

## HIGH MECHANICAL STRENGTH WOOD POLYMER COMPOSITES BY USE OF A NEW POLYURETHANE BINDER SYSTEM

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A new type of binder for wood particles or fibres was developed using a recycled polyol from polyurethane or PET wastes and a polyisocyanate as raw materials. The binders developed with various ratios of hydroxyl and isocyanate groups are solid at room temperature with melting points between 40 and 60°C. Between 5 and 20% of these were mixed with the wood products and compression-moulded at temperatures between 80 and 100°C and 0.75 to 2.05 kp/mm<sup>2</sup> pressure to give composites of tensile strength up to 47 N/mm<sup>2</sup> or flexural strength up to 58 N/mm<sup>2</sup>.

*Keywords:* Wood; Composites; Polyurethane; PET; Recycling; Polyols

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### INTRODUCTION

Wood Polymer Composites (WPC) occupy a small but rapidly growing niche in several industries (Simonsen 1996). They are used as replacements for lumber as laminated veneer lumber or medium density fibreboard, millwork, decking, a variety of products in building, in automobiles, and even in aeroplanes. The market for specialty additives used in natural and wood fibre polymer composites was valued in 2001 at \$57 million (Principia Consulting 2002). Thus, combining wood and synthetic polymer materials of various types is the basis of a growing industry (Rials 2000). The combination of wood in different forms such as powder, fibre, sawdust, chips or the like and suitable polymers or monomers to form polymers by a polymer reaction offers a broad spectrum of products to fit into a variety of applications. Polymers used to produce such composites include phenolic resins (Hae 1975), acrylates or methacrylates both as monomers to impregnate wood or to be used as a binder, e. g. in the form of a dispersion (Dotzauer German patent 1991), urea-formaldehyde resins (Michanickl US Patent 1995), or polyisocyanates (Iwata German patent 2000; Oldemeyer German patent 1991) or polyurethanes (Ambrose European patent 1984). The density of the wood is increased by use of monomers to penetrate the cells of wood and fill the voids. The strength of wood is similarly increased but still more by chemical bonding of the basic macromolecules of wood. The chemical bonding can be generally achieved by any reactive group for the hydroxyl groups of the wood, e. g. acrylics, carboxylic acids, isocyanates, epoxies a.s.o. Further, combinations of two or more of such monomers maybe used (Ellis 1997). Thus, the chemical combination of diacrylates, hydroxyethyl methacrylate, and hexamethylene diisocyanate greatly decreased wetting and penetration of water into the wood (Ellis

1999). The use of binders prepared from polyisocyanates to bond wood particles is well known, and the combination of the polyisocyanate (in general polymeric 4,4'-diphenylmethane diisocyanate) and water or a polyol or polyolmixture is frequently used (Dietrich German patent 1996; Gaul, German patent 1983; König German patent 1990; Oldemeyer German patent 1993). Further, as polyisocyanates one may use the reaction products of such polyisocyanates and polyols, so called prepolymers with various isocyanate content (Behrendt 2004).

In this paper we report on another type of binder to be used in the preparation of WPC, leading to another processing technology. The aim of this work was to obtain a new type of wood composite materials with high mechanical properties.

## EXPERIMENTAL

Binders were prepared of polymer 4,4'-diphenylmethane diisocyanate (Lupranat® M20A of Bosig Baukunststoffe GmbH) and two types of polyols based on specially designed polyols derived on one hand from polyurethane flexible foam wastes (Behrendt US patent 2004) or on the other hand from PET (Behrendt German patent 1999).

The polyols were characterised by:

- hydroxyl number according to DIN 53 240,
- acid number according to DIN 53 402
- amine number according to DIN 16 945 and
- viscosity measured on Rheo Stress 300 at 25°C.

The binders were characterised by:

- isocyanate content according to DIN 53 185,
- melting temperatures were determined by DSC on Netzsch DSC 204 with heating rate of 1 K/min in the range of 20 to 250 °C

The detailed processes are described elsewhere. Here, only a general description is given for both processes:

- (1) Polyol V1: Into a 100 l jacketed stainless steel reactor are charged 31.5 kg of dipropylene glycol and 5.5 kg of di-n-butyl amine. The reactor is heated to 165°C and 63.0 kg of polyurethane high resiliency foam flakes are added as fast as possible with agitation. After completion of the addition, the contents of the reactor are heated to 200°C and the contents agitated at this temperature for another 30 minutes. The contents are cooled down and recovered. No further treatment is performed. The recycling polyol had a hydroxyl number of 301 mg KOH/g, amine number of 53 mg KOH/g and a viscosity of 3,810 mPas (25°C). The polyol will be named V1 in the text to follow.
- (2) Polyol V2: The process is identical but the reactants composition is as follows: 65.6 % b.w. HR-Foam ; 29.2 % b.w. dipropylene glycol; 5.2 % b.w. di-n-butyl amine. To the polyol thus prepared are added 30.1 % of polypropylene glycol with an average molecular weight of 2000 (Lupranol® 1000, BASF). The hydroxyl number of the mixture was determined to be 237 mg KOH/g, the amine number 48.7 mg KOH/g and the viscosity 4,000 mPas (25°C).

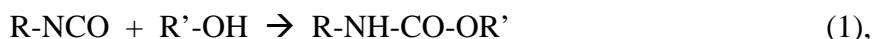
- (3) Polyol LF 126: Into a 400 l jacketed stainless steel reactor are charged 155 kg of diethylene glycol. This is heated with agitation to 180°C. Into the glycol are added 10 kg of glycerol and 550 g of tin catalyst. Into this mixture are introduced by conveyor 154 kg of PET granules. The mixture is heated to 250°C with agitation and held at this temperature for another 4.5 hours while 32 kg of ethylene glycol is distilled off. After completion, an aromatic polyester polyol is obtained having a hydroxyl number of 320 mg KOH/g, an acid number of 0.45 mg KOH/g and a viscosity of 3,180 mPas (25°C).
- (4) The binders were prepared in 10 l reactors into which at first the calculated amount of isocyanate was placed into which by agitation the polyol was added stepwise in such a manner as not to exceed a temperature of 80°C. In the case of binders GP 22, GP 25, GP 27, GP 30 prepared from aromatic polyester polyol and p. MDI the reaction mixture was agitated for another 150 min. The obtained binders were cooled to room temperature. After conditioning for about 20 hours the binders were recovered and milled to a particle size of 2 to 4 mm. The milled binders were flushed with nitrogen and stored in a container preliminarily filled with nitrogen.
- (5) Composites were prepared by using the previously obtained binders and pine wood with a particle size of 2 to 4 mm, an acidity 0.03 %, a specific volume of 8 dm<sup>3</sup>/kg, and water content of 5%. A two step procedure was applied. The wood material is introduced into a 5 l reactor and a stirrer started. Into this, the calculated amount of binder is added and stirring continued for about 30 minutes at room temperature. After this time the additive is introduced into the mixture and mixing continued for another 30 minutes. The homogenous mixture is portioned and placed in the respective amounts into the moulds. On the mixture is applied the temperature both by mould and stamp, the pressure, and the time are given in the description. After the time planned, the moulded composites are recovered by cooling the mould and stamp to room temperature and recovering. The moulded composites are conditioned for 12 days at room temperature before mechanical testing (Georgieva German patent 2005) on a Zwick Z 20 (universal testing machine in the tensile or flexural strength mode according to DIN EN ISO 527-1).

## RESULTS AND DISCUSSION

Wood polymer composites are prepared either with thermoplastic binders such as polypropylene or with liquid binders such as liquid polyisocyanates or dispersions. In the case of hydrocarbon thermoplastics there is hardly a real bonding between the hydrophilic wood particles and the hydrophobic polymer matrix. Furthermore, the polymer has to be used in proportions exceeding 50% by weight. To improve the bonding between wood and thermoplastic material, a coupling agent is frequently used, e.g. a copolymer with maleic acid anhydride (Klemm 2005). By the maleic acid structural component a reaction is possible between the free hydroxyl groups of the cellulose and the carbonic anhydride to form carboxylic ester bonds and setting free a limited number of carboxylic acid groups. The esterification reaction proceeds rather slowly and needs to be carried out at relatively low temperatures so as not to damage one of the components.

To overcome these difficulties we developed another route to wood polymer composites with chemical bonds between the binder matrix and the filler. This route may be described as follows:

- (1) The reaction between wood particles and binder is performed between hydroxyl groups of the cellulose and isocyanate groups of the binder according to the well known general equation



- (2) The binder is composed of a mixture of long and short chain polyhydroxyl compounds as derived from the solvolysis of polyurethane high resiliency foams with an average functionality in the range of ca. 2.25 and a polymeric isocyanate of a functionality of ca. 2.85 to produce a branched binder where the long chain polyhydroxyl compound acts a flexibilizer,
- (3) The binder contains additionally micro dispersed oligoureas as produced during the solvolysis from the originally employed polyisocyanate being able to form strong hydrogen bonds and enhancing with them the adhesive forces of binder and wood filler,
- (4) The reaction of isocyanate and hydroxyl groups is catalyzed by the catalysts present in the solvolysis products obtained by the chemical degradation of the polyurethane foams (of the original foams) leading to short reaction times at rather mild temperatures,
- (5) The binders produced are designed in a way so as to melt completely at temperatures in the range of 50 to 90°C and being able to flow under the conditions of pressure to coat the particles to a high degree.

### Preparation of the Binders

To prepare the binders, the polyols were reacted with polymeric 4,4'-diphenylmethane diisocyanate (p-MDI) in the metal reactor as described. The main parameters of the binders thus prepared from the polyurethane solvolysis products are presented in Table 1 and those of the binders produced from the aromatic polyester polyol in Table 2.

**Table 1.** Examples of Binders Produced from Polyol V1 and V2

Binder	1-22	1-25	1-27	2-100
<b>Composition</b>				
Polyol V 1 (% by weight)	38.8	35.8	34.0	0
Polyol V 2 (% by weight)	0	0	0	39.5
Lupranat® M20S (% b.w.)	61.2	64.2	66.0	60.5
Eq (polyol) : Eq (NCO)	1 : 2.2	1 : 2.5	1 : 2.7	1 : 2.7
<b>Properties</b>				
NCO – Content (%)	6.77	6.75	6.4	8.0
Melting peak (°C) (DSC)	49.2	45.4	66	57

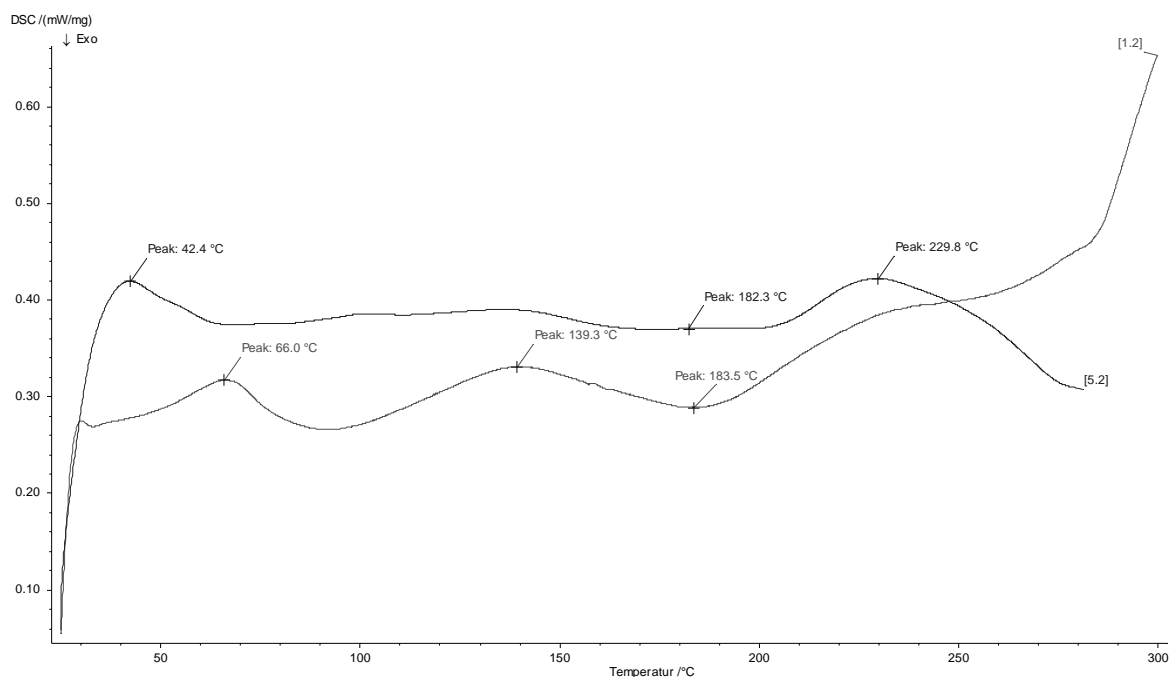
By choosing the ratio of the equivalents of isocyanate and hydroxyl group we established the amount of free isocyanate groups. All binders were characterized by DSC measurements to make sure that all hydroxyl groups had reacted and that there would not occur any post curing, resulting in a change of properties. Melting peaks also were

obtained from the DSC curves. The latter depend to a lesser extent on this ratio but more on the mode of preparation and possible side reactions. Because of the rather high degree of catalytic activity, nitrogen side reactions such as trimerization of the isocyanate groups may occur and increase both melting point and melt viscosity (Fig 1, 1.2). Thus, the melting areas at rather low indices were established in the low melting region. Despite the low melting areas the binders were subjected to a milling process without any problems due to frictional heat.

**Table 2.** Binders Prepared from an Aromatic Polyester Polyol and p-MDI

Binder	GP22	GP25	GP27	GP30
<b>Composition</b>				
Polyol LF 126 (% b. w.)	37.2	36.3	32.6	30.3
Lupranat M20S (% b.w.)	62.8	65.7	67.4	69.7
Eq (polyol) : Eq (NCO)	1 : 2.2	1 : 2.5	1 : 2.7	1 : 3.0
<b>Properties</b>				
NCO – Content (%)	4.54	4.90	5.88	8.68
Melting peak (°C) (DSC)	58.2	53.3	53.5	54.7

In case of the aromatic polyester polyols there is no catalyst available in the polyol itself, thus not leading to side reactions and a clear dependence of the isocyanate content on the ratio of the equivalents of isocyanate and hydroxyl groups (Fig. 1, 5.2). Despite the rather low melting temperatures the binders could be milled in the same way as above without difficulties arising.



**Figure 1.** DSC of binder 1-27 [1.2] and binder GP 27 [5.2]

### Composite Preparation

Composites were generally prepared by mixing of the corresponding wood material and finely ground isocyanate binder. The thoroughly mixed materials were subjected to a press with heated moulds for a certain time at a pre-determined temperature. The typical first formulation for starting a series of experiments was 80 % by weight of wood material and 20 % by weight of binder. To avoid damage of the wood particles or fibres the pressing temperature was kept as low as possible just to allow flow of the molten binder between the particles. The time of applying temperature and pressure was adjusted to a degree of conversion of the isocyanate groups greater than 90% as seen from infrared spectra. The pressure applied was in general in the range of 0.75 kp/mm<sup>2</sup>.

By using binders with different isocyanate content derived from corresponding ratios of hydroxyl and isocyanate groups of the materials reacted, it was shown that the highest mechanical strength was obtained at an isocyanate content of 6.4 % (sample GW 27-0). As the conditions to prepare the composites were held constant in the course of this investigation, no further optimization with respect to those conditions was made (see Table 3).

**Table 3.** Composites of Wood Particles of 4 mm Diameter and Binders with Various Isocyanate Contents

Wood polymer composite	GW 22-0	GW 25-0	GW 27-0	GW 100-0
<b>Formulation</b>				
Wood (% b. w.)	80	80	80	80
Binder 1-22 (% b. w.)	20	0	0	0
Binder 1-25 (% b. w.)	0	20	0	0
Binder 1-27 (% b. w.)	0	0	20	0
Binder 2-100 (% b. w.)	0	0	0	20
<b>Reaction conditions</b>				
Temperature (°C)	100	100	100	100
Pressure (kp/mm <sup>2</sup> )	0.75	0.75	0.75	0.75
Pressing time (min)	10	10	10	10
<b>Properties</b>				
Tensile strength (N/mm <sup>2</sup> )	37.5 ± 7.2	42.1 ± 8.9	43.2 ± 4.4	-
Elongation at break (%)	1.08 ± 0.24	0.97 ± 0.24	1.69 ± 0.14	-
E modulus (N/mm <sup>2</sup> )	4744 ± 876	5455 ± 253	4828 ± 571	-
Flexural strength (N/mm <sup>2</sup> )	38.5 ± 9.4	43.5 ± 9.9	45.9 ± 10.3	32.9 ± 8.7
Elongation at break (%)	1.63 ± 0.24	1.64 ± 0.15	1.73 ± 0.3	1.96 ± 0.35
E modulus (N/mm <sup>2</sup> )	2864 ± 685	3708 ± 785	3276 ± 800	2430 ± 599

When using different ratios of wood particles and binder under the same conditions of preparation, the decreases in the amount of binder lead to nearly the same properties to 15 % of binder but decreased sharply below this value. At 5 % of binder only 20% of the flexural strength was found, showing that there is a minimum of binder and reactive groups necessary for good properties. This limit is obviously reached at 15 % (see Table 4).

**Table 4.** Composites Made from Different Ratios of Wood Particles and Binder

Wood polymer composite	GW 27-0	GW 27-3	GW 27-4	GW 27-5
<b>Formulation:</b>				
Wood (% b. w.)	80	85	90	95
1-27 (% b. w.)	20	15	10	5
<b>Reaction conditions</b>				
Temperature (°C)	100	100	100	100
Pressure (kp/mm <sup>2</sup> )	0.75	0.75	0.75	0.75
Pressing time (min)	10	10	10	10
<b>Properties</b>				
Tensile strength (N/mm <sup>2</sup> )	43.2 ± 4.4	34.9 ± 7.6	17.2 ± 5	13.1±2.2
Elongation at break (%)	1.69 ± 0.14	0.87 ± 0.25	0.42 ± 0.25	0.38±0.1
E modulus (N/mm <sup>2</sup> )	4828 ± 571	5118 ± 231	4375 ± 485	3381±359
Flexural strength (N/mm <sup>2</sup> )	45.9 ± 10.3	44.4 ± 4.9	31.2 ± 4.7	9.1±1.8
Elongation at break (%)	1.73 ± 0.3	1.71 ± 0.08	1.42 ± 0.19	1.04±0.25
E modulus (N/mm <sup>2</sup> )	3276 ± 800	3089 ± 438	2861 ± 361	1419±209

In the following series the effect of pressing time at fixed conditions (pressure and temperature) and composition on the mechanical properties of the composites was investigated (see Table 5).

**Table 5.** Composites Made with Pressing Time between 5 and 20 Min

Wood polymer composite	GW 27-10	GW 27-3	GW 27-12	GW 27-14
<b>Formulation</b>				
Wood (% b. w.)	85	85	85	85
Binder 1-27 (% b. w.)	15	15	15	15
<b>Reaction conditions</b>				
Temperature (°C)	100	100	100	100
Pressure (kp/mm <sup>2</sup> )	0.75	0.75	0.75	0.75
Pressing time (min)	5	10	15	20
<b>Properties</b>				
Tensile strength (N/mm <sup>2</sup> )	19.7 ± 2	34.9 ± 7.6	23.1 ± 2.8	23.3 ± 3.1
Elongation at break (%)	0.62 ± 0.08	0.87 ± 0.25	0.62 ± 0.12	0.74 ± 0.17
E modulus (N/mm <sup>2</sup> )	3840 ± 567	5118 ± 231	4280 ± 438	4190 ± 490
Flexural strength (N/mm <sup>2</sup> )	23.1 ± 2.5	44.4 ± 4.9	24.9 ± 3	21.4 ± 2.8
Elongation at break (%)	0.98 ± 0.11	1.71 ± 0.08	1.35 ± 0.05	1.31 ± 0.15
E modulus (N/mm <sup>2</sup> )	2801 ± 233	3089 ± 438	2295 ± 301	2057 ± 250

As seen from Tables 4 and 5, the mechanical properties determined as the flexural strength had their highest values at 20 % binder and 10 min pressing time. A higher temperature was characterized by a slight drop in the value; the reason was assumed to be a beginning degradation of the wood particles.

In case of binders prepared from aromatic polyester polyols (APP) and polyisocyanates, the same methods were applied. Examples of binders based on the APP mentioned are given in Table 2. By choosing appropriate ratios of hydroxyl groups to isocyanate groups, binders with isocyanate contents in the range between 4.5 and 8.7 % were obtained. These had main melting peaks in the DSC between 60 and 40°C. The binders were obtained in big lumps but were milled without cooling or using cryo techniques to powder, showing no decrease in isocyanate content or melting behaviour, so that it is believed that they are unchanged by such processes. Further, the binder

powders were stored under a blanket of nitrogen for more than one year, and the loss in isocyanate content was less than 3 %. As with the binders discussed above by this process, stable, highly effective binders for wood materials can be produced.

From the binders described above, composites were prepared using similar conditions as in case of the binders produced from the polyurethane solvolysates. Composites prepared with the binder GP27 having an isocyanate content of 5.9% are shown in Table 6.

**Table 6.** Wood Composites Prepared with Binder GP 27 and Different Ratios of Wood and Binder

Wood polymer composite	3-27-081	3-27-08	3-27-082	3-27-083
<b>Formulation</b>				
Wood (% b. w.)	80	85	90	95
Binder GP 27 (% b. w.)	20	15	10	5
<b>Reaction conditions</b>				
Temperature (°C)	80	80	80	80
Pressure (kp/mm <sup>2</sup> )	0.75	0.75	0.75	0.75
Pressing time (min)	10	10	10	10
<b>Properties</b>				
Tensile strength (N/mm <sup>2</sup> )	46.6 ± 6.7	44.7 ± 5.5	38.4 ± 3.4	24.3 ± 2.2
Elongation at break (%)	0.81 ± 0.14	0.90 ± 0.12	0.80 ± 0.14	0.60 ± 0.09
E modulus (N/mm <sup>2</sup> )	5800 ± 622	5180 ± 827	5640 ± 383	4410 ± 596
Flexural strength (N/mm <sup>2</sup> )	57.7 ± 5.6	56.9 ± 9.6	47.2 ± 8.6	27.0 ± 5.1
Elongation at break (%)	1.38 ± 0.06	1.35 ± 0.14	1.15 ± 0.16	1.10 ± 0.07
E modulus (N/mm <sup>2</sup> )	5150 ± 616	5050 ± 1236	5390 ± 1127	3450 ± 601

The data of Table 6 show a significant dependence of the mechanical properties on the proportion of binder used. In this series, the drop in mechanical properties is clearly to be seen after passing the ratio of 85 % wood and 15 % binder. Lower concentrations led to serious losses in mechanical strength. With a binder concentration of 10%, composites with rather high values could be obtained, and these may be further increased by optimization of the technical process of preparation.

A similar investigation was performed employing different times of pressing. The description of samples and their mechanical properties is shown in Table 7. The pressing time at fixed ratio of binder and wood particles as 15 and 85, as well as pressure and temperature, were kept constant. Pressing time was increased from 5 to 20 minutes. When employing this ratio there is no significant increase in mechanical properties between 5 and 20 minutes pressing time. The small differences are within the range of statistic error.

Summing up these experiments, the optimum conditions of producing wood polymer composites from this type of binder and using this technology optimum conditions are a pressing temperature of 80°C with a pressure of 0.75 kp/mm<sup>2</sup>, using a pressing time of 10 minutes at a binder concentration of 15%.



**Table 7.** Wood Composites Prepared with Binder GP 27 and Different Pressing Time

Wood polymer composites	3-27-084	3-27-08	3-27-085	3-27-086
<b>Formulation</b>				
Wood (% b. w.)	85	85	85	85
Binder GP 27 (% b. w.)	15	15	15	15
<b>Reaction conditions</b>				
Temperature (°C)	80	80	80	80
Pressure (kp/mm <sup>2</sup> )	0.75	0.75	0.75	0.75
Pressing time (min)	5	10	15	20
<b>Properties</b>				
Tensile strength (N/mm <sup>2</sup> )	42.6 ± 4.9	44.7 ± 5.5	42.6 ± 2.6	45.8 ± 5.6
Elongation at break (%)	0.99 ± 0.13	0.90 ± 0.12	0.90 ± 0.11	0.91 ± 0.16
E modulus (N/mm <sup>2</sup> )	5180 ± 688	5180 ± 827	5310 ± 389	6030 ± 254
Flexural strength (N/mm <sup>2</sup> )	53.1 ± 9.7	56.9 ± 9.6	55.3 ± 4.9	55.5 ± 3.8
Elongation at break (%)	1.30 ± 0.1	1.35 ± 0.14	1.28 ± 0.12	1.34 ± 0.21
E modulus (N/mm <sup>2</sup> )	4750±1038	5050±1236	5970 ± 869	5080 ± 539

## CONCLUSIONS

1. It could be demonstrated that wood composites may be obtained by using a completely new strategy involving the mixing of the wood particles or fibers with solid binders bearing a content of reactive isocyanate groups between 4.5 and 8%.
2. The wood composites thus prepared have tensile strength up to 47 N/mm<sup>2</sup> or flexural strength up to 58 N/mm<sup>2</sup>. The elongation of break usually is better than 1% and under optimum conditions reaches more than 2%, showing that this type of composites is highly elastic and does not tend to be brittle.
3. The reaction conditions as found in the case of pressing are rather mild; i.e. temperatures are between 80 and 100°C, while the application of this temperature is in the range of 10 minutes, depending both on the process and thickness of the plate material.
4. The use of two types of binders, both based mainly on recycling polyols, one prepared from flexible polyurethane industrial waste the other from PET waste, offers additional advantages both with respect to the quality of the products and to the economy of the process.
5. Finally, the described wood composites are based on wood material otherwise rarely used and on binders produced by a new process mainly based on recycled materials.
6. These features, together with the low cost technology, have important economical advantages when used in places where state-of-the-art products have either too high prices or too high evolution of VOC's. These considerations may add further value to the new products.
7. Alternatively, similar products may be obtained by use of binders derived from polyester resins, such as used in powder coatings or the wastes produced in such processes which are known as overspray (Behrendt 2004; Georgieva German patent 2005).

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