted activating agents has not proved effective; moreover, it results in undesirable transport of acids to a major depth of the particles and, in pressing, to undesirable overpressure of steam resulting even in the rupture of the composite after the pressure relief. Apart from that the presence of water results in the shifting of the equilibrium of hydrolyzing reaction towards the hydrolysis products, impairing the condensation reactions. One of the solutions of this problem is the use of such activating agents whose effect will be brought about only by the thermal dissociation reaction. For instance:

$$NH_2CO\ NH_3HSO_4 \underset{}{\overset{T}{\rightleftharpoons}} NH_2CO\ NH_2 + H_2SO_4$$
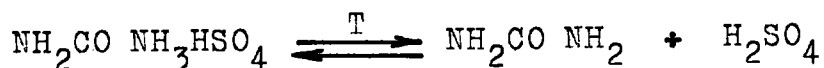
The reaction kinetics of the polymer origin from the phytomass can be described by the reaction scheme as a sequence of the following reactions:

Activating agent —▸ dissociation of the activating agent on
the phytomass —▸ origin of components capable of polymerization
—▸ origin of impregnated polymer

From the reaction kinetics also the requirements imposed
on the technological process follow. The duration of the sub-
sequent reaction is connected with the temperature, i.e. with
the heating of the mass to the temperature at which the re-
actions take place. For the individual activating agents the
optimum technologial conditions must be found, connected with
the duration and the temperature of pressing and the pressure
used.

Possibilities of Modification of Properties

The properties of the composite material can be modified
in various ways. For instance, the mechanical properties can
be improved by the incorporation of the possible reaction of
furfural hydrogenation into furylalcohol whose ability to form
copolymers with aldehydes, alcohols and carboxyl acids is well
known.

For this purpose minority components are added to the
reaction mix, such as Al, Mg, Zn in pulverized form, which
results, in acid environment, in the generation of hydrogen
in statu nascendi. An addition of aluminium at the rate of
0.5 % by weight results in a 30% improvement of mechanical
properties, which can be considered as a partial verification
of the hypothesis of furfural hydrogenation in the process of
in-situ composite generation.

The ways to the improvement of water-resistance of the
composite material are based on the mechanism of hydrophobiz-
ation of composites with binders, in which the water resistance
is determined by the character of the binder filling the pores
in the wood mass and thus preventing the swelling of the par-

11

ticles. Apart from that in the manufacture of classical materials also a hydrophobization emulsion is applied to the wood mass together with the binding emulsion; the hydrophobization emulsion contains parafin which stops those parts of the pores for which the binder was not available. In the case of the binderfree composite the mechanism of hydrophobization is not so explicit, which follows directly from the method of production and the structural arrangement of the system. The whole void volume is not filled with the binder, the porosity is continuous and water may easily penetrate into the material.

The fundamental and indispensable prerequisite for the water-resistance of the new material is the activation of the whole or at least of the majority of the surface of all particles, and the generation of a skin of the new polymer, generated in the course of the technological process, on their surface which is sufficiently water-resistant. The given method of application of the activating agent can ensure the covering of the whole particle surface by the generated polymer only exceptionally. For this reason three methods of improvement of water resistance of the new material were designed and tested.

The first method consists in higher batching of small size particles to which a higher quota of activating agent is applied. These particles form a pseudo-continuous phase in the composite material, consisting practically only of the generated polymer, which prevents water penetration similarly as in the case of classical materials.

The second method improves the water resistance of the new material by an admixture of inert thermoplastics, added to the particles before pressing in pulverized form /e.g. emulsified PVC/ with particle size of about 1 μm. It is assumed that, due to an electrostatic charge, these thermosets will envelop the individual particles also in the places which have not come into contact with the activating agent, and will form on them during pressing, due to temperature and pressure, a sintered layer preventing water penetration into them.

LABORATORY AND PILOT PRODUCTION TESTS

The actual manufacture of the composite material in the
form of chipboard-like materials was tested in the laboratory,
in an experimental plant and in a pilot plant. The suspended
particles are provided with the activating agent applied in the
form of mist. After the sorption of the activating agent the
particles are prepared for pressing. Acid activating agents are
not chemically bound during the production process, as a rule;
consequently, the residual acidity must be removed. This can
be achieved by an addition of neutralizing agents on the basis
of urea, weak lyes or other salts, such as ammonium sulphide,
ammonium phosphate, etc. The added compounds are capable of
forming a salt with the acid and thus reducing the pH of the
extract to an acceptable value. The mixture of particles with
the activation agent and other components is then pressed by
a specific pressure of 2 - 3 MPa at 180°C for the period cor-
responding with 1 minute per 2 mm of element thickness.

CONCLUSION

A number of laboratory tests have proved beyond doubt that
the described original process /5, 6, 7, 8/ can be used for the
manufacture of a phytomass composite material with the properties
satisfying and exceeding the requirements of the contemporary
standards valid for the classical binder-based composites of
wood mass both in respect of mechanical properties and water
resistance. The authors have succeeded in solving all basic
problems connected with the integral process of depolymeriz-
ation and repolymerization of the substances in the phytomass.

With the exception of the special equipment for the applic-
ation of the activating agent all other technological steps of
the manufacture of the binderfree composite material are ana-
logous with classical production methods and do not require
any special equipment.

The main advantage of the designed production method is
the complete elimination of emissions of harmful substances in

13

the course of production and in use and, consequently, a significant improvement of environment. The designed production method enables also the utilization of inferior raw materials incl. bark, "green" phytomass, etc. Substantial is also the reduction of the price of the products and the elimination of the problems connected with the provision of binders.

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