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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 of lignin (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. The SEM analysis 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, such as tensile strength, hardness, resilience and abrasiveness, confirmed these findings.

KEYWORDS:

Softwood Lignin;

24 Natural rubber composites;
25 Scanning Electron Microscopy;
26 Thermal analysis;
27 Mechanical properties;
28 Equilibrium swelling measurements
29

30 **1. INTRODUCTION**

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

42 One of the most recent issues in green chemistry is finding the possibility to
43 maximize the application of lignin by-products, which are produced in vast amounts
44 by the paper and pulp industries, in the field of polymer technology. Presently, ca. 50
45 million tons of lignin by-products produced annually by the industries are used as a



46 fuel for the energy production (Faruket al., 2016a). Only 2 % of this valuable raw
47 material is used for other applications because of the complex structure and
48 heterogeneity of lignin, which causes difficulties during delignification on a
49 commercial scale that is conducted by the pulp and paper industries (DeWild et al.,
50 2014; Neutelings, 2011).

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

59 The varying occurrence of bond types depends on the origin of lignin, i.e. the
60 sources of softwood or hardwood, which results in different percentages of bond
61 content. Bjornsson indicated that generally hardwoods contain less lignin than
62 softwoods (Bjornsson, 2014). The exact lignin structure not only depends of the type
63 of biomass, but also of the type of delignification process used, which modifies lignin
64 to a certain degree (Hatakeyama and Hatakeyama, 2010). The application of various
65 delignification methods results in a variety of lignin products. The main types of lignin
66 can be divided into liginosulfonates, kraft lignin, and organosolv lignin (Holladay et al.,
67 2007).

68 The delignification process affects the content of impurities in the obtained
69 products and, consequently, their further applicability. Liginosulfonates can be used

70 as dispersants, emulsion stabilizer, carbon black, industrial binders, agricultural
71 chemicals or concrete additives due to their medium purity (residual sulfur). Kraft
72 lignin also contains some ash and sulfur, and can be used as emulsifiers,
73 dispersants, carbon fibers or binders. Organosolv lignin, which is sulfur free, has the
74 highest degree of purity. Because of this property, it is possible to use organosolv
75 lignin for the synthesis of aromatic polyols, new diacids, carbon fibers, activated
76 carbon, phenolic resins, phenol derivatives and antioxidants (Faruket al., 2016a;
77 Holladay et al., 2007).

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

95 aromatic oil-based materials (Alexander and Thachil, 2006). The same observation
96 was later reported by Mohapatra and Nando (Mohapatra and Nando, 2014).

97 The main aim of this research was to prepare and characterize natural rubber-
98 based composites filled with various amounts of lignin, and obtained with the use of
99 glycerolysate. This experimental set up was an exemplification of the application of
100 the chemical recycling of polymer product as a novel plasticizer in the natural rubber
101 matrix. The synthesis of the plasticizer used in our study had been based on the
102 decomposition of polyurethane waste by means of chemicals, heat and catalysts.
103 Polyurethanes are in the sixth place in the ranking of the most used polymers in the
104 global market. The polyurethane waste constitutes ca. 6 % of all plastic waste
105 (Kopczyńska and Datta, 2016). As a result, the chemical recycling processes of
106 polyurethanes are one of the most prolific development tasks in the materials
107 engineering (Simonet al., 2014). Moreover, the most investigated are the wastes of
108 flexible polyurethane foams due to their extensive application and the resulting high
109 volume of waste that entails environmental and economic problems (Nikjeand Nikrah,
110 2007). Glycerolysate is the product of thermo-mechanical recycling of polyurethane,
111 with the use of glycerine as a decomposition prime mover. The process is called
112 glycolysis or glycerolysis, and it is the transesterification reaction between hydroxyl
113 groups in glycol or glycerol (glycerine), respectively, which interchanged the ester
114 groups in the polyurethane chains (Simónet al., 2016). The decomposition product of
115 polyurethane is a mixture of compounds and monomers. Until now, glycerolysates
116 were most frequently used to synthesize polyurethanes, mainly in the form of foams
117 (Simónet al., 2016) or elastomers (Datta,2010; Datta and Pasternak, 2005), in which
118 polyols were partially or completely replaced by the product of the chemical recycling
119 of polyurethane.



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

125 **2. EXPERIMENTAL**

126 **2.1. MATERIALS**

127 Natural rubber used to prepare the composites was purchased from Torimex
128 Chemicals Ltd Sp. z o. o., KonstantynówŁódzki, Poland (density 0.92 g/cm^3 , weight
129 average molecular weight, $M_w = 800\,000 \text{ mol/g}$). Lignin (INDULIN AT – kraft pine
130 lignin – softwood lignin) used in this study was obtained from MeadWestvaco
131 Corporation, Specialty Chemical Division, South Carolina, USA. INDULIN AT with a
132 density of ca. 1.25 g/cm^3 was dried prior to use at 100°C for 12 hours in air. After
133 drying, it was applied as a filler in the rubber mix. Sulfur with a density of about 1.8-
134 2.1 g/cm^3 and a molecular weight of 32.1 g/mol was also purchased from Torimex
135 Chemicals Ltd Sp. z o. o. Other ingredients, listed below, were purchased from
136 BrenntagPolska Sp. z o. o., Kędzierzyn - Koźle, Poland:

- 137 • stearic acid with a density of about $0.85 - 0.99 \text{ g/cm}^3$ and a molecular weight
138 of 284.5 g/mol ,
- 139 • zinc oxide with a density of about 5.6 g/cm^3 and a molecular weight of 81.4
140 g/mol ,
- 141 • stabilizer AR (fenyl- β -naphthylamine): density 1.16 g/cm^3 , molecular weight
142 219.3 g/mol ,

- 143 • accelerator T (tetramethylthiuram disulfide): density 1.5 g/cm³, molecular
144 weight 240 g/mol.

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

149 **2.2. THE PREPARATION OF COMPOSITES**

150 Five different composite specimens were prepared. Four composite samples
151 contained different lignin contents, namely, 5, 10, 20 and 40 phr, and were coded
152 WLI5G, WLI10G, WLI20G and WLI40G, respectively. The reference sample without
153 lignin was also prepared (WLI0G). Before mixing, the natural rubber was annealed in
154 air to improve the mastication process. The natural rubber was subjected to the
155 mixing process in a BUZULUK open-roll machine (Datta and Głowińska, 2011). Then
156 the ingredients were added in the quantities shown in Table 1. The friction ratio
157 between the two rolls was about 1.1:1. All composites were vulcanized at a
158 temperature of 146 °C with the use of hydraulic press produced by ZUP Nysa. The
159 applied pressure was ca. 5 MPa. The vulcanization temperature was chosen in
160 accordance with the reports by Jacob et. al. (Jacob et al., 2004) and Chonkaew et. al.
161 (Chonkaew et al., 2010).

162

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

164

165 **2.3. CHARACTERIZATION OF THE COMPOSITES**

166 Fourier Transform Infrared Spectroscopy was used to obtain the spectra of the
167 samples of five composites, pure lignin, natural rubber, and glycerolysate. The
168 measurements were carried out using a Nicolet 8700 FTIR spectrometer (Thermo
169 Electron Corporation) with the use of ATR technique. The resolution was 4 cm^{-1} .
170 Sixty-four scans in the wavenumber range from 4500 to 500 cm^{-1} were taken.

171 Scanning Electron Microscopy was used to characterize the cross-section
172 morphology of the composites. The study was performed with the use of a Phenom
173 G2 PRO scanning electron microscope (Phenom-World corporation) at the
174 accelerating voltage of ca. 5 kV.

175 Dynamic mechanical tests were carried out with the use of a DMA Q 800
176 analyzer (TA Instruments). The measurements were performed in accordance with
177 ISO 6721-1, which allowed to obtain the values of storage modulus and tangent delta
178 (damping factor) curves. The specimens with dimensions 30 x 5 x 2 mm were
179 analyzed at a heating rate of ca. 4 $^{\circ}\text{C}/\text{min}$ for the temperature range from -100 to
180 150 $^{\circ}\text{C}$. The tests were performed in air, with a frequency of 1 Hz.

181 Thermogravimetric analysis allowed to characterize the thermal stability of the
182 prepared composites. The measurements were carried out with the use of a
183 NETZSCH TG 209F3 analyzer. The specimens weighing ca. 5 mg each were
184 analyzed under nitrogen atmosphere. The temperature used ranged from 35 to
185 600 $^{\circ}\text{C}$ at a heating rate of 20 $^{\circ}\text{C}/\text{min}$.

186 The mechanical properties, such as tensile strength, elongation at break, and
187 permanent elongation after break, were determined with the use of a Zwick/Roell
188 Z020 universal testing machine. The tests were performed in accordance with ISO
189 37, with the crosshead speed set to 300 mm/min and the 20 kN load cell. The

190 dumbbell-shaped specimens of all composites were tested. The obtained results are
191 reported as average values calculated from three samples.

192 The hardness measurements were performed with a Shore type A Durometer
193 (Zwick/Roell). The circular specimens with a thickness of 6 mm were tested in
194 accordance with the standard ISO 868. The presented results are the mean values of
195 hardness based on ten independent measurements.

196 A Schob machine was used to analyze the rebound resilience of the obtained
197 materials. Tests were performed on the circular, 6-mm thick samples in accordance
198 with ISO 4662. The mean values calculated from ten measurements are reported for
199 all the composites.

200 The density of the produced materials was determined by using an electronic
201 analytical balance equipped with a kit for measuring the density of solids. During the
202 single test the sample was weighed in air and in the liquid of known density, namely,
203 methanol with a density of ca. 0.790 g/cm³. All measurements were performed at a
204 temperature of 23°C in accordance with ISO 2781. The presented results are the
205 mean values calculated from three independent measurements.

206 The abrasion resistance was investigated with the use of a Schopper-
207 Schlobbach instrument. All specimens were circles of diameter 17 mm. Tests were
208 performed on three samples of each material in accordance with ISO 4649. The
209 average values were calculated from three independent measurements. The
210 abrasiveness V (cm³) was defined as a volume loss, and determined from equation
211 (1):

212

213
$$V = (m_0 - m_1) * m_t / (\rho * \Delta m_w) \quad (1)$$

214

215 where: m_0 (g) and m_1 (g) are the sample mass before and after the test, respectively;
216 m_t (g) is a theoretical loss of weight of the reference mixture (assumed value of 0.2
217 g); ρ (g/cm³) is the density of tested sample; and Δm_w (g) is the average weight loss
218 of reference mixture with the known abrasiveness (assumed value of 0.1095 g).

219 The swelling parameters, such as swelling index, volume fraction of rubber
220 network, molecular weight between crosslinks, and the crosslink density, were
221 determined by employing the equilibrium swelling method. The tests were carried out
222 according to the descriptions presented in the literature (Abdelmouleh et al., 2007;
223 Bahl et al., 2014; Gregorová et al., 2006; Kosikova et al., 2007). The rectangular
224 specimens with the average dimensions 15 x 15 x 2 mm were immersed in pure
225 toluene (purchased from POCH, Gliwice, Poland). The measurements were carried
226 out at room temperature for 7 days (168 hours). In this time period, samples were
227 taken out from the immersion liquid to determine the weight change. The samples
228 were dried on paper for one minute in air, then weighted and placed again in toluene.
229 After obtaining the equilibrium swelling state, the samples were dried in air for 7 days
230 and then subjected to annealing at a temperature of 80°C for 3 hours (Riyajan, 2015;
231 Stelescu et al., 2014). The swelling ratio was calculated according to the following
232 equation (2):

233

234
$$SR = (m_a - m_b) / m_b * 100 \% \quad (2)$$

235

236 where: $m_b(g)$ and $m_a(g)$ are the mean weights of analyzed samples before and after
 237 swelling in the immersion liquid, respectively. In the next step of the procedure, the
 238 volume fraction of rubber network, $V_{fr}(-)$, was calculated from equation (3):

239

$$240 \quad V_{fr} = V_r / (V_r + V_s) = (m_r/\rho_{rr}) / (m_r/\rho_{rr} + m_s/\rho_s) \quad (3)$$

241

242 where: V_r (cm^3) and V_s (cm^3) are the mean volumes of rubber and solvent in the
 243 swollen sample, respectively; $m_r(g)$ and $m_s(g)$ are the mean weights of rubber and
 244 solvent in the analyzed samples after swelling in the immersion liquid, respectively;
 245 $\rho_{rr}(\text{g}/\text{cm}^3)$ and ρ_s (g/cm^3) are the respective densities of rubber ($0.9125 \text{ g}/\text{cm}^3$ for
 246 natural rubber) and solvent ($0.867 \text{ g}/\text{cm}^3$ for toluene) in the composites.

247 The average molecular weight between crosslinks, M_c (g/mol) was determined
 248 by using the Flory–Rehner theory according to the following equation (4):

249

$$250 \quad M_c = \frac{-\rho_r \times V_s \times \left(V_{fr}^{\frac{1}{3}} - \frac{1}{2} V_{fr} \right)}{\ln(1 - V_{fr}) + V_{fr} + (\chi \times V_{fr}^2)} \quad (4)$$

251

252 where: $\rho_r(\text{g}/\text{cm}^3)$ means the density of lignin-rubber composites; V_s is the molar
 253 volume of solvent ($106.52 \text{ cm}^3/\text{mol}$ for toluene); and χ is the Huggins parameter,
 254 defining the interaction between the polymer and solvent (0.38 for natural rubber-
 255 toluene).

256 The crosslink density, v (mol/cm³), was determined from equation (5):

257

$$258 \quad v = \rho_r / M_c \quad (5)$$

259

260 where: ρ_r (g/cm³) means the polymer density (lignin-rubber composite), and M_c
261 (g/mol) is the average molecular weight of polymer.

262 **3. RESULTS AND DISCUSSION**

263 **3.1. FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY**

264 Fourier Transform Infrared analysis was used to investigate the chemical
265 structure of the prepared lignin/rubber composites, pure lignin, natural rubber and
266 glycerolysate used. The FTIR spectra of all composite samples (Figure 1a)
267 demonstrated similar profiles.

268

269 **Figure 1** a) FTIR spectra of the composites, pure lignin, natural rubber and
270 glycerolysate; b) FTIR spectra of the obtained specimens for the wavenumbers
271 ranging from 1800 to 800 cm⁻¹.

272

273 More differences were associated with the varying intensity of characteristic
274 peaks. For the samples without the natural rubber, the characteristic wide vibration
275 was present in all spectra in the wavelength range between 3570 and 3170 cm⁻¹,
276 which was attributable to the stretching vibrations of hydroxyl groups derived from



277 lignin and glycerolysate (Kubačková et al., 2013). The strong peaks with the highest
278 intensity at 2960, 2918 and 2850 cm^{-1} correspond to the stretching vibrations of the
279 CH_3 , CH_2 , CH groups from cis-1,4-polyisoprene macromolecules and glycerolysate
280 (Riyajan, 2015) , however, the lignin particles also revealed a small shift in this
281 wavenumber range.

282 For a better visibility, the FTIR spectra of samples in the wavelength range
283 from 1800 to 800 cm^{-1} were presented in Figure 1 b. The intensive peak at 1596 cm^{-1}
284 is attributable to the symmetric aromatic skeletal vibration indicated by lignin
285 macromolecules (Faruket al., 2016c). Other strong bands at 1515 cm^{-1} are related to
286 the asymmetric aryl ring stretching corresponding to lignin (Faruket al., 2016c). The
287 absorption at ca. 1445 cm^{-1} was assigned to the deformation vibrations of methyl
288 groups $-\text{CH}$ is related to the lignin aromatic rings, and also to the natural rubber
289 chains (Joseph et al., 2010). The band near 1377 cm^{-1} is attributable to the
290 asymmetric vibrations of the methyl $-\text{CH}$ groups derived from the natural rubber
291 chain as well as glycerolysate (Datta and Włoch, 2015). The absorption at ca. 1266
292 cm^{-1} was assigned to the stretching vibrations of the $-\text{C}-\text{O}$ groups present in the
293 phenolic rings of lignin. The peaks at ca. 1127 and 1030 cm^{-1} were attributed to the
294 aromatic $-\text{CH}$ groups in-plane deformation stretching originating from lignin (Faruket
295 al., 2016c). In the case of glycerolysate, the most intensive peak at a wavenumber of
296 1094 cm^{-1} was attributable to the stretching vibration of the $\text{C}-\text{O}$ group. The peak
297 near the wavelength of ca. 839 cm^{-1} was related to the variations of $-\text{CH}$ groups in
298 the rubber chains (Lin et al., 2015).

299 It is noteworthy that the intensity of characteristic peaks did not increase with
300 the increasing amount of lignin in the composites. That can be explained by the

301 formation of lignin agglomerates, which occurs as the amount of lignin increases. The
302 accumulation of lignin particles results in the disturbance of the spectrum.

303 The interaction between the lignin units and the natural rubber chain can be
304 explained based on the FTIR results. Jiang et al. (Jianget al., 2013) described the
305 interaction between lignin and the poly(diallyldimethylammonium chloride)
306 (PDADMAC) chain by comparing the shifts in the FTIR peaks corresponding to the
307 stretching vibration of the -CH groups due to the presence of double bonds. The
308 authors also indicated that lignin interacts with the rubber chains in the same way
309 because of the similarity between the chain skeletons of NR and PDADMAC. In
310 Figure 1 b, the peaks at 1515 and 1596 cm^{-1} in the spectrum of pure lignin shift to the
311 respective locations at 1545 and 1600 cm^{-1} in the spectra of composites. A small shift
312 from a wavenumber of 1445 cm^{-1} to 1450 cm^{-1} is also visible, which is associated with
313 the vibration of the natural rubber chain. This little shift indicates a noncovalent
314 interaction between the NR chain and lignin due to the adsorption of NR onto lignin.
315 The similar results were presented by Pillai and Rennekar (Pillai and Rennekar,
316 2009), and Yang and co-workers (Yanget al., 2005).

317 **3.2. SCANNING ELECTRON MICROSCOPY (SEM)**

318 The cross-sections of specimens were assessed by the scanning electron
319 microscopy in order to characterize the lignin dispersion in the composites. In
320 addition, the SEM micrographs revealed the interaction between the lignin powder
321 and the natural rubber matrix. Figures 2a and 2b show the specimens without lignin
322 and those containing 5 phr of lignin, respectively. It has been demonstrated that the
323 dispersion of this lowest quantity of lignin was satisfactory, without any visible
324 agglomerates. Other specimens, i.e. WLI10G, WLI20G and WLI40G showed the

325 accumulation of lignin particles. The lignin agglomerates were of irregular shape with
326 approximate dimensions from several to several tens of micrometers (Jianget al.,
327 2015). This finding explains the formation of hydrogen bonds between the lignin
328 particles. It also indicates that the aggregation of lignin is unavoidable in the natural
329 rubber matrix without additional modifications (Jianget al., 2013). Moreover, it is well
330 known that the composites with highly dispersed filler in the rubber can bear higher
331 stress in comparison to the composites containing the filler agglomerates. The
332 concentration of lignin particles in the obtained composites results in a decrease in
333 resistance (Jianget al., 2015). It is noteworthy that the observed agglomerates did not
334 expand with increasing lignin content in the composites, however, their number
335 increased. This can be explained by the glycerolysate content, which can suppress
336 the accumulation of lignin particles into larger agglomerates despite the lignin
337 polydispersity, and its propensity to form larger agglomerates with increasing lignin
338 concentration.

339

340 **Figure 2** SEM images of a) reference samples, WLI0G; b) samples containing 5 phr
341 of lignin, WLI5G; c) samples with 10 phr of lignin, WLI10G; d) samples with 20 phr of
342 lignin, WLI20G; and e) samples with 40 phr of lignin, WLI40G.

343

344 **3.3. DYNAMIC MECHANICAL ANALYSIS (DMA)**

345 The dynamic mechanical behavior of the lignin-rubber composites was
346 investigated with the use of dynamic mechanical analysis. The variation of the
347 storage modulus logarithm, $\log E'$ versus temperature, and variation of tangent delta,
348 $\tan \delta$ versus temperature were determined (Figures 3 and 4).



349

350 **Figure 3** The logarithm of storage modulus (Log E') of the lignin-rubber composites
351 plotted versus temperature.

352

353 The characteristics of the Log E' vs. temperature curve are typical for thermoplastic
354 polymers with high molecular weights. The relationship between the storage modulus
355 and temperature for the temperature range from -100 to ca. -50°C was linear. The
356 underlying cause of this behavior is the presence of natural rubber which, at the
357 aforementioned temperature range, occurs is the glassy state, and does not generate
358 the reinforcing effect with the filler (Braset al., 2010). After achieving the temperature
359 of ca. -50°C, a sharp decreasing trend was observed in the curve. This phenomenon
360 is related to the alfa transition temperature of the natural rubber matrix. The midpoint
361 of the decreasing curve at the temperature range from ca. -50 to ca. 0°C indicates
362 the position of the glass transition temperature, T_g (Chonkaew et al., 2010;
363 Geethamma et al., 2005). This point is closely associated with the relaxation of the
364 long chain sequences of natural rubber. Cooperative motion of macromolecules
365 induce the dissipation of energy at the temperature of maximum $\tan \delta$ (Figure 4)
366 (Abdelmouleh et al., 2007). The curve characteristics at around 0°C are related to the
367 melting of the remaining crystalline regions in the macromolecule matrix (Gopalan
368 Nair and Dufresne, 2003).

369

370 **Figure 4** Tan δ as a function of temperature of the lignin-rubber composites.

371

372 The addition of the various amounts of lignin to the composites resulted in a
373 decrease in the alfa transition temperature. The lowest value, i.e. ca. -44 °C was
374 determined for the specimens containing 10 and 40 phr of lignin (Table 2). These
375 results can be explained by impaired chain mobility due to the lignin addition, which is
376 an obstacle for generating significant reinforcement in the composite (Chonkaew et
377 al., 2010). The highest $\tan \delta$ peak was observed in the reference sample. With
378 increasing lignin content, the peak intensity decreased. Because the filler particles
379 were surrounded by the rubber matrix and the hydrogen bonds formed, the
380 movement of macromolecule chains was reduced, which resulted in the decreased
381 intensity of the peaks (Kargarzadeh et al., 2015).

382

383 **Table 2** Alfa transition temperature [°C] of the lignin-rubber composites.

384

385 **3.4. THERMOGRAVIMETRIC ANALYSIS (TGA)**

386 The thermal stability of the composites, reference sample and pure lignin was
387 investigated with the use of thermogravimetric analysis. The measurements allowed
388 for plotting the thermogravimetric (TGA; Figure 5) and differential thermogravimetric
389 (DTG; Figure 6) graphs.

390

391 **Figure 5** Thermogravimetric (TGA) curves for pure lignin, reference samples, and
392 lignin-rubber composites with different lignin content.

393

394 **Figure 6** Differential thermogravimetric (DTG) curves for pure lignin, reference
395 samples, and lignin-rubber composites with different lignin content.

396

397 Both aforementioned figures present one step of thermal decomposition for all
398 samples. The highest rate of weight loss was observed in the sample of pure lignin.
399 The samples of lignin-rubber composites showed an increase in the weight loss rate
400 with increasing lignin content. In comparison to the reference sample, the composites
401 containing higher lignin levels lost weight at the lower temperature (a 5% weight loss
402 temperature). This was caused by the effect of lignin on the thermal properties of the
403 prepared composites. Despite the aforementioned finding, the maximum rate of mass
404 loss for all the composites occurred at the same temperature (390°C), except for the
405 reference sample and pure lignin. For the latter two, the maximum rate of weight loss
406 was observed at the lower temperature. In the case of temperatures of 50% and 80%
407 weight loss, the samples displayed a similar range of maximum rate. Table 3
408 presents the thermal degradation characteristics for all the analyzed samples.

409

410 **Table 3** Thermal degradation characteristics of the lignin-rubber composites and pure
411 lignin, where $T_{5\%}$ is a temperature of 5% weight loss, $T_{50\%}$ is a temperature of 50%
412 weight loss, $T_{80\%}$ is a temperature of 80% weight loss, and T_{\max} is a temperature of
413 the maximum rate of weight loss. Residue at 600°C [%].

414

415 The residual weight after TGA analysis (at 600°C) increased with increasing
416 lignin content. This resulted from the presence of the highest lignin content. The

417 residue at 600°C comprised of ash, which consisted of organic and inorganic
418 impurities. The impurities play an important role because they influence the thermal
419 properties of lignin. The content of contaminants reduced the possibility of lignin
420 softening in the composites, and decreased the quality of the filler. Moreover, due to
421 the presence of impurities, thermal motion is hindered thereby preventing the thermal
422 processing (Hu,2002; Kadla et al., 2002).

423 **3.5. MECHANICAL PROPERTIES**

424 The mechanical properties of the composites, such as tensile strength,
425 elongation at break, and permanent elongation after break, were investigated. In
426 order to characterize the prepared materials, their hardness, rebound resilience,
427 density and abrasiveness were measured. Figure 7 shows the effect of varying
428 amounts of lignin on the tensile strength of the composites.

429

430 **Figure 7** Stress-strain curve of the rubber composites.

431

432 It was found that the tensile properties of the samples decreased with
433 increasing lignin content. The composites with a low amount of filler (WLI5G and
434 WLI10G) showed a decrease in the elongation at break and tensile strength. The
435 specimens containing 10 phr of lignin displayed the characteristics which were similar
436 to those of the reference sample, however, they had lower tensile strength. In the
437 case of the samples containing 20 and 40 phr lignin, they were characterized by the
438 higher (WLI20G) or similar (WLI40G) elongation at break, and lower tensile strength
439 than the reference sample. The lignin admixture in the composites caused a

440 decrease in the deformation resistance of rubber chains. Yu et al. (Yu et al., 2015)
441 obtained similar results. Table 4 presents the results of tensile measurements.

442

443 **Table 4** The effect of lignin content on the tensile properties of lignin/natural rubber
444 composites.

445

446 The interaction between the rubber chain and the filler particles hindered the
447 return of macromolecules to the pre-test state. For this reason, the lignin rubber
448 composites showed an increase in the permanent elongation after break. The
449 specimen containing 5 phr of lignin was an exception because its permanent
450 elongation decreased.

451 In Table 5 the results of hardness, resilience, density and abrasiveness
452 measurements are presented.

453

454 **Table 5** The results of hardness, resilience, density and abrasiveness tests for the
455 analyzed composites.

456

457 For the samples with 5 and 10 phr of lignin added, hardness of the analyzed
458 composites slightly increased. In the case of the remaining filled samples, the
459 hardness values decreased. It is known that the hardness of composites is closely
460 related to the crosslink density (Stelescu et al., 2014). The maximum hardness at ca.
461 45 °Sh A was measured in the sample containing 5 phr of lignin. A decrease in

462 hardness with increasing lignin content was correlated with the reduced crosslink
463 density. The differences were observed in the case of the composite samples
464 containing 5 phr of lignin. Those samples were characterized by higher hardness
465 than the reference sample and other specimens. Thereby, the crosslink density of
466 this particular composite displayed the greatest value.

467 Rebound resilience is also correlated with the crosslink density of composites.
468 It was clearly demonstrated in this study that with increasing lignin content the
469 crosslink density decreased (except for WLI5G), and thus the elasticity was also
470 reduced which led to more rigid composites. Stelescu et al. obtained similar results
471 (Stelescu et al., 2010).

472 Density is strictly related to the lignin amount, therefore, the highest density
473 was measured in sample WLI40G, while the lowest, in WLI0G.

474 The composite with a 5 phr of lignin admixture showed the lowest
475 abrasiveness compared to the remaining composites. This finding is clearly
476 connected to the crosslink density of this specimen, which was the highest. For the
477 remaining composites, the abrasion resistance decreased with increasing lignin
478 content.

479 **3.6. EQUILIBRIUM SWELLING PROPERTIES**

480 The effect of lignin content on the composite network structures was
481 investigated via the equilibrium swelling test. The following parameters were
482 determined: the volume fraction of rubber, molecular weight between the crosslinks,
483 crosslink density, and swelling ratio all of composites. Table 6 presents the results of
484 those measurements.

485

486 **Table 6** The results of equilibrium swelling measurements performed on the lignin-
487 rubber composites.

488

489 With increasing lignin content the swelling ratio of the composites decreased
490 (Table 6) in comparison to the reference specimen. The swelling ratio increased only
491 in the case of the composites with the highest lignin content. M. Jacob et al. (Jacobet
492 al., 2004) pointed out that the solvent diffusion mechanism in the rubber matrix is
493 correlated with the polymer's ability to form voids suitable for the solvent uptake. With
494 increasing lignin content in the composites, the number of voids in the rubber matrix
495 decreased, locking the pathways for the solvent, and thus the solvent uptake also
496 decreased. The highest value of the swelling ratio of the specimen with a 40 phr
497 lignin content is related to the most numerous formation of agglomerates with the
498 highest volume. The aforementioned amount of lignin in the composite is too high for
499 the successful hydrogen bond formation between the lignin particles and the natural
500 rubber matrix. As a result, the lignin particles can leach out from the samples during
501 the swelling ratio measurements, which makes the high solvent uptake possible. The
502 swelling ratio is related to the crosslink density. (Jacobet al., 2004; Park and Cho,
503 2003) suggested that the maximum interaction between the rubber chain and filler,
504 and the lowest crosslink density are characteristic for the composites with the highest
505 admixture of lignin. The obtained results showed that the lignin content caused a
506 decrease in the crosslink density (Table 6). Lignin in the natural rubber vulcanizates
507 lowers the number of polysulfidic crosslinks between the rubber chains if the disulfidic
508 and monosulfidic crosslinks remain constant (Faruket al., 2016b). The decreased

509 amount of polysulfides lowers the hardness, resilience, abrasion resistance and
510 tensile properties (Stelescu et al., 2010). The lignin particles mask some of the sites
511 on the natural rubber molecules, that otherwise would have been available for
512 crosslinking (Kumaran et al., 1978) , and cause a decrease in the network density.
513 Due to the occurrence of masked crosslinking sites, the distance between the
514 network nodes increases. The larger distance between the networks leads to the
515 polymer chain tangling. The increased molecular weight between crosslinks (see
516 Table 6) is a proof of the increased complexity of natural rubber macromolecules
517 between the network nodes.

518 During the equilibrium swelling measurements the values of weight loss were
519 recorded over time (Figure 8). The samples containing 5 and 10 phr of lignin
520 displayed a lower weight change than the reference samples. The sample with a 5
521 phr lignin content showed the lowest weight loss. The two composites with the
522 highest lignin contents displayed a higher weight loss than the reference samples.
523 The performed measurement allowed for concluding that a low lignin content in the
524 composites containing glycerolysate as a plasticizer, resulted in a decrease in the
525 solvent (toluene) absorption.

526

527 **Figure 8**Weight loss during the swelling measurements performed on the lignin-
528 rubber composites.

529

530 **4. CONCLUSIONS**

531 The softwood-lignin/natural rubber composites were successfully prepared
532 with the use of a novel plasticizer. Nowadays, the plasticizers mainly originate from
533 the petrochemical resources. Glycerolysate used in this work is the product of the
534 chemical recycling of polyurethanes. The results of the presented research
535 demonstrated that the mechanical and thermal properties of softwood-lignin/natural
536 rubber composites obtained with the use of glycerolysate as a plasticizer are similar
537 to those of the lignin-containing composites prepared with other commercially
538 available plasticizing agents. In addition, the data showed that the composite
539 containing 5 phr of lignin displayed the best properties. Specimen WLI5G had the
540 highest values of hardness and abrasiveness, and superior tensile properties. The
541 Scanning Electron Microscopy (SEM) confirmed a positive interaction between the
542 rubber chains and the lignin particles. The SEM images of composite WLI5G showed
543 good dispersion of lignin, without the lignin agglomerates. The prepared four
544 composite formulas with increasing lignin content allowed the determination of
545 maximum lignin content in the composite that would not alter the material's positive
546 properties. The composite containing the highest amount of lignin (WLI40G) had the
547 biggest and most numerous agglomerates and, consequently, the worst mechanical
548 (the lowest values of tensile strength, elongation after break, etc.) and thermal
549 properties (e.g. the fastest weight loss). This observation has been confirmed by the
550 results of swelling measurements, where sample WLI40G displayed the highest
551 swelling ratio. The application of lignin that is the product of natural origin, and the
552 use of the product of the chemical recycling of polyurethanes makes the described
553 procedure eco-friendly. Its economic advantages should also be considered.
554 Glycerolysate, used as a plasticizing agent, is less expensive than the commonly
555 employed plasticizers derived from petrochemicals. In summary, this work is a



556 promising development in the field of natural product utilization, and the application of
557 the products of chemical recycling in the natural rubber matrix.

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562

563

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712 Figure Captions

713 **Figure 1** a) FTIR spectra of the composites, pure lignin, natural rubber and
714 glycerolysate; b) FTIR spectra of the obtained specimens for the wavenumbers
715 ranging from 1800 to 800 cm^{-1} .

716 **Figure 2** SEM images of a) reference samples, WLI0G; b) samples containing 5 phr
717 of lignin, WLI5G; c) samples with 10 phr of lignin, WLI10G; d) samples with 20 phr of
718 lignin, WLI20G; and e) samples with 40 phr of lignin, WLI40G.

719 **Figure 3** The logarithm of storage modulus ($\text{Log } E'$) of the lignin-rubber composites
720 plotted versus temperature.

721 **Figure 4** $\text{Tan } \delta$ as a function of temperature of the lignin-rubber composites.

722 **Figure 5** Thermogravimetric (TGA) curves for pure lignin, reference samples, and
723 lignin-rubber composites with different lignin content.

724 **Figure 6** Differential thermogravimetric (DTG) curves for pure lignin, reference
725 samples, and lignin-rubber composites with different lignin content.

726 **Figure 7** Stress-strain curve of the rubber composites.

727 **Figure 8** Weight loss during the swelling measurements performed on the lignin-
728 rubber composites.

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

| COMPONENT | QUANTITIES OF INGREDIENTS (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 | 2 | 2 | 2 | 2 | 2 |
| Lignin (INDULIN AT) | 0 | 5 | 10 | 20 | 40 |
| Sulphur | 3 | 3 | 3 | 3 | 3 |

730

731 **Table 2** Alfa transition temperature [°C] of the lignin-rubber composites.

| Composite | Alfa transition temperature |
|-----------|-----------------------------|
| | T_{α} [°C] |
| WLI0G | -38 |
| WLI5G | -40 |
| WLI10G | -44 |
| WLI20G | -41 |
| WLI40G | -43 |

732

733 **Table 3** Thermal degradation characteristics of the lignin-rubber composites and pure
 734 lignin, where $T_{5\%}$ is a temperature of 5% weight loss, $T_{50\%}$ is a temperature of 50%
 735 weight loss, $T_{80\%}$ is a temperature of 80% weight loss, and T_{\max} is a temperature of
 736 the maximum rate of weight loss. Residue at 600°C [%].

| Sample | Thermal degradation characteristic [°C] | | | | |
|--------|---|------------|------------|------------|-------------------------|
| | $T_{5\%}$ | $T_{50\%}$ | $T_{80\%}$ | T_{\max} | Residue at 600°C [%] |
| WLI0G | 308 | 393 | 430 | 386 | 6 |
| WLI5G | 303 | 396 | 433 | 390 | 8 |
| WLI10G | 298 | 394 | 431 | 390 | 8 |
| WLI20G | 290 | 395 | 438 | 390 | 11 |
| WLI40G | 270 | 395 | 447 | 390 | 15 |
| lignin | 267 | 567 | - | 382 | 48 |

737

738 **Table 4** The effect of lignin content on the tensile properties of lignin/natural rubber
739 composites.

| COMPOSITE | Tensile strength [MPa] | Elongation at break [%] | Permanent elongation after break [%] |
|-----------|---------------------------|----------------------------|---|
| WLI0G | 16.25 ± 1.1 | 717 ± 12 | 18.1 ± 1.0 |
| WLI5G | 15.16 ± 0.4 | 626 ± 15 | 15.5 ± 1.1 |
| WLI10G | 14.22 ± 1.6 | 706 ± 15 | 18.4 ± 0.4 |
| WLI20G | 14.39 ± 0.7 | 733 ± 3 | 18.2 ± 0.5 |
| WLI40G | 8.39 ± 0.7 | 682 ± 26 | 21.9 ± 0.5 |

740

741 **Table 5** The results of hardness, resilience, density and abrasiveness tests for the
 742 analyzed composites.

| COMPOSITE | HARDNESS [°Sh A] | RESILIENCE [%] | DENSITY [g/cm ³] | ABRASIVENESS [cm ³] |
|-----------|---------------------|-------------------|------------------------------|------------------------------------|
| WLI0G | 43.6 ± 0.3 | 58.7 ± 2.0 | 0.9724 ± 0.0003 | 0.0899 ± 0.0080 |
| WLI5G | 45.5 ± 0.5 | 57.6 ± 0.8 | 0.9846 ± 0.0021 | 0.0847 ± 0.0170 |
| WLI10G | 44.3 ± 0.5 | 57.3 ± 0.9 | 0.9922 ± 0.0006 | 0.1179 ± 0.0143 |
| WLI20G | 41.2 ± 0.3 | 52.0 ± 1.1 | 1.0099 ± 0.0004 | 0.1469 ± 0.0221 |
| WLI40G | 38.3 ± 0.4 | 38.7 ± 0.7 | 1.0420 ± 0.0009 | 0.1999 ± 0.0487 |

743

744 **Table 6** The results of equilibrium swelling measurements performed on the lignin-
 745 rubber composites.

| COMPOSITE | SWELLING RATIO SR [%] | VOLUME FRACTION V_{fr} [-] | MOLECULAR WEIGHT BETWEEN CROSSLINKS M_c [g/mol] | CROSSLINK DENSITY $v \times 10^{-3}$ [mol/cm ³] |
|-----------|-----------------------------|------------------------------------|---|--|
| WLI0G | 290.8 ± 3.1 | 0.2374 ± 0.0026 | 191.6 ± 2.1 | 5.01 ± 0.05 |
| WLI5G | 280.9 ± 0.3 | 0.2371 ± 0.0003 | 194.2 ± 0.2 | 5.07 ± 0.01 |
| WLI10G | 278.4 ± 0.9 | 0.2313 ± 0.0007 | 200.4 ± 0.6 | 4.95 ± 0.01 |
| WLI20G | 279.9 ± 1.6 | 0.2156 ± 0.0011 | 218.2 ± 1.0 | 4.62 ± 0.02 |
| WLI40G | 308.2 ± 2.9 | 0.1771 ± 0.0018 | 268.6 ± 2.6 | 3.88 ± 0.04 |

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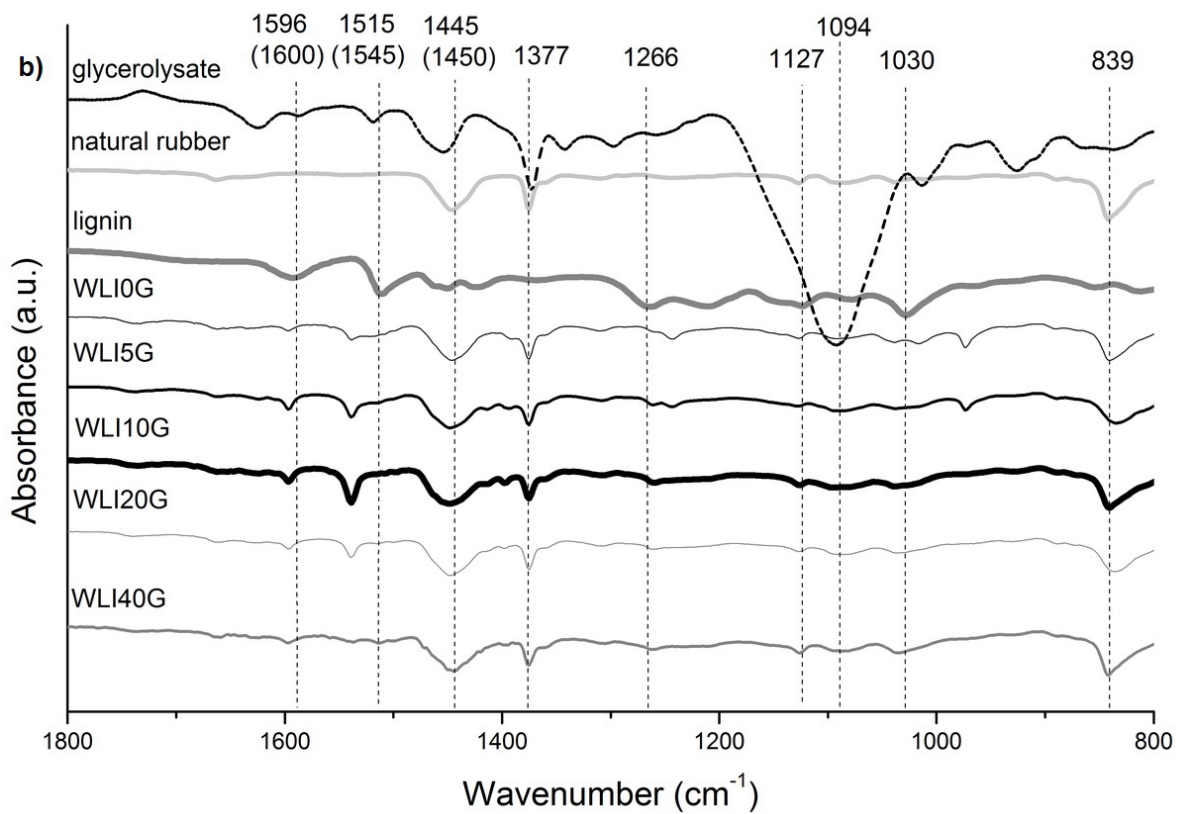
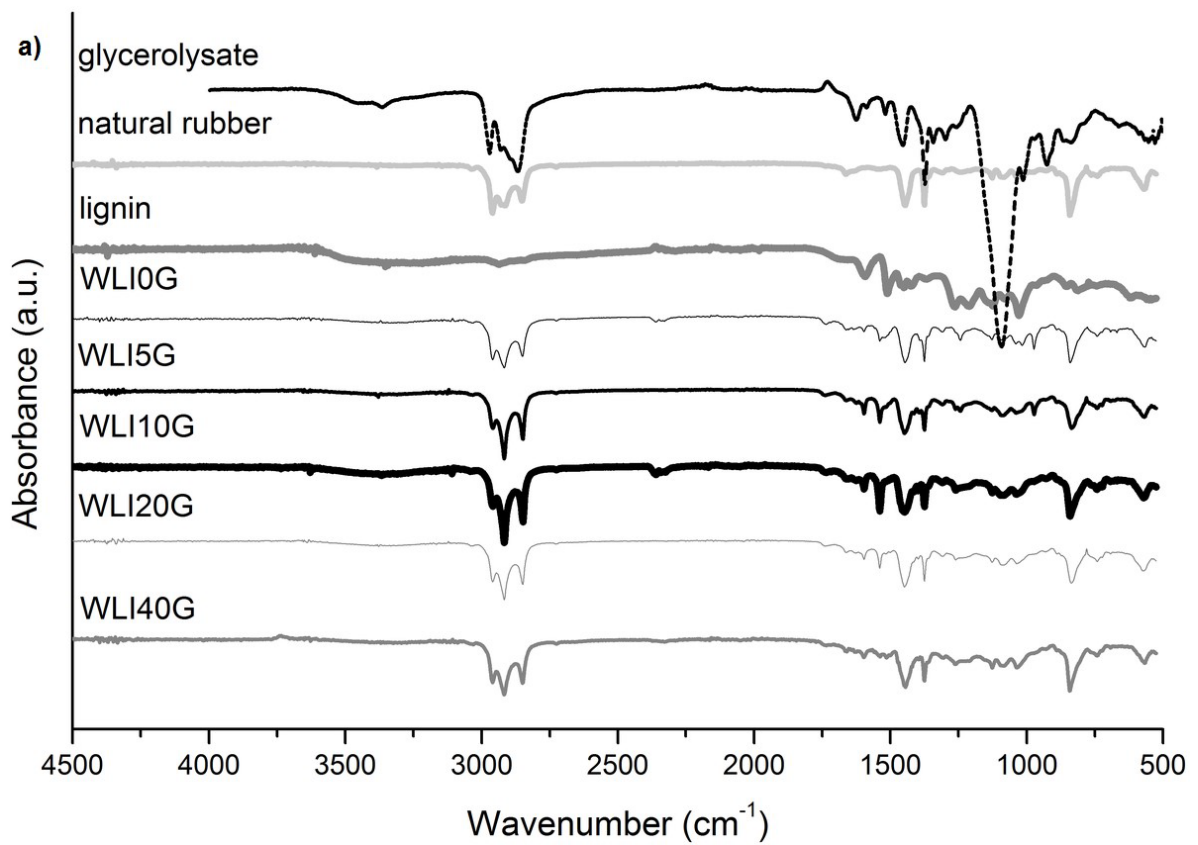
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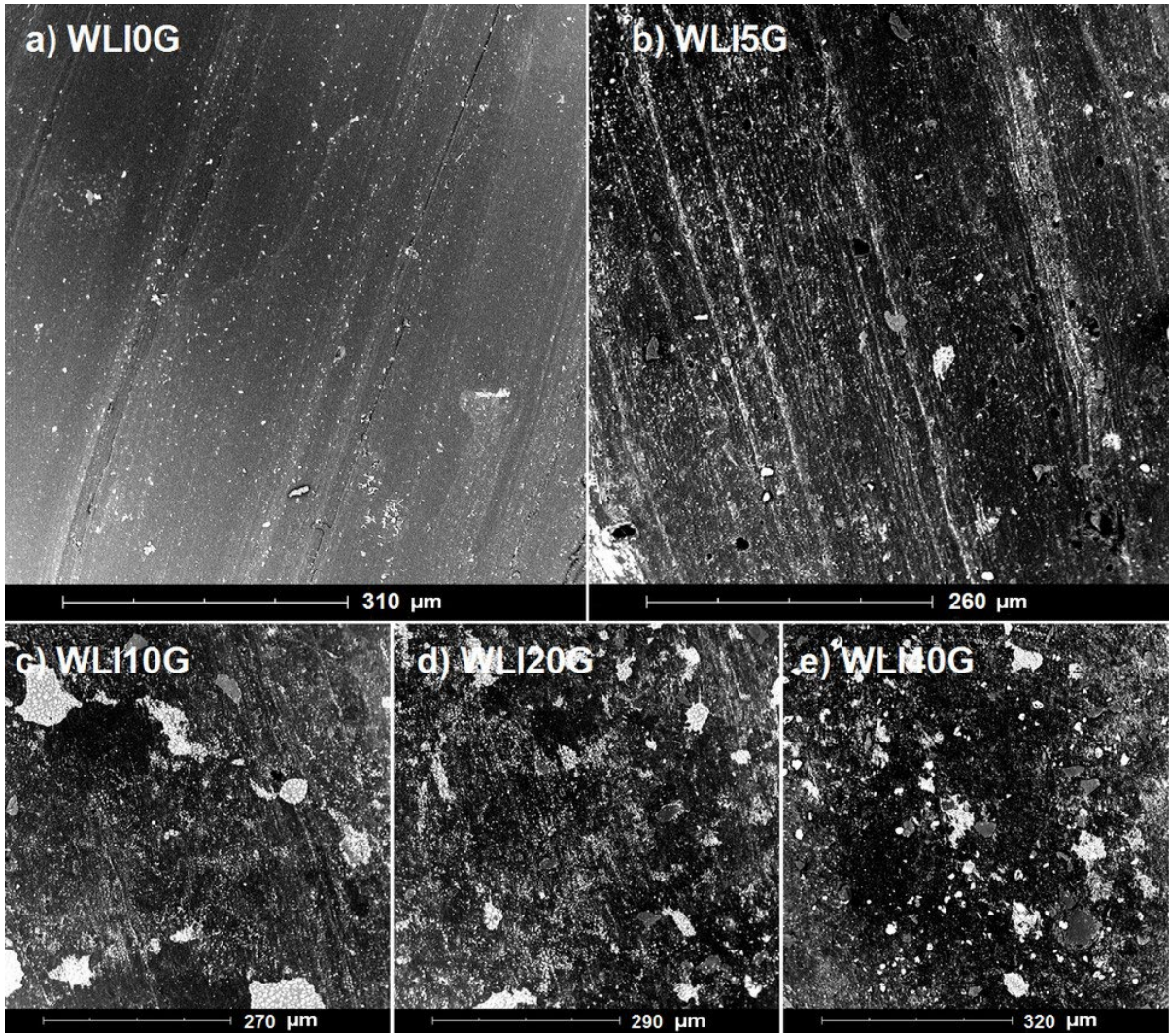
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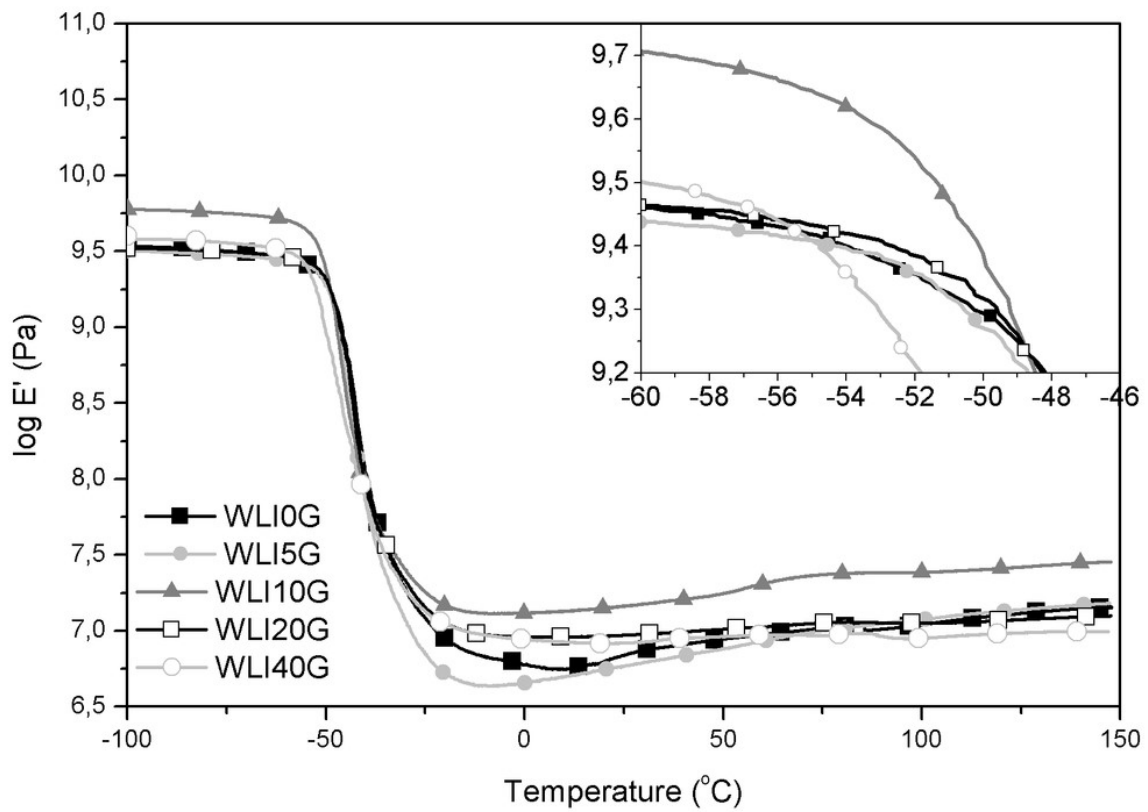
756 Figure 1

757



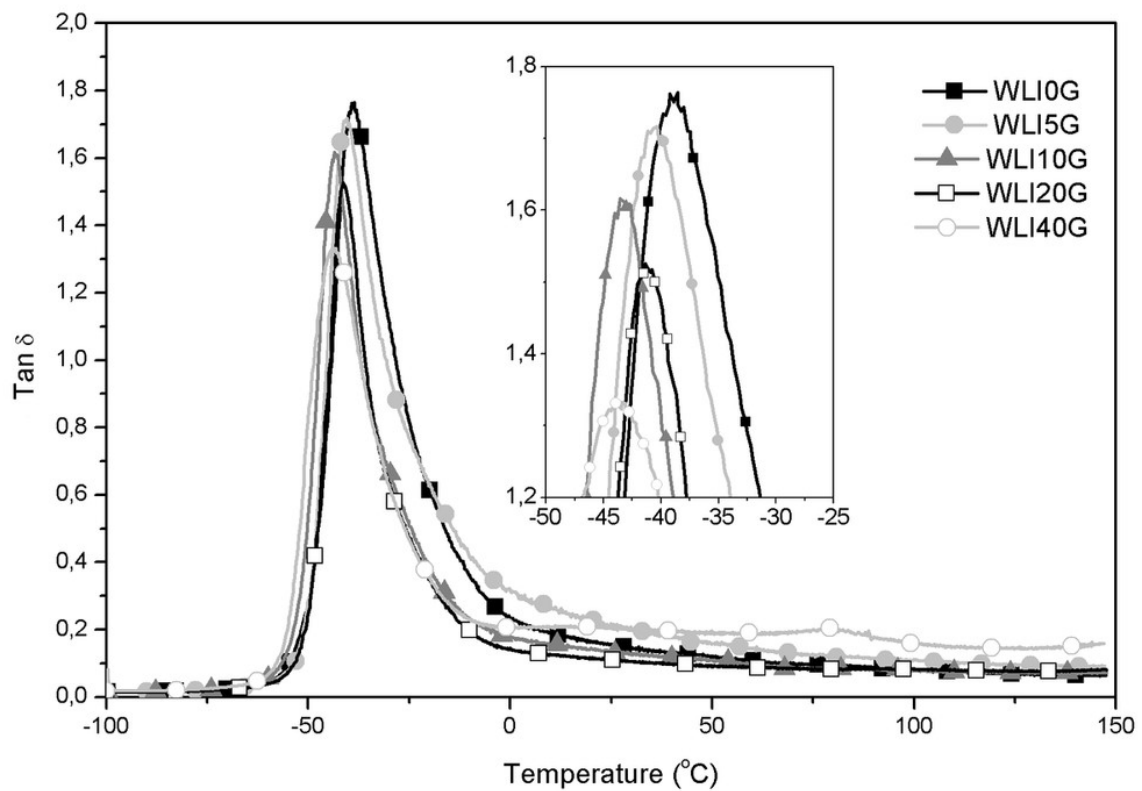
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759 Figure 2



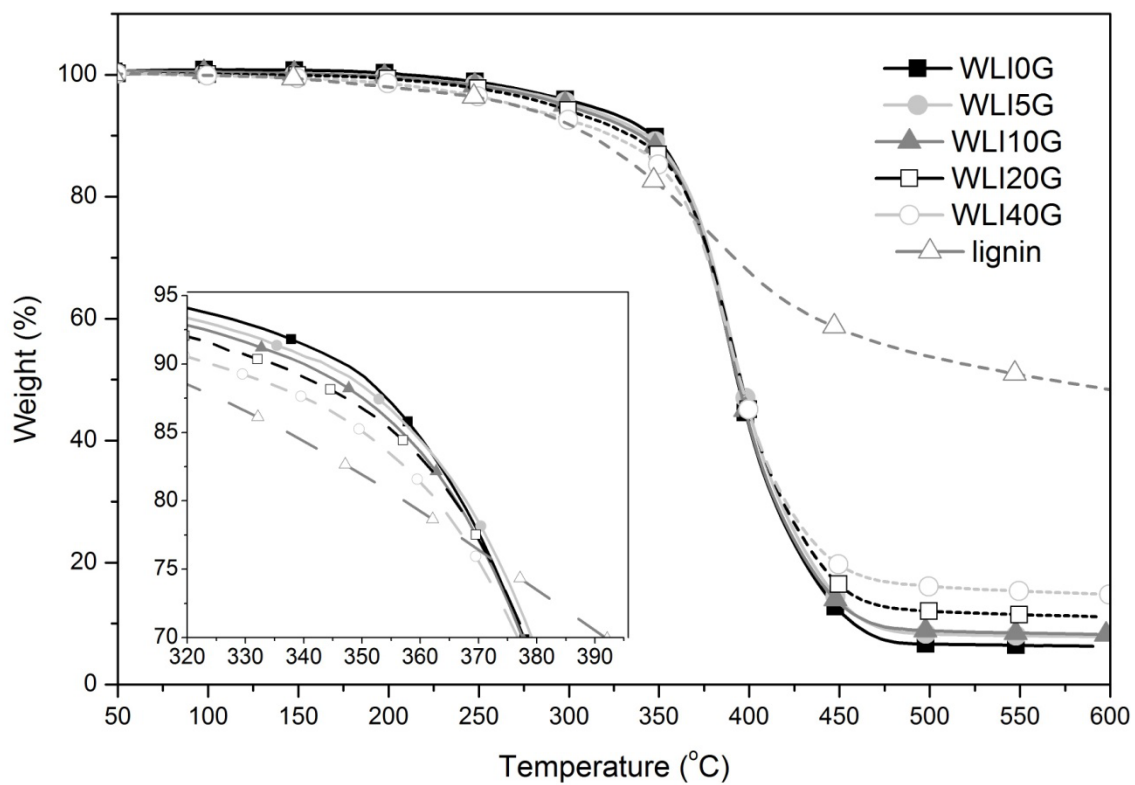
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761 Figure 3



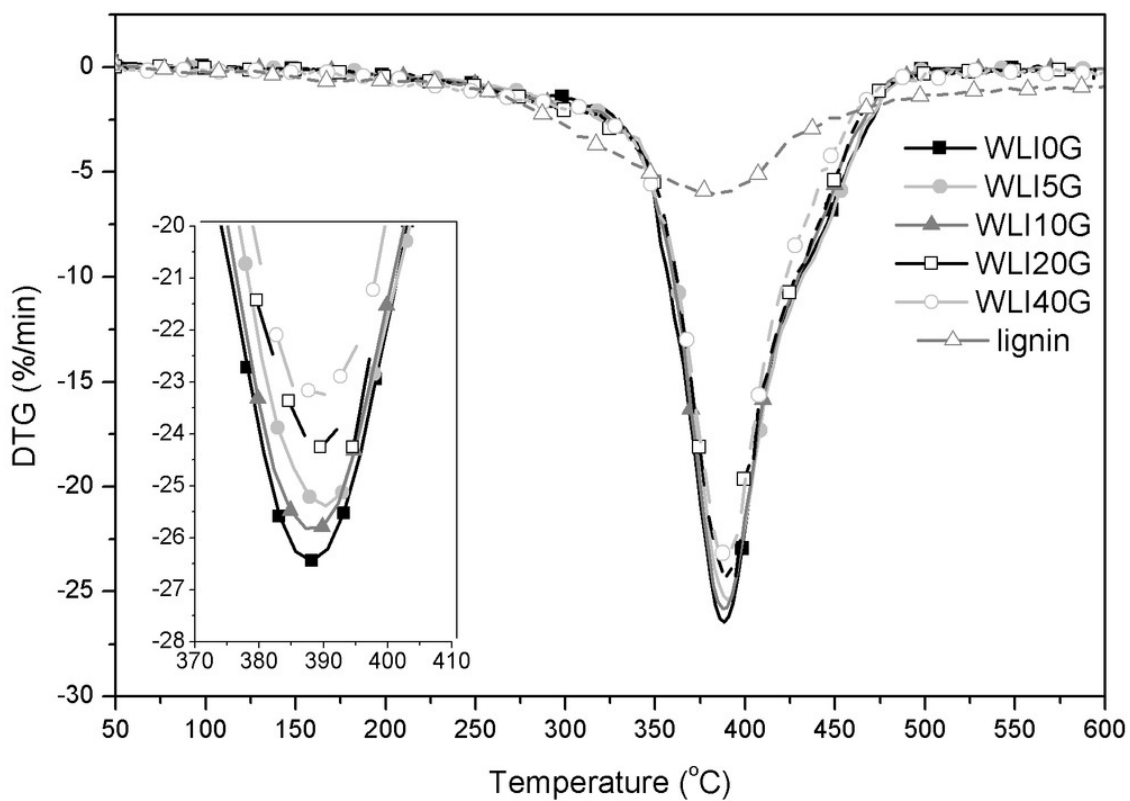
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763 Figure 4



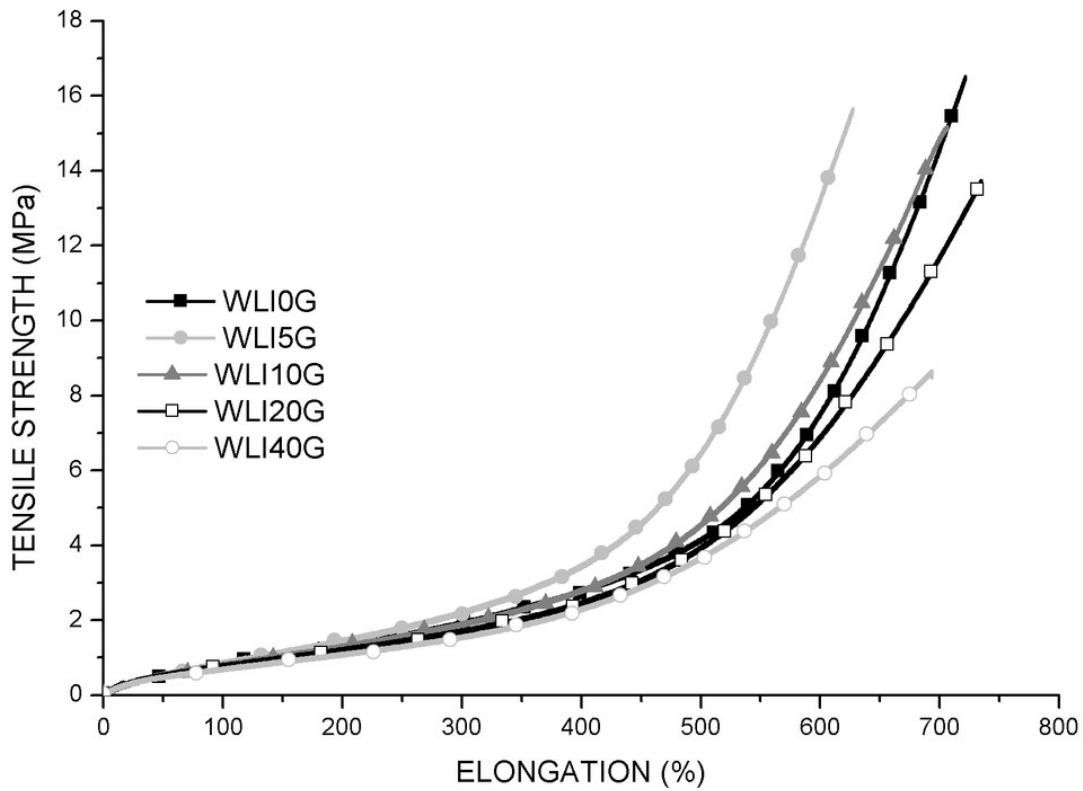
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765 Figure 5



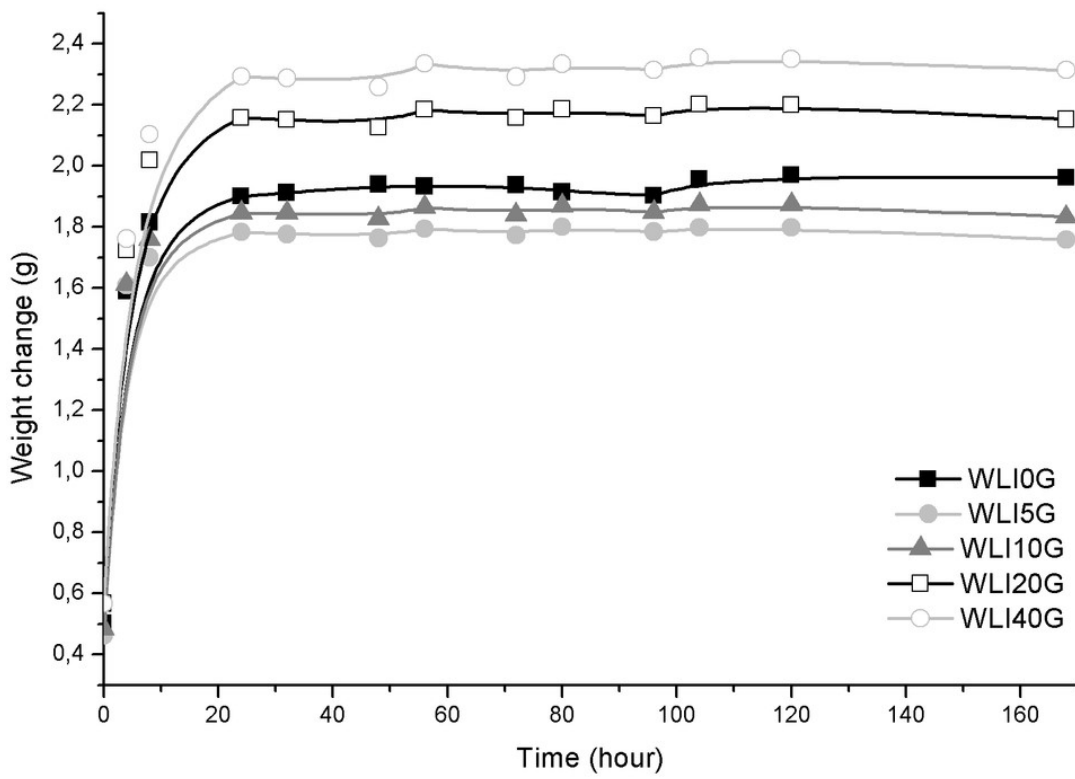
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767 Figure 6



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769 Figure 7



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771 Figure 8