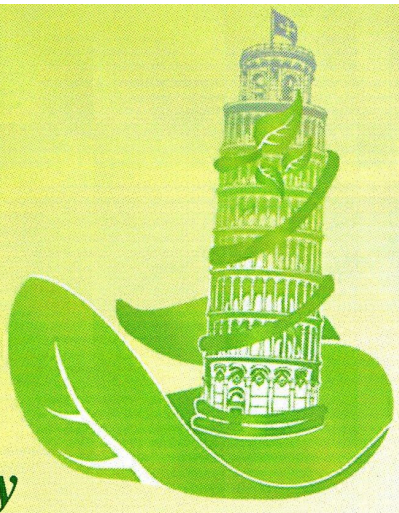
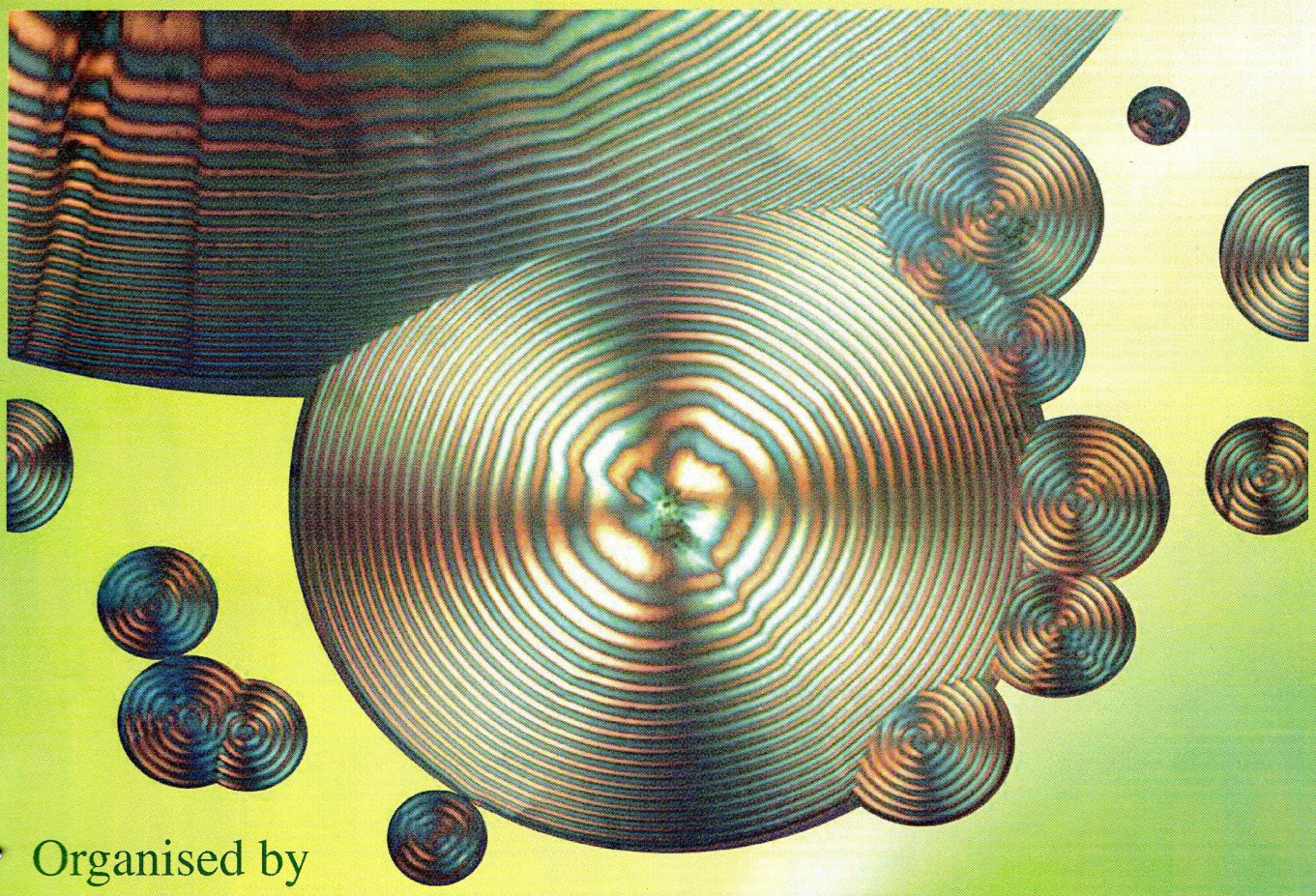
4th Workshop

Green Chemistry and Nanotechnologies in Polymer Chemistry



4-6 September 2013 – Pisa, Italy



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POLYURETHANE FOAM FROM INDUSTRIAL WASTE OF PLYWOOD PRODUCTION

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Concept

This study shows the possibility of using birch bark, a by-product of plywood production, for preparing polyurethane foam. A birch bark lignocellulose component – inner bark – was liquefied to obtain a polyurethane raw material – polyol mixture. Outer bark, containing valuable biologically active pentacyclic triterpenes (betulin, lupeol, betulinic acid, etc.), after extracting those compounds, was subjected to hydrothermal treatment in alkaline medium, and the other main inner bark component – suberin – was depolymerised. The obtained suberinic acid triethanolamine ester, as a polyol component, was used for polyurethane foam synthesis. Both types of polyols gave polyurethane foams with good physical properties. Such a complex approach has shown that it is possible to prepare new products with a high added value from waste natural raw materials.

Motivation and Objectives

In modern plants, 2.7 to 2.8 m^3 of solid volume veneer blocks are consumed to produce 1 m^3 of plywood. After the hydrothermal treatment and debarking of blocks, waste bark is obtained, which makes up 12.5% of the wood mass, while 16-20% of bark is composed of outer birch bark. Recalculating, outer bark makes up 2.0-3.4% of the veneer log mass. Bark is currently burned in boiler houses. Its average combustion heat is 25-26 MJ/kg.

The high combustion heat of outer bark is ensured by its component composition: pentacyclic lupane-type triterpenes – 35-38% of the mass, saturated C16-C22 fatty acid, epoxy- and oxy- fatty acid polyester – suberin, which makes up 30-40% of the mass, lignin – 7.1%, cellulose – 8.5%, and polyphenols, tannins and polysaccharides [1]. The inner bark components' composition is close to that of wood: cellulose – 23.4% of the mass, pentosans – 21.8%, holocellulose – 38.7%, lignin – 18.1%, and small amounts of triterpenes, for example, betulin – 0.37-0.43% of the mass [1].

Close assessment of both outer birch bark and inner birch bark components' composition sets thinking of a more efficient way of their use merely as a fuel. Such an avenue could be obtaining of polyols and further processing into polyurethanes, especially into polyurethane foams. Figure 1 shows the flow diagram of obtaining polyols from birch bark.

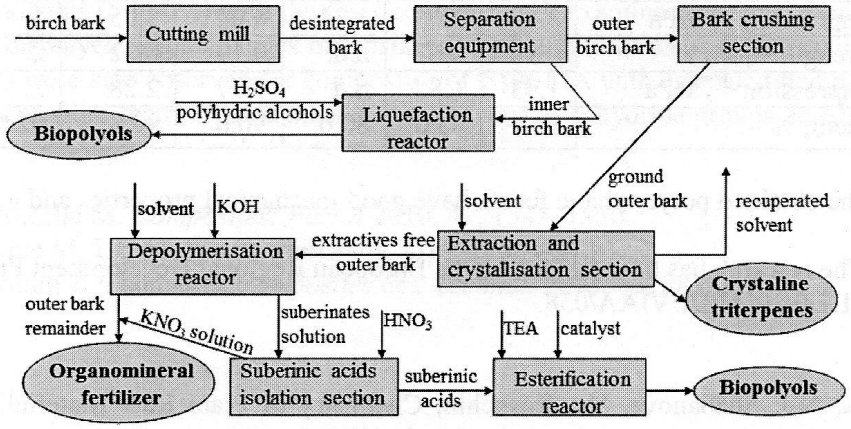

Figure 1 Flow diagram of obtaining polyols from birch bark

Results and Discussion

Birch bark from a veneer plant debarker was ground in a cutting mill up to a particle size of 2-5 mm. Outer bark was separated from the inner bark by the flotation method (31.5-33.0% and 67.0-68.5% respectively). The material was dried. Outer bark was granulated in a flat matrix granulator. The granules, preparing for extraction,

were crushed and the fraction with a particle size of 0.4-2.0 mm was extracted with ethanol, isopropanol or petroleum ether in an intensive mass exchange apparatus. Extractives' (30-38% from the granule mass) main components were triterpenes, containing up to 75-90% betulin.
The extractives free outer bark was subjected to the alkaline hydrolytic suberin depolymerisation reaction. Potassium hydroxide in isopropanol solution (outer bark – isopropanol - potassium hydroxide mass ratio 1:9:0,33). Suberinic acid salts were evaporated till a dry state. The salts, water solution acidified with nitric acid till pH 2.5-3.5, were separated by centrifugation and dried in a vacuum.
Birch inner bark was liquefied in the milled form (fraction 0.125-0.400 mm) in a mixture with polyethylene glycol (PEG 400) and glycerol (weight ratio 1:1,6:1,4) catalysing with concentrated sulphuric acid (3% from polyhydric alcohol mass). The reaction proceeded at 150°C, mixing by refluxing for 3 h according to [2]. In the cooled reaction mixture, the sulphuric acid was neutralised with a potassium hydroxide solution.
During the thermochemical conversion, solvolysis and depolymerisation take place simultaneously. The crystallinity and degree of polymerisation of cellulose are important factors in the process of liquefaction in polyhydric alcohols medium [3]. In this respect, the liquefaction process with inner bark polysaccharides proceeds favourably, since both the crystallinity and degree of polymerisation of cellulose in this case are at a lower level.
Polyols from suberinic acids were synthesised by esterification with triethanolamine in an inert atmosphere at a temperature of 170-175°C. The synthesis was accomplished, when the acid number was below 5 mg KOH/g.
Polyurethane foams were prepared from suberinic acid esters with the OH number 440 mg KOH/g (Z1) and 432 mg KOH/g (Z4), adding polyether polyols with the OH number 400 mgKOH/g and the additives – flame retardant, blowing agent, catalyst, stabiliser and polyisocyanate with the NCO group content 31.5%.
Polyurethane foams from liquefied inner bark were prepared using preparations with the following OH numbers (mgKOH/g) and moisture: 1208 and w = 3.9% (Z3), 940 and w = 2.2% (Z11) and 658 and w = 3.9% (Z14). Modifying polyols, flame retardants, blowing agents, catalysts and stabilisers were added [4]. The properties of the obtained polyurethane foams are listed in Table 1. Instead of petroleum derived glycerol, crude glycerol, a by-product of the biodiesel production process was tested with success (Z11).

Table 1 Properties of inner bark and suberinic acid polyol polyurethane foams

Indices	Liquefied inner bark polyols			Suberinic acid esters polyols		ISO/WD8873-1 Requirements
	Z3	Z11	Z14	Z1	Z4	
Apparent core density, kg/m^3	39.1	28.8	32.8	49.0	36.7	28
Compressive strength //, MPa	0.16	0.11	0.12	0.28	0.27	0.17
Modulus of compression //, MPa	3.49	3.06	3.34	6.04	5.05	...
Compressive strength $\perp$, MPa	0.10	0.07	n.d.	0.19	0.12	...
Modulus of compression $\perp$, MPa	1.93	1.80	n.d	3.97	2.28	...
Closed cell content, %	94.7	83.0	80.0	90.0	94.8	92.0

Table 1 shows that the obtained polyurethane foams have good mechanical properties and a closed cell structure.

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