OXIDE CERAMIC NANOPARTICLES INTO FREE-FORMALDEHYDE WOOD ADHESIVE

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INTRODUCTION

Despite the toxicity of formaldehyde, dangerous for the human health and environment, the **use of resin based on formaldehyde as wood adhesive** in the industrial production process of wood panels remains due to technical performance and economical reasons.

Synthetic resins free of formaldehyde have a higher price and are commonly used in **specific types of products**, such as pMDI.

Bio-based resins represents the only alternative for the production of free-formaldehyde resins **non-derived from petroleum**. These resins cannot provide **enough hardness** and **moisture resistance** in wood panels.

EcoPressWood European project is focused on the development of a **bio-based free formaldehyde resin** from residues of biodiesel production. To improve the hardness and moisture resistance of wood panels an extra **reinforcement provided by oxide ceramic nanoparticles** is analyzed.

Conventional oxide ceramic nanoparticles make a great commercial impact due to their **low cost** of production and that can be **easily synthesized**. Threrefore they have been used to **reinforce polymeric materials** with improved properties.

Several studies have analyzed the **use of oxide ceramic nanoparticles** in the formulation of free-formaldehyde resins used **as wood adhesives**. The results of these nanofilled resins are promising and show a marked improvement over conventional resins.

OBJECTIVE

To analyze the effect of adding oxide ceramic nanoparticles into comercial free-formaldehyde wood adhesive resins for preparing particleboards. Analyze their stability into the resin and the effect in the final properties of the particleboards performed.

EXPERIMENTAL PROCEDURE

MATERIALS Acrodur 950 L, an acrylic formaldehyde-free binder for wood resin

Resin properties	
Chemical nature	Aqueous solution of a modified polycarboxylic acid
Solid content %	46
pH	3.16
Viscosity (mPa·s)	900-2500
Density (g/cm³)	1.2
Miscibility with water	Yes

Oxide ceramic nanopowder particles,, Al_2O_3, ZnO, ZrO_2, TiO_2

Nanoparticle	Supplier	Particle size (nm)	Superficial area (m2/g)
Al_2O_3	Io-li-tec	20	<200
SiO_2	Evonik	12	200
TiO_2	Io-li-tec	10-25	50-150
ZnO	Io-li-tec	20	50
ZrO_2	Tecnan	10-15	70-110

EXPERIMENTAL TECHNIQUES

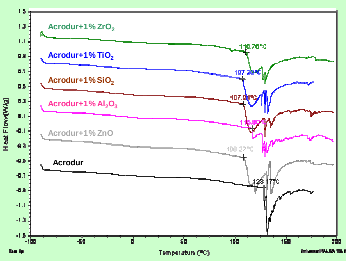
Nanoparticles at concentrations of 1-5%wt are added in the resin. Dispersions have been carried out by a high speed homogenizer (IKA RW20) at 2000 rpm during 2 h. The dispersions obtained have been followed in order to see their stability with time by their observance.

A **Differential Scanning Calorimeter (**Q200, TA Instruments**)** was used **to determine the Tc** (temperature to start the curing process) of the resin **and the Tg** (glass transition temperature). Conditions: drying of resin at 65ºC for 60 min and ramp from -90 ºC to 200 ºC at 10 ℃/min; inert atmosphere of N_2(g).

Particleboards have been performed at **lab scale** (10x10 cm) with spruce particles (1.25-3.15mm), resin content of 23%w/w, thickness 7.7 mm, 80 bar press, press time 78 s/mm and press Tª 185 +- 3ºC. To characterize the wood panels samples tensile resistance or internal bond strength (EN 319), dimensional stability or thickness swellig (EN 317) and density (EN 232) have been measured.

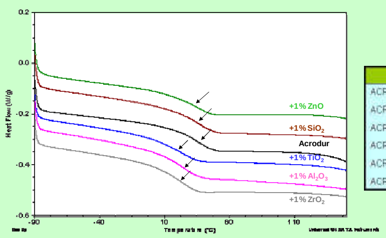
RESULTS

Differential Scanning Calorimetry



Sample	Tc (°C)
ACRODUR	128.2 ±0.1
ACRODUR + **1wt% SiO_2**	107.9 ±0.1
ACRODUR + **1wt% TiO_2**	107.2 ±0.1
ACRODUR + **1wt% Al_2O_3**	116.8 ±0.1
ACRODUR + **1wt% ZnO**	108.3 ±0.1
ACRODUR + **1wt% ZrO_2**	110.8 ±0.1

It is shown a **decrease** of the **starting curing temperature** with the addition of **nanoparticles at 1wt%**. TiO_2 produces the highest decrease (22ºC less) while Al_2O_3 the minor (11ºC less) regarding the reference sample.



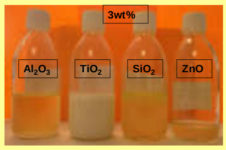
Sample	Tg (°C)
ACRODUR	36±1
ACRODUR + **1wt% SiO_2**	32±1
ACRODUR + **1wt% TiO_2**	20±1
ACRODUR + **1wt% Al_2O_3**	22±1
ACRODUR + **1wt% ZnO**	30±1
ACRODUR + **1wt% ZrO_2**	20±1

The addition of **nanoparticles at 1wt% decreases** the **glass transition temperature**. The least temperature obtained is produced with the addition of TiO_2 and ZrO_2, and the highest with SiO_2, regarding the reference sample.

Dispersions

ZrO_2 and Al_2O_3 → settle down

SiO_2, Al_2O_3 and ZnO → are stable

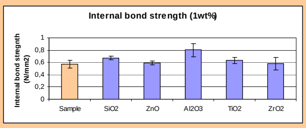


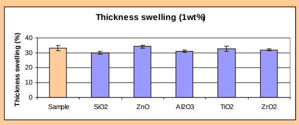
SiO_2 and ZnO → are stable around two weeks after stirring

Al_2O_3 and TiO_2 → settle down in few hours, dispersions are not stable

Mechanical properties of particleboards

1wt% of nanoparticles into the resin

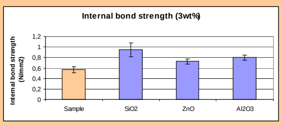


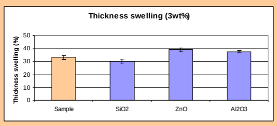


Nanoparticle	Density (Kg/cm³)
Sample	670 ± 6
SiO_2	660 ± 10
Al_2O_3	673 ± 3
TiO_2	638 ± 23
ZnO	651 ± 8
ZrO_2	671 ± 4

Improvement in internal bond strength (EN 319) and **thickness swelling** (EN 317) with the use of **SiO_2** and **Al_2O_3** at 1wt%

3wt% of nanoparticles into the resin





Nanoparticle	Density (Kg/cm³)
Sample	670 ± 6
SiO_2	657 ± 7
Al_2O_3	672 ± 3
ZnO	677 ± 10

Improvement in **internal bond strength** (EN 319) and **thickness swelling** (EN 317) with the use of **SiO_2** at 3wt%

CONCLUSIONS

- Dispersions of SiO_2 and ZnO at 1, 3 and 5wt% in the acrylic resin at 2000 rpm for 2 hours showed to be stable with time
- The oxide ceramic nanoparticles selected **decrease the temperature** value required **for starting of curing process and** the **glass transition temperature** when they are added at 1wt% in the acrylic resin
- The study of the effect of nanoparticles on commercial acrylic resin show an **improvement** in the **mechanical properties** with the addition of **SiO_2 and Al_2O_3 at 1wt%,** and also **SiO_2 at 3wt%.**

ACKNOWLEDGEMENTS

• Thanks to the European Commission. The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n°605236.

• Thanks to all the Consortium members of Ecopresswood project for their work during the project.

• Thanks to BASF for supplying us the commercial resin used in this study.