EFFECT OF WATER GLASS-POLYVINYL ALCOHOL FOR MERCERIZATION ON RICE HUSK AND STRAW FIBERS FOR PARTICLEBOARD

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Abstract: *particleboard made of rice husk and straw fibers is required to manufacture some furniture instead of wood. The most important problem to use these agricultural wastes as the reinforcement fibers is the integrating problem between the matrix and fibers, thus, mercerization. Rice straw and husk fibers are hydrophilic, but polyethylene as the binder is hydrophobic. So rice husk and straw must be treated to integrate them into organic matrix. Water glass, polyvinyl alcohol, urea-formaldehyde resin and other additional agents for mercerization could make the surfaces of natural fibers compact and hydrophobic, so help them to distribute into matrix. In this case, zinc-aluminum phosphate and polyphosphate, sodium silicofluoride and aluminum hydroxide were used as curing agent for water glass. In addition to these, urea formaldehyde also improved the adhesive ability of the water glass. This paper dealt with the effect of water glass and polyvinyl alcohol on the rice husk and straw fibers for particleboard when compared with mercerization based on maleic anhydride.*
Keywords: *water glass, polyvinyl alcohol, mercerization, rice husk, rice straw, particleboard, benzoyl group, polyphosphate, aluminum hydroxide, curing agent, polyethylene, composite.*

ВЛИЯНИЕ ВОДНОГО СТЕКЛА И ПОЛИВИНИЛОВОГО СПИРТА НА МЕРСЕРИЗАЦИЮ РИСОВОЙ ШЕЛУХИ И СОЛОМЫ РИСА ДЛЯ ДРЕВЕСНОСТРУЖЕЧНЫХ ПЛИТ

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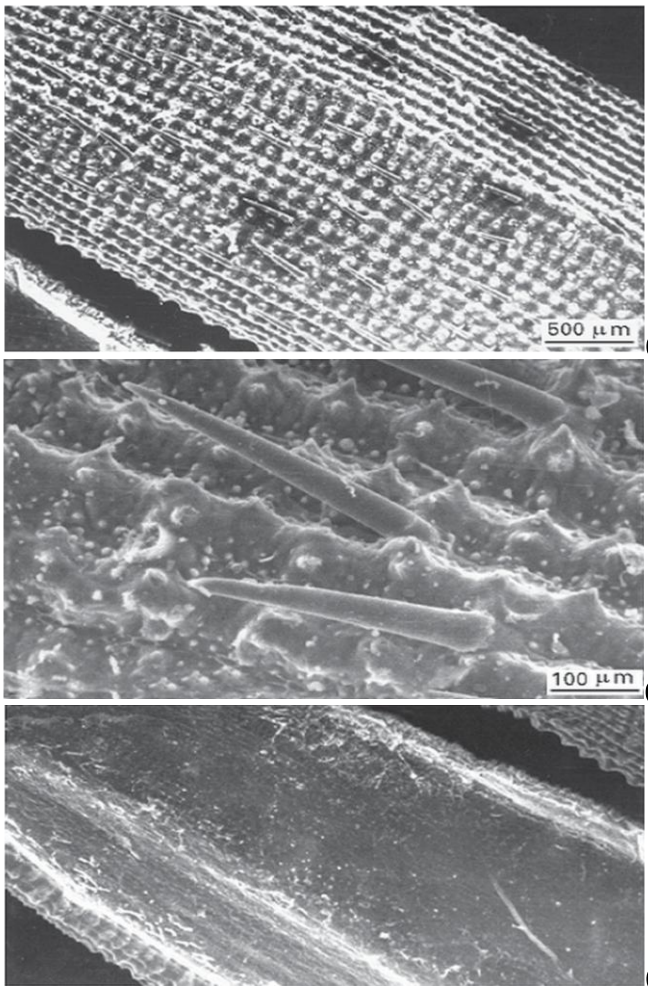
Аннотация: *ДСП, изготовленная из шелухи риса и соломы, требуется для производства мебели вместо древесины. Наиболее важной проблемой для использования этих сельскохозяйственных отходов в качестве армирующих волокон является интегрирующая проблема между матрицей и волокнами, таким образом, мерсеризация. Солома из рисовой соломы и шелухи являются гидрофильными, а полиэтилен в качестве связующего является гидрофобным. Так что рисовая шелуха и солома должны быть обработаны, чтобы интегрировать их в органическую матрицу. Водное стекло, поливиниловый спирт, мочевиноформальдегидная смола и другие дополнительные вещества для мерсеризации могут сделать поверхности натуральных волокон компактными и гидрофобными, что поможет им распространяться в матрице. В этом случае в качестве отвердителя для жидкого стекла использовали фосфат цинка и алюминия, полифосфат, силикофторид натрия и гидроксид алюминия. В дополнение к этму формальдегид мочевины также улучшил адгезионную способность водного стекла. В данной статье речь шла о влиянии жидкого стекла и поливинилового спирта на рисовые волокна шелухи и соломы для древесностружечных плит по сравнению с мерсеризацией на основе малеинового ангидрида.*
Ключевые слова: *Водное стекло, поливиниловый спирт, мерсеризация, рисовая шелуха, рисовая солома, древесностружечная плита, бензоильная группа, полифосфат, гидроксид алюминия, отвердитель, полиэтилен, композит.*

1. Introduction

1.1. The surface characteristics of the rice fiber

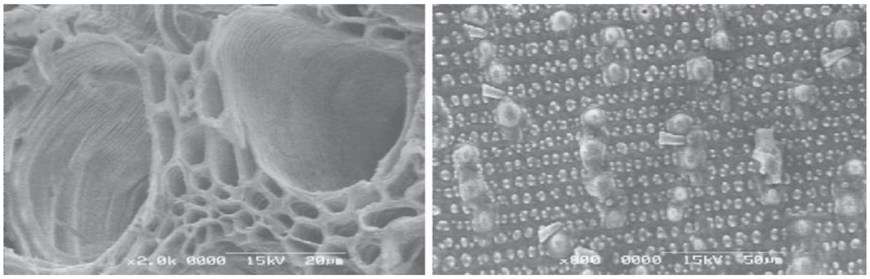
Rice husk and straw fibers are one of the bio-mass produced in agricultural industry. Rice residue is either disposed of as waste by being burnt in the field or used as animal food and bedding material. [4] The amount of rice husk and straw is not so small, and if it is not underutilized efficiently, it might affect the global warming by being burnt, and also saving the forest and petroleum resource. Today the interesting of the furniture gets higher and to meet it, variable kinds of composites made of wood are utilized, but wood resource is limited and the cultivation of them takes a long time. In case of rice husk and straw, the amount of production is constant every year in some countries use rice as main food. Now all over the world the study on used non-wood bio-fibers such as straw and rice husk fiber in place of wood for manufacturing particleboard will save existing wood. A composite is a combination of two or more materials held together by physical entanglement or a chemical matrix. [1]. Rice is harvested mechanically or manually, and the rice straw is cut off to around 400 mm length by downstream machinery, and then both rice straw and rice husk are ground to the desired particle size in a rotary knife cutter. After grinding, they would be washed with water to remove dust and impurities and dried in an oven at around 70~80°C.



(a) (b) (c)

Fig. 1. SEM micrographs of a rice husk: (a) and (b) outer surface and (c) inner surface

On outer surface of the rice husk there are well-structured corrugated cuticles, as shown in Fig. 13.2(a). As it is magnified, the outer surface has spiky trichomes, as shown in Fig. 13.2(b). These trichomes are mostly made of a form of silica called opaline silica, which is hydrated and amorphous in form. The silica content of the outer surface of the rice husk makes it abrasive and resistant to moisture. The inner surface of husk is very smooth as shown in Fig. 13.2(c).



(a) (b)

Fig. 2. SEM micrographs of a rice straw stem: (a) transverse section and (b) longitudinal section

SEM micrographs of traverse and longitudinal sections of a rice straw stem are shown in Fig. 2 [3].

1.2. The several methods for fiber surface treatment

The strong adhesion between the fiber and the matrix is the key to high strength. So many researches to modify surfaces of rice husk and the straw had been suggested in order to improve the mechanical properties. A coupling agent, at first, coats fiber surface and then bonds with matrix. There are several kinds of methods for treatment, thus, such as Mercerization, Maleic anhydride-grafted polymers, silane treatment, Acetylation, Benzoylation, Grafting of acrylic acid acrylonitrile, Permanganation, Peroxide treatment.

Mercerization: It is the widely used method for surface treatment of rice straw and husk, using alkali which makes the amount of hemicellulose and lignin reduce, therefore causes fibrillation of rice fibers or stream which makes the fibrous matter from the rice husk remove [5].

Maleic anhydride-grafted polymers: It is a usual choice for rice straw and husk. Heating polyethylene in maleic anhydride solution generates polyethylene macroradicals which may set off the polymerization of maleic anhydride or join the developing chains of poly (maleic anhydride) by reaction of peroxide radicals with polyethylene and by reaction of polyethylene–maleic anhydride radicals with polyethylene chains.

Silane treatment: Rice straw and husk interact with silane in two steps. Thus, in the first step, silane monomers are converted into silanol reactive groups upon hydrolysis, liberating alcohol molecules. And then, in the second step, silanol and rice straw and husk fibers develop interlinking through self-condensation, adsorption and chemical grafting.

Acetylation: It is an esterification reaction which has plasticize rice straw and husk fibers by-introducing acetyl functional groups (CH3COO–). The reaction of rice straw and rice husk with acetic anhydride is shown below.

$RS/RH–OH + CH_3 –C(=O)–O–C(=O)–CH_3 \rightarrow RS/RH–OCOCH_3$
$+ CH_3COOH$

This makes the fibers hydrophobic in nature and improves the water resistance and dimensional stability of the composite.

Benzoylation: Introducing benzoyl functional groups (C6H5C=O) at the fiber surface increases the water resistance by below reaction.

$RS/RH–OH + NaOH \rightarrow RS/RH–O^- Na^+ + H_2O$

$RS/RH–O^- Na^+ + benzoyl–Cl \rightarrow RS/RH–benzoyl + NaCl$

Grafting of acrylic acid acrylonitrile: The reaction of Acrylonitrile (CH_2=CHCN) as coupling agent with surface hydroxyl groups of RS/RH is shown below.

$RS/RH–OH + CH_2 =CHCN \rightarrow RS/RH–OCH_2CH_2CN$

Permanganation: MnO_3^- ion formation affects production of cellulose radicals, and highly reactive Mn^{3+} ions set off graft copolymerization.

Peroxide treatment: A schematic reaction between RS/RH fibers and polypropylene, initiated by organic peroxide, is shown below.

RO–OR → 2 RO•
RO• + PP–H → ROH + PP•
RO• + RS/RH–H → ROH + RS/RH•
PP• + RS/RH• → PE–RS/RH

2. Method of surface treatment for rice straw and husk with water glass

2.1. Mechanism of mercerization

Strong adhesion between rice straw or rice husk and polyethylene as the matrix enhances stress transfer and load distribution all along the interface. Therefore, researches for surface modification were conducted to increase this interface adhesion and thus improve the mechanical properties of the composite. Rice husk and straw are hydrophilic and it has hydroxyl groups. In this case it is difficult to fix each other because rice straw and rice husk contain cellulose, which is hydrophilic in nature, whereas the polymer matrix is hydrophobic. As mentioned above, there are trichomes made of amorphous silica called opaline silica on the surface of RS fiber. These are also hydrophilic. If RH fiber were treated with NaOH, these trichomes would react with NaOH during long term, so the strength of the composite will get lower. Of course, trichomes should contribute to increase the strength of composite instead of reacting off. If urea is added into soluble glass, its cohesive force can be improved without modifying the viscosity.[6] So sodium silicate(water glass), polyvinyl alcohol and urea formaldehyde resin were utilized for treating surfaces of natural fibers instead of sodium hydroxide. Here especially water glass is required for trichomes and UF resin is necessary for matrix which is hydrophobic and cellulose fibers which are hydrophilic. Polyvinyl alcohol is for releasing the emission of formaldehyde. Benzoyl functional groups (C6H5C=O) also is required for reaction between RS/RH fibers and water glass. Sodium silicofluoride, zinc polyphosphate and ammonium polyphosphate are used for water glass as the curing agent, and ammonium chloride as the acid-cure catalyst is used for UF. The curing reaction of water glass is shown below.

Na2O•nSiO2+CO2+mH2O=Na2CO3+nSiO2•mH2O

The process is very slow, so soluble glass is often heated or mixed with sodium fluosilicate (Na2SiF6) as an accelerator for hardening to quicken the hardening speed. Sodium fluosilicate is added into soluble glass will react as follows, speeding up the precipitation of silicic acid gel.

2[Na2O•nSiO2]+Na2SiF6+mH2O = 6NaF+(2n+ 1)SiO2•mH2O

The reaction of water glass with zinc phosphate and aluminum phosphate is shown below.

3Na2O•nSiO2+Zn3(PO4)2+mH2O = 2Na3PO4+3Zn(OH)2↓+3nSiO2•(m-3)H2O

3Na2O•nSiO2+2AlPO4+mH2O = 2Na3PO4+2Al(OH)3↓+3nSiO2•(m-3)H2O

or

RS/RH–OH + NaHSiO3 → RS/RH–$O^{-}\ Na^{+}$ + H2SiO3

RS/RH–$O^{-}\ Na^{+}$ + benzoyl–Cl → RS/RH–benzoyl + NaCl

H2SiO3(among RS/RH, and from water glass) + CaO → CaSiO3 +H2O

3H2SiO3+ 2Al(OH)3 → Al2(SiO3)3+ H2O

Instead of zinc and aluminum phosphate, the zinc and aluminum polyphosphate will react with water glass more and more. This reaction will help the curing of the water glass.

2.2. The new method for mercerization

After the formation of the hydroxyl methyl urea at a pH of about 8–9, the appropriate amount of the hydroxyl methyl urea should account for 10% of the weight of soluble glass. The formaldehyde-to-urea ratio is 1.6. The module of water glass is 3.1 and its density is 1.29 g/㎤, which is made in Kim Chaek University of Technology of DPR of Korea. The component of complex curing agent (CCA) for soluble glass and urea is shown below.

Table 1. Component of CCA

Sodium silicofluoride	Zinc polyphosphate	Aluminum polyphosphate	Aluminum hydroxide	Zinc and magnesium oxide
15	30	30	5	20

CCA should account for 20% of the weight of soluble glass. At first CCA will be mixed uniformly with 45~500 ㎛ RH and 100~1000 ㎛ RS fiber with around 10% moisture. And then the hydroxyl methyl urea and soluble glass would be mixed also with CCA and RS/RH fiber. This compound was transferred into the oven and allowed to dry for 1 h at the temperature of 60-80℃ and put at room temperature for 24 h. And then it was ground in the ball mill among the 5% polyvinyl alcohol solution of 5% of the weight of soluble glass to prevent formaldehyde emissions. Here the ammonium chloride is added. This was removed into the oven and allowed to spray and dry under the condition of thermo fan 60-80℃. Finally the treated RS/RH fibers were mixed with polyethylene as matrix for making the particleboard as traditional methods.

2.3. Result

In comparison with maleic anhydride mercerization, the mean density values obtained for RS/RH particleboard were 536 kg/m^3, it is about 30% higher. This is because of water glass and urea. After 24 h of immersion of the specimen in water samples treated by water glass had got lower 12%. Modulus of elasticity (MOE) and Modulus of rupture (MOR) were increased 20% respectively.

3. Conclusion.

It had been shown that it is possible to utilize water glass and urea for mercerization of rice husk and straw fiber particleboard. In this paper the new curing agent for water glass which was used for manufacturing RS/RH fiber particleboard had been dealt. Due to the same structure of silica water glass was more suitable and fixed well. To solve the poor water resistance of water glass and urea, zinc-aluminum phosphate and polyphosphate and pH condition for UF was dealt. The agricultural waste, RH/RS might be efficiently used for particle board. In future more and more studying, instead of wood production RS/RH fiber will contribute to human's life.

References

1. *Bassyouni M., Taha I., Abdel-hamid, S.M.-S. and Steuernagel L.*, 2012. Physicomechanical properties of chemically treated polypropylene rice straw bio- composites. Journal of Reinforced Plastics and Composites, 31, 303–312.
2. *Ryu S.-E. , Kim T.-N. and Kang T.-K.*, 1997. Pulverization of rice husks and the changes of husk densities. Journal of Materials Science. 32. 6639–6643.
3. *Zhang Q. and Cai W.*, 2008. Enzymatic hydrolysis of alkali-pretreated rice straw by Trichoderma reesei ZM4-F3. Biomass and Bioenergy. 32. 1130–1135.
4. *Buzarovska A., Bogoeva G.G., Grozdanov A., Avella M., Gentile G. and Errico M.*, 2008. Potential use of rice straw as filler in eco-composite materials. Australian Journal of Crop Science. 1 (2). 37–42.
5. *Liao Z., Song G., Shi F., Yin Z., Yang Y., Niu Z. and Tang G.*, 2011 . Preparation and characterization of PLA/rice straw fi ber composite. Applied Mechanics and Materials. 71. 1154–1157.
6. Building Materials in Civil Engineering A volume in Woodhead Publishing Series in Civil and Structural Engineering, 2011. Pages 29–45, 423.