OBTAINING OF CELLULOSE POLYMER COMPOSITES ON THE BASIS OF AROMATIC POLYOL AND SECONDARY FIBROUS MATERIAL

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Abstract

The development of composite materials and their production technologies is one great innovation in history of materials science. Of special interest are wood polymer composites, possessing high physical and mechanical properties and special characteristics for the aims of automotive industry, electronics and many other aims. Lignocellulose materials are preferred as components in such composite articles in view of their possibilities for regeneration and ecological pure nature. New wood polymer cellulose materials with high physical and mechanical properties for different sphere of application are developed.

Key words: *cellulose, composites, aromatic polyester polyol, secondary cellulose fibrous material*

1. INTRODUCTION

Composite materials appear in the middle of the 20th century as a promising class of engineering materials, giving new directions of modern technology. In general, any material consisting of two or more components having different properties and the presence of phase boundary between them can be described as a composite material.

Development of science and technology is not possible without intensive use of polymers. It can hardly be found an area of industry that does not use the polymer composites. Both polymers and wood give a new product wood- polymer composite, which combines a number of valuable properties (strength, dimensional stability, low cost, etc.).

The chemical composition and structure of the polymers do not determine uniquely the properties of the product but they give information for the rheological behaviour during composite formation. There is a relationship between polymer composition and material's properties which is fundamental in composite processing [1, 2].

Development of wood- polymer composites is a new stage in the progress of the polymer industry. The new properties of these materials make them not only attractive, but define them as materials of the future or so called "modern (advanced) materials" [3]. In recent years there has been an increased use of wood polymer composites in automotive industry, housing, aircraft manufacturing, etc. [4- 6].

Wood components are natural polymers and their interface has a large quantity of functional polar groups, especially the cellulose. Wood, paper and plastics could be major components in composites and offer great opportunities for recycled ingredients [7].

Bonding at the interface can be achieved by modifying the filler- matrix surface with various surface-active additives or coupling agents [8]. The hydrophilic nature of wood particles and cellulose fibres

offers additional advantages, in comparison with inorganic fillers. The possibility for incorporation of different chemical groups on the surface is already provided [9].

Several classes of adhesives used in wood bonding involve the use of isocyanates. Isocyanates are widely used because of their reactivity with groups that contain reactive hydrogen, such as amine and hydroxyl groups at room temperature. Isocyanates are most often used to produce polyurethanes by reacrting with liquid polyols [10].

Isocyanate adhesives have shown increased use because of their high reactivity and efficiency in bonding. Polymeric diphenylmethane diisocyanate (pMDI), commonly used in wood bonding is a mixture of monomeric diphenylmethane diisocyanate and methylene- bridged polyaromatic polyisocyanates [11].

In the present investigation, a new prepolymer based on polymeric diphenilmethane diisocyanate (pMDI) was obtained and the effect of wood particles and cellulose fiber as fillers on the mechanical properties of composites was studied.

2. MATERIALS AND METHODS

2.1. Materials and test apparatus

Aromatic polyester polyol H100 (OHn 254 mg KOH/g, Acid number 0.71 mg KOH/g and viscosity of 5340 mPa.s) was supplied by Recyclit GmbH, Wildau, Germany. For drying it is kept for 3h at temperature of 120°C under vacuum.

Lupranat® M20A Elastogran GmbH (deaerated at temperature of 70°C). The chemical structure of pMDI is shown in Fig.1.

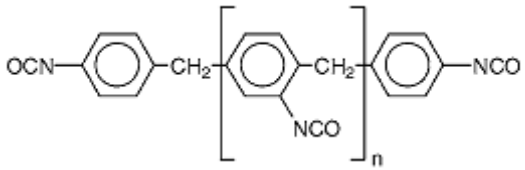


Figure 1 Chemical structure of polymeric 4, 4'- diphenylmethane diisocyanate (pMDI).

Wood particles and cellulose fibers waste were supplied by Department of Cellulose, Paper and Packaging, University of Chemical Technology and Metallurgy, Sofia, Bulgaria. They were dried at 150°C for 3h before mixing with the polyol and polyisocyanate. The experiments were carried out with wood particles from softwood: particle size at about 140 μm, specific volume of 8 dm3/ kg and moisture content of 5wt%, wood acidity 0.030%, resin content at about 2% and cork content at about 0.34%.

NETZSCH DSC 204 PHOENIX®. This instrument works according to the heat flow principle and is characterized by a three-dimensional symmetrical construction with homogeneous heating.

Brabender® W350 Lab Station measuring mixer. The measuring mixers consist of a mixer backstand with gear unit and a detachable mixer bowl [12].

40-t heating lab-press is used for composite material plate preparation. Hot press technique was used.

Universal testing machine “Zwick Z020” was used for the mechanical properties measurements.

2.2 Procedure for composite fabrication

Adhesives of lingo-cellulosic materials for construction boards or panels have been primarily limited to phenol formaldehyde, urea formaldehyde and pMDI. Along with these conventional adhesive, it has been reported that polyurethane materials can also serve as wood binders with adequate properties for different applications.

At room temperature the wood particles/cellulose fiber wastes were weighted and mixed with stiring with pMDI and polyol in desired proportions. Composite materials are post cured at room temperature until complete solidification. About 5 hours are needed to complete the reaction. After mixing the components the progress of reaction is observed by measuring the temperature. The reaction is exothermic. The temperature of the mass should not exceed 80ºC, due to the formation of trimers.

For the purposes of this study two series of composite materials were prepared (Table I and II).

Table I. Preparation of composite samples with wood particles filler

Sample	OH : NCO, Eq	H 100, g	M20A, g	Wood particles, %
TI 1.1part	1: 2	81.9	109	10 (9.1g)
TI 1.2part	1: 2	72.8	109	20 (18.2g)
TI 1.3part	1: 2	61.7	109	30 (27.3g)
TI 1.4part	1: 2	52.6	109	40 (36.4g)
TI 1.5part	1: 2	45.5	109	50 (45.5g)

Table II. Preparation of composite samples with cellulose fiber waste

Sample	OH : NCO, Eq	H 100, g	M20A, g	Waste cellulose fibers, %
TI 1.1cell	1: 2	81.9	109	10 (9.1g)
TI 1.2 cell	1: 2	72.8	109	20 (18.2g)
TI 1.3 cell	1: 2	61.7	109	30 (27.3g)
TI 1.4 cell	1: 2	52.6	109	40 (36.4g)
TI 1.5 cell	1: 2	45.5	109	50 (45.5g)

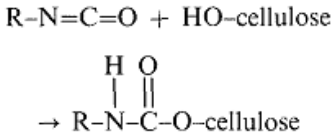
2.3 Mechanical properties

Tensile properties of the composite specimens were measured using universal testing machine "Zwick Z020" Zwick GmbH & Co. KG, Ulm, Germany. The cross head speed was 5 mm min^{-1}. The reported properties were measured at break. Fracture energy was calculated from the area under the stress-strain curve. A minimum of 5 samples were tested in each series. The test results were automatically calculated by a Zwick TestXpert V.9.0 computing system .The coefficient of variation of the reported properties was less than 10%.

3. RESULTS AND DISCUSSION

Methylene diisocyanate (MDI) is widely used as bonding agent in wood particle boards [13]. In the present study a mixture of polyisocyanate and polyol were used as bonding agents. The tensile strength is increased by 50% filler concentration (cellulose fiber waste) when compared to composite materials with wood particles filler.

The better performance with isocyanate can be attributed to the formation of urethane bonds between the OH group of cellulose and isocyanate. The possible bonding mechanism can be explained as follows:



The isocyanate group reacts readily with the OH groups of the cellulose to form a urethane structure [14]. Solvent extraction studies confirmed that the isocyanate was chemically bonded with cellulose [15]. The chemically bonded wood surface is molecularly bridged during compounding to the thermally activated surface of the polymer matrix.

The isocyanate content was measured according to DIN 53 185 [16].

Table III. Isocyanate content of composite materials with wood particles filler

Sample	*Isocyanate content, %*
TI_1.1part	4.5
TI_1.2part	4.8
TI_1.3part	5.3
TI_1.4part	5.5
TI_1.5part	5.9

Table IV. Isocyanate content of composite materials with cellulose fiber waste filler

Sample	Isocyanate content, %
TI_1.1cell	4.4
TI_1.2 cell	3.9
TI_1.3 cell	3.7
TI_1.4 cell	3.1
TI_1.5 cell	2.8

In the samples with wood particles filler there is an increase in isocyanate content value. This may be due to the fact that the components of wood contains excess of OH-bonded groups that can not react with NCO-groups, in contrast to cellulose. All OH-groups located on the surface of the cellulose fiber are easily accessible. Wood particles have less active surface, compared with wood flour or short

cellulose fibers. Reducing the isocyanate content of composite samples indicates that the NCO-groups enter into reaction with free OH-groups of short cellulose fibers, probably those on the surface. The results showed interaction on the phase boundary between the two components of composites. Cellulose can successfully replace the polyol within the specified cases.

Differential scanning calorimetry (DSC) is a technique for measuring the energy necessary to establish a nearly zero temperature difference between a substance and an inert reference material, as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate [17].

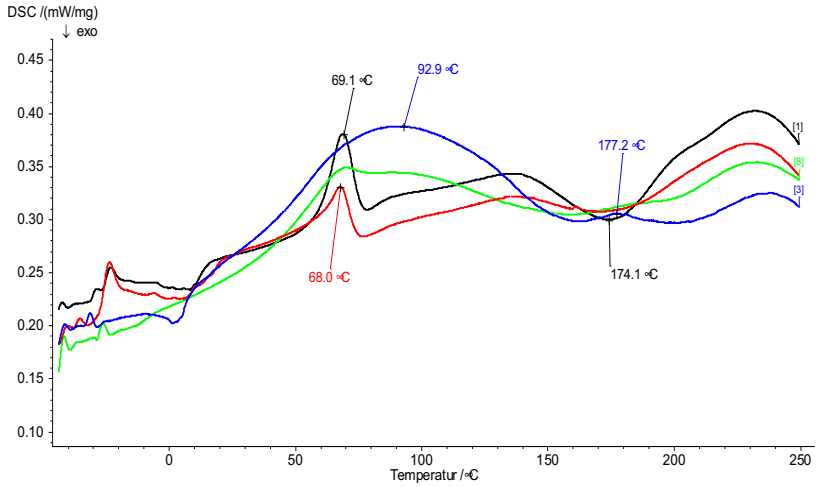


Figure 2 DSC analyses of composite materials TI_1.1part, TI_1.2part, TI_14.part, TI_1.5 part

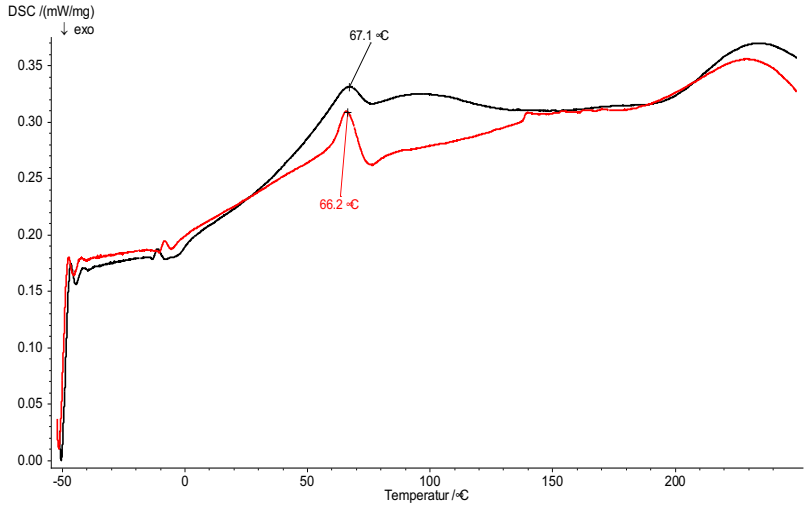


Figure 3 DSC analysis of composite material TI_ 1.3part (TI 1.3 part- before kneading in Brabender®, TI 1.3.1 part- after kneading)

No definite glass transition was observed (Figure 3). The only difference is seen at about +70°C. The broad endothermic peak there seems to originate from water or solvent evaporation. The peak at 67°C has changed in shape and become smaller and better defined after kneading. It is, therefore, not showing a reaction or the result of a reaction but maybe a crystallization phenomenon. It has to be checked if there is some ingredient suitable for crystallization and melting in the range of 220°C. The only difference is that by kneading water is evaporated.

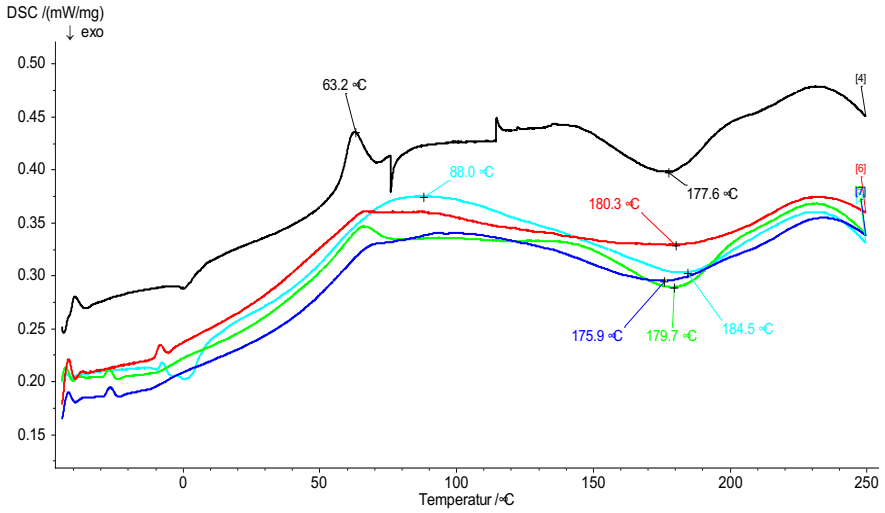


Figure 4 DSC analyses of composite materials TI_1.1cell, TI_1.2cell, TI_1.3cell, TI_1.4cell, TI_ 1.5.cell

With increasing the amount of cellulose the amount of evaporating water increases. As there is seen a small endotherm peak at 63°C there is a melting or solvent evaporation phenomenon. A glass transition is not to be seen. The decrease in intensity of the 250°C endotherm peak with increasing amount of cellulose fibers waste seems to hint to a degradation of the other component.

Before using the hot press technique composite materials are heated at temperature of 100ºC and time of 5 minutes in Brabender® W350 Lab Station.

The hot press technique is also called compression molding of thermosets. In this process the materials for composite samples are placed in heated mold. The process is primarily used for making simple shapes such as flat plates. The conditions for the composite fabrication are given in Table V.

Table V. Compounding and molding conditions

Brabender® W350 Lab Station	
Mixing temperature	70 to 100 ºC
Mixing time	5 min
Compression molding	
Molding temperature	100 ºC
Molding time	5 to 10 min
Molding pressure	9.6 MPa
Mold cooling time	10 min

Table VI. Wood polymer composites- mechanical properties

Sample	Modulus of elasticity (E), [MPa]	Tensile strength (σM), [MPa]	Tensile elongation (εM), [%]	Elongation at break (εB), [%]
TI_1.1part	1682	10,4	1,56	1,57
TI_1.2part	2388	10,9	0,96	0.97
TI_1.3part	2239	10,1	0.99	0.99
TI_1.4part	2052	9,2	1,06	1.06
TI_1.1cell	2483	18,9	0,80	0,80
TI_1.2cell	2496	23,9	0,96	0,96
TI_1.3cell	3075	36,6	1,27	1,27
TI_1.4cell	3167	29,6	1,01	0,99
TI_1.5cell	3747	40,0	1,19	1,19

The data in Table VI show that the tensile strength and E- Modulus increase with increasing concentration of filler, as a significant difference is obtained by using short cellulosic fibers. Maximum is reached when using 50% waste cellulose fibers. This demonstrates better adhesion between the components of the composite material.

There is also a significant difference in the strength values between the two series of composite materials.

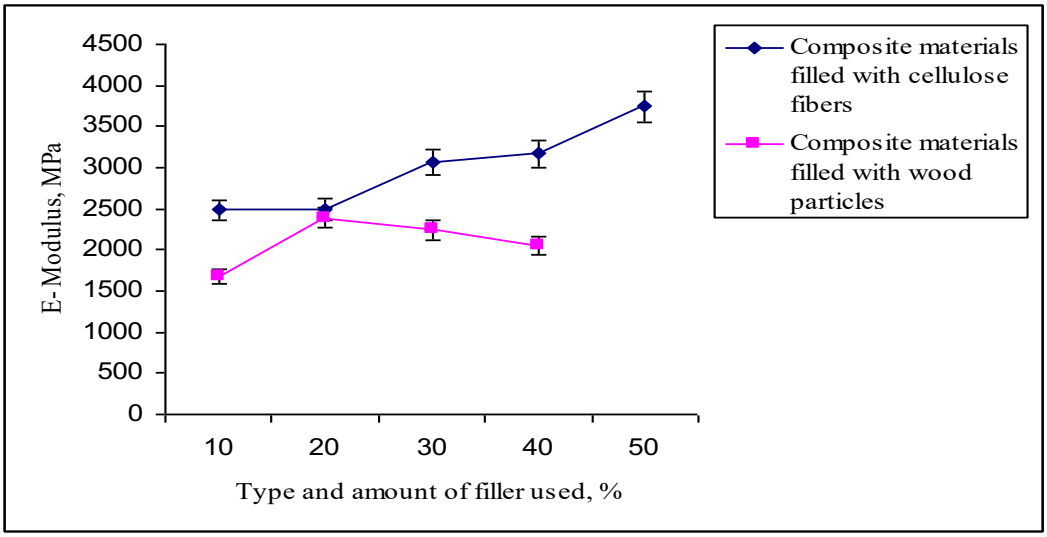


Figure 5 Changes in the E- Modulus, depending on the type and quantity of filler used

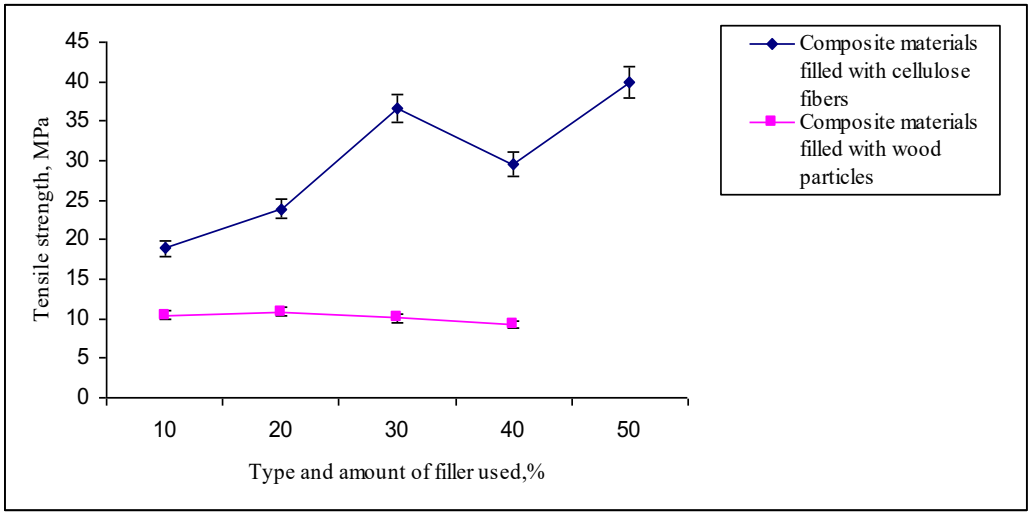


Figure 6 Changes in the tensile strength, depending on the type and quantity of filler used

In Figure 5 and 6 are shown graphically the changes in E- Modulus and tensile strength of composite materials. Data from Fig 8 shows a higher tensile strength of the composite materials filled with cellulose fibers in comparison with those filled with wood particles.

The next two figures (Figure 7 and 8) show the variation of tensile elongation and elongation at break after fracture of the specimens. Highest values of these two indicators are observed when using 10% wood filler particles and 30% short cellulosic fibers respectively.

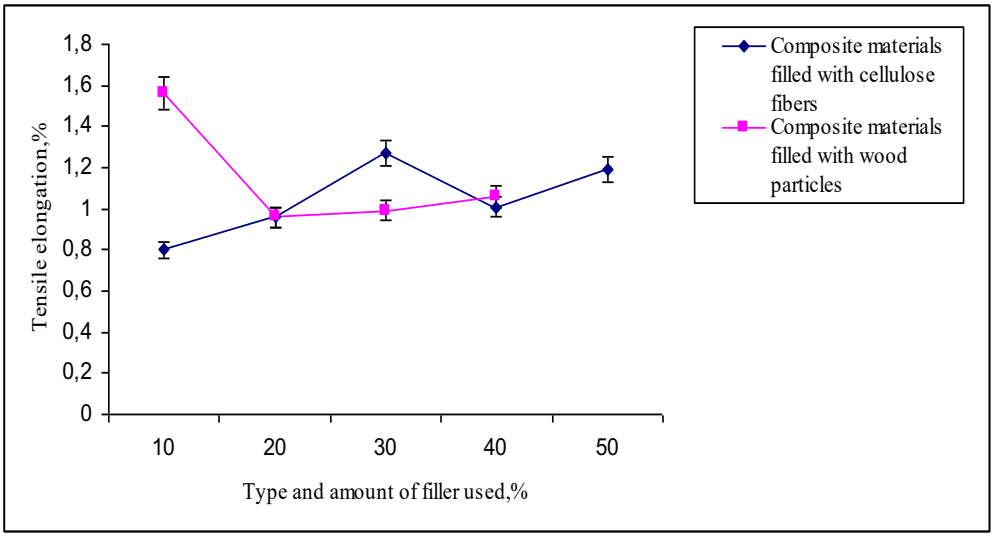


Figure 7 Changes in tensile elongation, depending on the type and amount of filler used

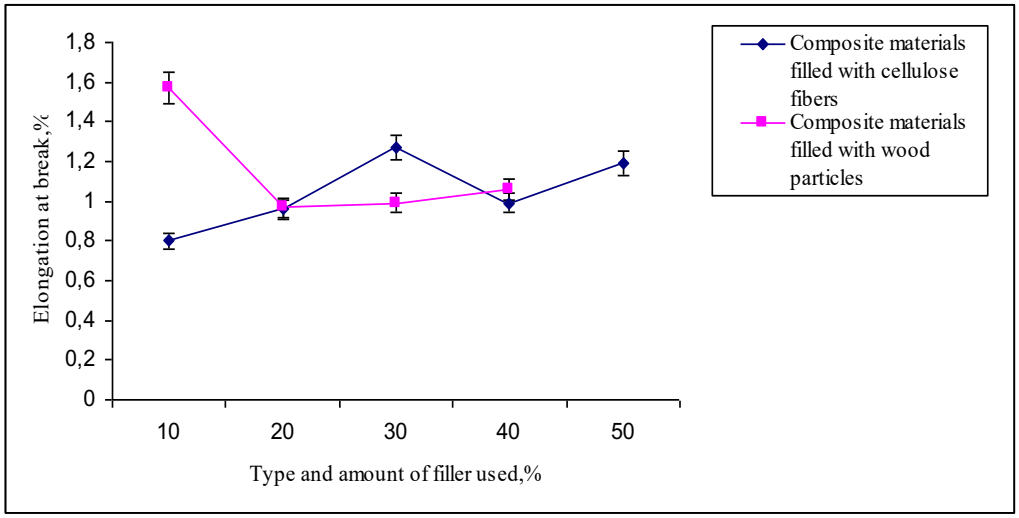


Figure 8 Changes in elongation at break, depending on the type and amount of filler used

4. CONCLUSIONS

Wood and cellulosic are polymer materials and their interface is of high complexity. In the test we used wood fiber and cellulose fiber waste as main element. The surface of these fibers has strong chemical polarity. In order to obtain composite materials with high mechanical properties we added isocyanate binder. This type of adhesive is highly effective in bonding wood/ cellulose fiber waste, added at room temperature. The adding quantities of isocyanate adhesive might be a main factor for improvement of the mechanical properties of the composites. The composite materials obtained by this process have high mechanical properties as it was shown by the tensile strength up to 40MPa.

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