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# Softwood-lignin/natural rubber composites containing novel plasticizing agent: Preparation and characterization

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ABSTRACT

Composite materials based on natural rubber were obtained by using glycerolysate (decomposition product of polyurethane) as a novel plasticizer. In order to determine the effect of various lignin content, four different filler amounts were used, namely, 5 phr (parts per 100 parts of natural rubber) of lignin (WLI5G), 10 phr (WLI10G), 20 phr (WLI20G), and 40 phr (WLI40G). The reference specimen without lignin (WLI0G) was also prepared. The resulting vulcanizates were analyzed by Fourier Transform Infrared Spectroscopy (FTIR) to determine the chemical interaction between the lignin powder and the natural rubber chain. Scanning Electron Microscopy (SEM) of the cross-sections of the obtained materials was carried out to determine the adhesion between lignin and rubber. The results of dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA) showed that the samples containing 5 and 10 phr of lignin had the best thermal properties. Also, the measured mechanical properties confirmed these findings.



## 1. Introduction

At present, many scientific teams work on the possibility to employ natural resources in the field of materials science and engineering. It is a consequence of the ending stocks of petrochemical resources such as coal, natural gas, and crude oil. One of the most important issues related to green chemistry is the utilization of renewable resources as a new application in the existing products. Moreover, the polymer recycling process and the utilization of polymer recycling products constitute the second most urgent task due to the increase in the waste quantity. It has been proven that the renewables and the products of polymer recycling can partially replace the primary resources used in the polymer synthesis and preparation. The resulting materials display the same, approximately the same, or even better properties.

One of the most recent issues in green chemistry is finding the possibility to maximize the application of lignin by-products, which are produced in vast amounts by the paper and pulp industries, in the field of polymer technology. Presently, ca. 50 million tons of lignin by-products produced annually by the industries are used as a fuel for the energy production (Haghdan et al., 2016). Only 2% of this valuable raw material is used for other applications because of the complex structure and heterogeneity of lignin, which causes difficulties during delignification on a commercial scale that is conducted by the pulp and paper industries (De Wild et al., 2014; Neutelings, 2011).

Lignin is a highly branched bio-macromolecule. It is composed of units such as paracoumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Jiang et al., 2014). These phenylpropane units have none, one, or two methoxyl groups at the positions 3 or 5 in the phenolic ring (Haghdan et al., 2016). The aforementioned molecules are linked together by different bond types, i.e. 5—O—4, β—O—4, β—1, β—5, β—β, etc. (Rogers, 2015). Chakar et al. (Chakar and Ragauskas, 2004) presented the percentages of different bonds in softwood lignin, β—O—4 being the most common one. This particular bond type is present in up to 50% of total bonds in softwood-lignin.

The varying occurrence of bond types depends on the origin of lignin, i.e. the sources of softwood or hardwood, which results in different percentages of bond content. Bjornsson indicated that generally hardwoods contain less lignin than softwoods (Bjornsson, 2014). The exact lignin structure not only depends of the type of biomass, but also of the type of delignification process used, which modifies lignin to a certain degree (Hatakeyama and Hatakeyama, 2010). The application of various delignification methods results in a variety of lignin products. The main types of lignin can be divided into lignosulfonates, kraft lignin, and organosolv lignin (Holladay et al., 2007).

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The delignification process affects the content of impurities in the obtained products and, consequently, their further applicability. Lignosulfonates can be used as dispersants, emulsion stabilizer, carbon black, industrial binders, agricultural chemicals or concrete additives due to their medium purity (residual sulfur). Kraft lignin also contains some ash and sulfur, and can be used as emulsifiers, dispersants, carbon fibers or binders. Organosolv lignin, which is sulfur free, has the highest degree of purity. Because of this property, it is possible to use organosolv lignin for the synthesis of aromatic polyols, new diacids, carbon fibers, activated carbon, phenolic resins, phenol derivatives and antioxidants (Haghdan et al., 2016; Holladay et al., 2007).

Plasticizers, represented by freely available, non-volatile compounds, are widely used in the polymer production due to the important role they play in the resulting products. They improve processability during the polymer preparation as well as add flexibility to the final materials (Vieira et al., 2011). Over the past years, due to the increasing interest of polymer industries in biopolymers, biorenewables and the products of the chemical recycling of polymer waste, many publications appeared in which the addition of a biopolymer plasticizer and/or biodegradable plasticizing materials of natural origin had been described. Altenhofen Da Silva and coworkers utilized the product of the polyesterification of rice fatty acid as a plasticizer in the poly(vinyl chloride) and natural rubber films. The results of this research indicate that the addition of natural plasticizer increased the elongation at break compared to pure polymer film. In terms of thermogravimetric analysis no significant differences were detected between the plasticized material and pure natural rubber-based product (Da Silva et al., 2011). Alexander and Thachil investigated differences between cardanol and aromatic oil emloyed as plasticizers. It was demonstrated that cardanol, used as a plasticizing agent in the natural-rubber matrix, gave mechanical properties similar to those obtained with the aromatic oil-based materials (Alexander and Thachil, 2006). The same observation was later reported by Mohapatra and Nando (Mohapatra and Nando, 2014).

The main aim of this research was to prepare and characterize natural rubber-based composites filled with various amounts of lignin, and obtained with the use of glycerolysate. This experimental set up was an exemplification of the application of the chemical recycling of polymer product as a novel plasticizer in the natural rubber matrix. The synthesis of the plasticizer used in our study had been based on the decomposition of polyurethane waste by means of chemicals, heat and catalysts. Polyurethanes are in the sixth place in the ranking of the most used polymers in the global market. The polyurethane waste constitutes ca. 6% of all plastic waste (Kopczyńska and Datta, 2016). As a result, the chemical recycling processes of polyurethanes are one of the most prolific development tasks in the materials engineering (Simon et al., 2014). Moreover, the most investigated are the wastes of flexible polyurethane foams due to their extensive application and the resulting high volume of waste that entails environmental and economic problems (Nikje and Nikrah, 2007). Glycerolysate is the product of thermo-mechanical recycling of polyurethane, with the use of glycerine as a decomposition prime mover. The process is called glycolysis or glycerolysis, and it is the transesterification reaction between hydroxyl groups in glycol or glycerol (glycerine), respectively, which interchanged the ester groups in the polyurethane chains (Simón et al., 2016). The decomposition product of polyurethane is a mixture of compounds and monomers. Until now, glycerolysates were most frequently used to synthesize polyurethanes, mainly in the form of foams (Simón et al., 2016) or elastomers (Datta, 2010; Datta and Pasternak, 2005), in which polyols were partially or completely replaced by the product of the chemical recycling of polyurethane.

**Table 1**
Composition of lignin filled natural rubber-based composites.

| COMPONENT | QUANTITIES OF IGREDIENTS (phr) | | | | |
|---|---|---|---|---|---|
| | WLI0G | WLI5G | WLI10G | WLI20G | WLI40G |
| Natural rubber | 100 | 100 | 100 | 100 | 100 |
| Stearic acid | 3 | 3 | 3 | 3 | 3 |
| Zinc oxide | 5 | 5 | 5 | 5 | 5 |
| Stabilizer AR | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Accelerator T | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Glycerolysate (G) | 2 | 2 | 2 | 2 | 2 |
| Lignin (INDULIN AT) | 0 | 5 | 10 | 20 | 40 |
| Sulphur | 3 | 3 | 3 | 3 | 3 |

This paper describes novel elastic composites containing four different levels of lignin, and the same amount of plasticizer in the form of glycerolysate. The influence of lignin content on the structure, morphology, and the selected mechanical, thermal and chemical properties of the obtained composites was investigated.

## 2. Experimental

### 2.1. Materials

Natural rubber used to prepare the composites was purchased from Torimex Chemicals Ltd Sp. z o. o., Konstantynów Łódzki, Poland (density 0.92 g/cm$^3$, weight average molecular weight, $M_w$ = 800 000 mol/g). Lignin (INDULIN AT – kraft pine lignin – softwood lignin) used in this study was obtained from MeadWestvaco Corporation, Specialty Chemical Division, South Carolina, USA. INDULIN AT with a density of ca. 1.25 g/cm$^3$ was dried prior to use at 100 °C for 12 h in air. After drying, it was applied as a filler in the rubber mix. Sulfur with a density of about 1.8-2.1 g/cm$^3$ and a molecular weight of 32.1 g/mol was also purchased from Torimex Chemicals Ltd Sp. z o. o. Other ingredients, listed below, were purchased from Brenntag Polska Sp. z o. o., Kędzierzyn – Koźle, Poland:

- stearic acid with a density of about 0.85–0.99 g/cm$^3$ and a molecular weight of 284.5 g/mol,
- zinc oxide with a density of about 5.6 g/cm$^3$ and a molecular weight of 81.4 g/mol,
- stabilizer AR (fenyl-β-naphthylamine): density 1.16 g/cm$^3$, molecular weight 219.3 g/mol,
- accelerator T (tetramethyl thiuram disulfide): density 1.5 g/cm$^3$, molecular weight 240 g/mol.

The glycerolysate with a number average molecular weight of about 902.4 g/mol and a hydroxyl number of about 186.5 mg KOH/g was used as a plasticizer. This component was produced at the Department of Polymer Technology, Gdańsk University of Technology.

### 2.2. The preparation of composites

Five different composite specimens were prepared. Four composite samples contained different lignin contents, namely, 5, 10, 20 and 40 phr, and were coded WLI5G, WLI10G, WLI20G and WLI40G, respectively. The reference sample without lignin was also prepared (WLI0G). Before mixing, the natural rubber was annealed in air to improve the mastication process. The natural rubber was subjected to the mixing process in a BUZULUK open-roll machine (Datta and Głowińska, 2011). Then the ingredients were added in the quantities shown in Table 1. The friction ratio between the two rolls was about 1.1:1. All composites were vulcanized at a temperature of 146 °C with the use of hydraulic press produced by ZUP Nysa. The applied pressure was ca. 5 MPa. The vulcanization tem-

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