

## WOOD POLYMER COMPOSITES USING A BINDER BASED ON POLYURETHANE RECYCLING PRODUCTS

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Received 05 July 2007

Accepted 30 October 2007

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### ABSTRACT

A new type of binder for wood particles or fibres was developed using a recycling polyol from polyurethane 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 45 and 80 °C. 5 and 20 % of these were added to wood products and this mixture compression moulded to give the composites materials.

*Keywords:* wood, composites, polyurethane, recycling.

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### INTRODUCTION

Composites based on wood and various binders are frequently used in design and construction where a broad range of properties is established both by the type and shape of the wood particles and the binder used [1]. Phenolic resins, urea formaldehyde resins, acrylates, epoxies or polyurethanes are used as binders [2-5]. Recent developments favour aqueous dispersions of acrylics or polyurethanes instead of urea or phenolic resin due to the supposed elimination of formaldehyde from these polymeric binders. In another application polyisocyanates are used as liquids and directly combined with the wood particles in a spray and pressing process [6]. Handling of the polyisocyanates and their use in a spraying process constitutes always some safety problems.

In the present paper we report another opportunity of such processes by the use of specially developed

solid and easy and low melting polymeric binders with multitude of reactive groups. The process is based on the development of two new types of reactive precursors, i. e.

- specially designed polyol components derived from industrial polyurethane wastes and produced by a new solvolysis process [7];

- solid, low melting isocyanate containing prepolymers [8] with free isocyanate groups being stable over at least one year and containing catalysts to promote the reaction of the isocyanate and hydroxyl groups of the wood.

The process [8] to produce the composites is based on the properties of the solid prepolymers and is applied in the following stages:

- mixing of the powdered prepolymer with the wood particles in the appropriate proportion in a dry process;

- forming the mixture to the shape and magnitude of the composite intended;
- applying pressure and temperature to the mixture in a mould.

In this paper the preparation of the reactive intermediates and the process to produce such composites of various properties and fields of application is described.

## EXPERIMENTAL

### Materials

Dipropylene glycol (DPG) was obtained by Fluka AG and used without further purification, polypropylene glycol 2000 was a gift of Elastogran AG, Germany, di-n-butyl amine (DBA) was purchased from Merck KGaA, Darmstadt, Germany, and used without further treatment. The polymeric 4,4'-diphenylmethane diisocyanate (Lupranate® M20S) was a gift from Bosig Baukunststoffe GmbH. The types of polyurethanes used were samples from producers of Germany, Japan, Mexico, Poland, USA, Bulgaria, or Portugal. For the experiments to follow, mainly high resiliency foam (HR foam) of a German producer was used.

### Method to obtain a recycling polyol

The composition, the reaction condition and the characteristics of the recycling polyol are given in Table 1. The polyol was derived from flexible polyurethane foams by solvolysis [7]. The experiments were performed in a three necked glass flask with stirrer, thermometer, reflux and solids inlet. The liquids were placed into the reactor, heated to 180°C, and the PUR foam was introduced with stirring as fast as possible while the temperature was slowly increased to the final reaction temperature of 220°C and was kept after completion of the addition for another 30 minutes. The reaction mixture was cooled down, recovered and subjected to analysis for determination of the hydroxyl number (DIN 53 240), amine number (DIN 16 945) and viscosity (DIN 3219) using a Rheo Stress 300 (Haake GmbH).

The polyol was used without further purification.

Table 1. Formulation and characteristics of the recycling polyol.

Sample	BP 1
<b>Composition:</b>	
PUR-Foam , % <sub>mass</sub>	64
Dipropylene glycol, % <sub>mass</sub>	27
Poly(propylene glycol) 2000, % <sub>mass</sub>	5
Di-n-butyl amine, % <sub>mass</sub>	4
<b>Reaction conditions:</b>	
Temperature, °C	180-220
Addition time, min	120
Post reaction time, min	40
Post reaction temperature, °C	220
<b>Properties:</b>	
Hydroxyl number, mg KOH/g	301
Amine number, mg KOH/g	53
Viscosity (25°C), mPa	3810

### Method of obtaining of prepolymers

The preparation of the prepolymers [8] was performed in a stainless steel vessel with oil heating mantle, stirrer, nitrogen inlet, column, condenser, and bottom outlet. The polyisocyanate was introduced into the vessel, nitrogen applied for about 5 minutes and the temperature raised to 45°C. The polyol was added in steps not to exceed a temperature of 80°C. After completion of the addition, the temperature was kept at 80°C for three hours. After this phase, the prepolymer was recovered from the vessel by recovering through the bottom outlet onto Teflon® coated steel plates and cooled to ambient temperature. After conditioning for 24 hours it was milled using a lab mill to receive a powder with average particle diameter of less than 1 mm. The main parameters of prepolymers thus obtained are presented in Table 2. The isocyanate content was determined according to DIN 53 185.

The prepolymers obtained were used without further treatment. Under ordinary conditions they are stable up to two years.

Table 2. Examples of prepolymers produced from polyol BP 1.

Sample:	PP 1-1	PP 1-2	PP 1-3	PP 1-4	PP 1-5
Composition:					
Polyol BP 1, % <sub>mass</sub>	28.5	31.7	34.0	35.8	37.7
Lupranat M20S, % <sub>mass</sub>	71.5	68.3	66.0	64.2	62.3
Properties:					
NCO – content, %	11.28	9.58	8.36	7.05	4.87
Melting area, °C, (DSC)	56.2	66.4	49.3	58.4	64.8
Peak beyond melting peak, °C	113	182	130	133	131

### Method of obtaining and characterisation of the composites

Composites were prepared using a two-step process. The first step was mixing the wood particles with the calculated amount of powdered prepolymer in a drum. In the second step the mixture was placed into a mould (100 / 200 / 20 mm). The mould with the mixture was heated to the desired temperature of moulding and the predetermined pressure applied by a lab press type RSR 200 for the time given. After cooling the mould to 50°C the composite was removed.

Mechanical tests, i. e. tensile strength, elongation at break, elastic modulus, were performed with a Zwick Z20 Universalprüfmaschine (DIN EN 527-1) after conditioning the samples for seven days at room temperature.

Melting points were determined using a Netzsch DSC 102 with a heating rate of 1K/min between –100 and +200 °C.

### RESULTS AND DISCUSSION

The polyols used in this investigation were recycling polyols derived from HR foams. Their characteristic parameters are depicted in Table 1. They generally have a completely different structure and composition as virgin polyols and, hence, unique properties. Consequently, also the polyurethanes produced on their basis will have mechanical or thermal properties which differ from such polyurethanes being produced from ordinary polyols. The main components of the recycling polyols are:

- the polyether polyol originally used to prepare the polyurethane (main component),
- any short chain glycol, e. g. poly(ethylene glycol) 600 used in the formulation,
- all catalysts used, i.e. tertiary amines and tin compounds (the latter are fully active),
- silicones used as cell stabilizers,
- the short chain glycols of the reaction mixture,
- ω-hydroxyl-urethanes from the transesterification of the hydroxyl component at the urethane group,
- trisubstituted polyureas derived from the originally used isocyanate and the amine used in the reaction.

The recycling polyols constitute thus a mixture of various components which were controlled only by the composition of the solvolysis mixture. One essential feature is that the originally present isocyanates were first reacted to the urethanes and by the solvolysis process converted to trisubstituted polyureas with chain length up to several nanometers. These form a kind of nanofillers with some reactive (amino) groups left. They will further react with any isocyanate added. The catalysts originally present are further fully active in the mixture. This could result in instable liquid prepolymers leading to gelation.

The properties of the recycling polyol (BP1), e.i. hydroxyl number 301 mg KOH/g, amine number 53 mg KOH/g, viscosity at 25°C 3810 mPas are suitable for preparation of solid prepolymers. The hydroxyl and amine content are balanced to the amount of isocyanate

Table 3. Physical-mechanical properties of composites using prepolymer PP 1-3.

Sample	01	02	03	04
Formulation:				
Wood, % <sub>mass</sub>	75	80	85	90
Prepolymer, % <sub>mass</sub>	25	20	15	10
Reaction conditions:				
Temperature, °C	120	120	120	120
Pressing time, min	20	20	20	20
Pressure, kp/cm <sup>2</sup>	51.2	51.2	51.2	51.2
Properties:				
Tensile strength, N/mm <sup>2</sup>	39.7	20.2	18.4	9.4
Elongation at break, %	0.62	0.67	0.31	0.27
E modulus, N/mm <sup>2</sup>	6833	3293	5535	2795

Table 4. Physical-mechanical properties of composites produced of prepolymer PP 1-3.

Sample	021	022	023	024
Formulation:				
Wood, % <sub>mass</sub>	80	80	80	80
Prepolymer, % <sub>mass</sub>	20	20	20	20
Reaction conditions:				
Temperature, °C	120	120	120	120
Pressing time, min	20	20	20	20
Pressure, kp/cm <sup>2</sup>	102.4	153.6	204.8	256
Properties:				
Tensile strength, N/mm <sup>2</sup>	15.4	11.2	30.7	22.1
Elongation at break, %	0.38	0.29	0.77	0.54
E modulus, N/mm <sup>2</sup>	4360	3424	4434	4629

to be used to establish the melting areas useful in further processing.

The prepolymers prepared (Table 2) are powders stable at room temperature. They have an isocyanate content in the range of 4.87 to 11.28 %<sub>mass</sub>. The prepolymers still contain the catalysts of the original polyurethane which are fully active as are the isocyanate. It was found that the prepolymers are nevertheless stable at room temperature in a closed container up to two years. Their high reactivity toward hydrogen-active compounds together with the low melting point is of

advantage in producing composites from natural resource of various kinds.

The prepolymers were prepared at constant conditions reaction so as to measure the effect of the composition on the properties. In this series, the melting peak (determined by DSC) shows a minimum at an isocyanate content of 8.36 %<sub>mass</sub> at about 50°C with increasing values to both lower and higher isocyanate contents reaching in both cases about 65°C. The determination of the melting peaks was rather complex due to the complicated structure of the material having a great

Table 5. Physical-mechanical properties of composites produced of prepolymer PP 1-

Sample	023	053	054
Formulation:			
Wood, % <sub>mass</sub>	80	80	80
Prepolymer, % <sub>mass</sub>	20	20	20
Reaction conditions:			
Temperature, °C	120	120	120
Pressing time, min	20	30	40
Pressure, kp/cm <sup>2</sup>	204.8	204.8	204.8
Properties:			
Tensile strength, N/mm <sup>2</sup>	30.7	30.26	30.31
Elongation at break, %	0.77	0.42	0.56
E modulus, N/mm <sup>2</sup>	4434	5147	4225

number of different species with melting ranges between  $-65^{\circ}\text{C}$  (glass transition of the polyurethanes derived from the polyether triol) and  $+250^{\circ}\text{C}$  (melting point of the polyureas of MDI). The second peak observed usually in the range of  $130^{\circ}\text{C}$  degrees maybe attributed to the lower chain length  $\omega$ -isocyanato-oligourethanes of the glycols.

It is essential to keep in mind that despite of various ratios of hydroxyl and isocyanate groups the prepolymers exhibit similar melting points and melting behavior and, thus, having very little effect on further processing conditions.

The prepolymer PP 1-3 was used for obtaining composites. From Table 3 it can be seen that with decreasing amount of prepolymer there is a decrease in the tensile strength of the composite simultaneously with a reduction of the elongation at break. It is seen that in the range of 20 to 15 %<sub>mass</sub> of prepolymer the mechanical properties show a plateau and do not follow a straight line while with a higher portion of wood particles the decrease in properties is dramatical.

This results in the proposal to use for producing high quality wood products a prepolymer amount of about 20 %<sub>mass</sub>.

In a further series (Table 4) with constant proportions of wood particles and prepolymer the processing conditions were optimized. The effect of pressure

in the process is illustrated. The mechanical properties depend on the pressure in such a way as they pass a maximum with a certain pressure, here shown with sample 023, to result in maximum tensile strength and elongation at break. Higher pressure applied will reduce the mechanical properties again, presumably due to a breakdown of the wood structure.

In the following series was investigated the effect of pressing time at fixed conditions (pressure and temperature) and composition on the mechanical properties of the composites (Table 5). The time of pressing of the components in the mould at fixed conditions suggests that a longer pressing time than 20 minutes has nearly no effect on the mechanical properties. Small differences are usually within the range of statistical error.

It is seen from the experiments to prepare composites with wood that this new type of prepolymers is well suited to receive such composites with high mechanical strength even when employing rather mild conditions. Here, a press temperature of  $120^{\circ}\text{C}$  at a pressure of  $200\text{ kp/cm}^2$  for 20 minutes was found to be the optimum.

## CONCLUSIONS

According to the investigations shown the following conclusions can be reported:

Recycling polyols from HR PUR foam may be converted to a new type of stable prepolymers by reacting them with polyisocyanates. It could be shown that the reaction of polymeric MDI results in prepolymers being stable at room temperature and having a melting point exceeding 50°C so they are solid at room temperature and may be subjected to typical mechanical processing such as milling. It is surprising that material containing isocyanate groups between 4.87 and 11.28 %<sub>mass</sub> and highly active catalysts are stable over a period of two years even with no protection or nitrogen blanket. A new type of binder material has been developed which may have much more fields of application as was shown here.

The prepolymer binders are highly effective in bonding wood particles even at a rate of 15 %<sub>mass</sub> added under various of conditions. The composite material obtained by this process has high mechanical properties as was shown by the tensile strength being up to 40 N/mm<sup>2</sup> and the elongation at break between 0.27 and 0.77 %. So, the prepolymer binders add to the elasticity of the composites without affecting negatively the properties of wood.

All these applications make the developed polyols and the prepolymers valuable new intermediates for the production of composites.

#### Acknowledgements

*D. Georgieva acknowledges the receipt of a grant by the German Federal Ministry of Economy. The authors are grateful for generous gifts of the Bosig Baukunststoffe GmbH and Elastogran AG.*

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