



## CHEMISTRY AND MATERIALS SCIENCE

UDC

**Aleksander Hejna**

Doctor of Science, Assistant Professor, Department of Polymer Technology  
Gdańsk University of Technology, Republic of Poland

**Paulina Kosmela**

Doctor of Science, Assistant Professor, Department of Polymer Technology  
Gdańsk University of Technology, Republic of Poland

**Adam Olszewski**

Master of Science, PhD Student, Department of Polymer Technology  
Gdańsk University of Technology, Republic of Poland

**Łukasz Zedler**

Master of Science, PhD Student, Department of Polymer Technology  
Gdańsk University of Technology, Republic of Poland

**Krzysztof Formela**

Doctor of Science, Assistant Professor, Department of Polymer Technology  
Gdańsk University of Technology, Republic of Poland

**DETERMINATION OF THE HYDROXYL NUMBER OF GROUND  
TIRE RUBBER PARTICLES VIA MODIFIED TEST METHOD FOR  
ISOCYANATE GROUPS**

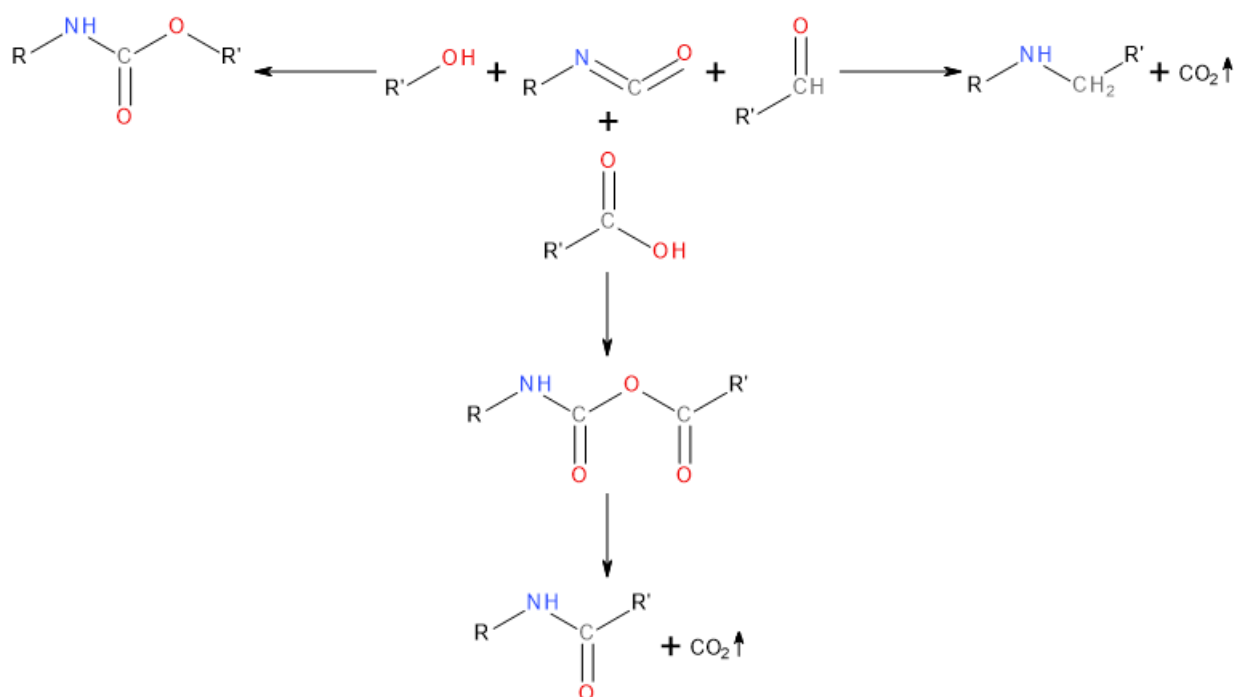
**Abstract:** Nowadays, considering the environmental trends and law regulations associated with the circular economy, it is very important to seek for the methods of by-products and waste utilization. The example of such material, which requires the attention and recycling method is ground tire rubber generated during recycling of post-consumer car tires. It can be introduced into various polymer matrices as a filler, but to enhance its effectivity it is essential to guarantee the interfacial compatibility. Therefore, the fast and simple methods for determination of the waste rubber chemical structure are needed. In

the presented paper, we are presenting the method for the determination of hydroxyl number of ground tire rubber, based on the modified standard test method for isocyanate groups. Hydroxyl number is used as a quantitative measure of the hydroxyl groups content, which is essential during manufacturing of multiple polymeric materials, such as polyurethanes, epoxy resins, polyesters or polyamides. Moreover, the presence of hydroxyls on the rubber surface may be exploited during compatibilization of composites.

**Keywords:** Ground tire rubber; hydroxyl number; isocyanate groups; titration; chemical structure

## Introduction

During manufacturing of polyurethanes (PU) it is very important to monitor the ratio between the free isocyanate and hydroxyl groups in the polyurethane system, since their reaction generates the polyurethane groups [1]. Isocyanates are also able to react with carbonyls and carboxyls, as presented in Figure 1.



**Fig. 1. Schematic reactions of isocyanate groups with hydroxyls, carbonyls and carboxyls**

The most important are hydroxyls, which as mentioned above take part in the actual polymerization reaction during manufacturing of polyurethanes. Their amount is



determined by the hydroxyl number, very important parameter of components applied for PU production [1]. Nevertheless, they also may be introduced into the system when fillers are applied. Hydroxyl groups are mostly present on the surface of various lignocellulose fillers [2], but may be also found on the surface of ground tire rubber (GTR) particles. They are generated during shredding of car tires, as a result of shear forces action. Moreover, during the treatments aimed at enhancement of GTR compatibility with polymer matrices, hydroxyl groups may appear as a result of thermooxidative treatment or addition of various modifiers [3]. Therefore, it is essential to monitor their content and include it during engineering the recipes for polyurethanes. In presented work, we evaluated the determination of the hydroxyl number of ground tire rubber particles via modified test method for isocyanate groups. This standard test method is described in the ASTM D2572 standard, and is widely applied during manufacturing of polyurethane materials. It can be used for the determination of free isocyanate groups content in isocyanates or prepolymers applied during manufacturing of polyurethanes.

### Materials and methods

Ground tire rubber obtained by ambient grinding of used tires (a combination of passenger car and truck tires in 50:50 mass ratio), whose average particle size is approximately 0.6 mm, was produced and provided by Recykl S.A. (Śrem, Poland).

The GTR was modified by the oxidation with 30% solution of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) or 15 % solution of potassium permanganate ( $\text{KMnO}_4$ ). The  $\text{H}_2\text{O}_2$  was acquired as solution, while  $\text{KMnO}_4$  in solid form, both from Sigma Aldrich (Poland). Other method of GTR modification included treatment with fresh (FO) and waste (WO) rapeseed oil, acquired from Lidl (Poland) and from a local restaurant (Gdańsk, Poland), respectively.

During the evaluation of the chemical structure of modified GTR following chemicals were applied: acetone, dibutylamine, chlorobenzene, hydrochloric acid, technical grade toluene diisocyanate (TDI), and 3',3'',5',5''-tetrabromophenolsulfonphthalein. All chemicals were acquired from Sigma Aldrich (Poland) and were used as received.



During oxidation, GTR was modified with a 30% solution of hydrogen peroxide and a 15% solution of potassium permanganate. Particles were premixed with the proper solution in different weight ratios: 1:2, 1:1, and 2:1 for 5 minutes at room temperature. Then, mixtures were left at room temperature for 72 hours and dried at 70 °C for 8 hours. For comparison, GTR dried at 70 °C for 8 hours was used as reference.

The oil treatment of ground tire rubber were described in our previous work [4]. Briefly, treatment of GTR was performed with EHP 2x20 Sline co-rotating twin-screw extruder from Zamak Mercator (Poland) with a screw diameter of 20 mm and an L/d ratio of 40. Before the modification, GTR was premixed with 20 or 40 phr (parts per hundred of rubber) of selected oil. Then, it was dosed into the extruder with a constant throughput of 2 kg/h. Barrel temperature in all zones was set at 200 °C. The screw speed was set at 50 or 150 rpm and 350 rpm, depending on the oil content. For each set of parameters, extrusion was carried out for at least 5 min after stabilizing the extruder's motor load, indicating the stabilization process. Samples were coded as GTR/XY/Z, where X stands for oil content, Y for type of oil, and Z for the screw speed.

Changes in the chemical structure of GTR were evaluated using a modified method for the determination of free isocyanate group content by titration with dibutylamine, according to ASTM D-2572. The 0.5 g samples of GTR were put in a glass flask with 0.5 g of toluene diisocyanate and 20 cm<sup>3</sup> of acetone. Mixtures were thoroughly mixed, sealed, and stored at room temperature for 24 hours. Proper amounts of dibutylamine solution in chlorobenzene and 3',3'',5',5''-tetrabromophenolsulfonphthalein were added. Then, mixtures were titrated with 0.1 M hydrochloric acid until the color change to yellow. Obtained results were compared with the free isocyanate content of neat toluene diisocyanate to determine the number of functional groups at the rubber surface able to react with isocyanates. As described earlier, such evaluation is essential for the potential application of modified GTR in manufacturing of polyurethane materials.





The free isocyanate content of the GTR/TDI mixture ( $\%_{NCO}$ ) was calculated according to the formula (1):

$$\%_{NCO} = \frac{(4.202 \cdot (V_B - V_s) \cdot N_{HCl})}{m_{TDI}} \quad (1)$$

where:  $V_B$  – the volume of HCl required for titration of the blank sample, ml;  $V_s$  – the volume of HCl required for titration of analyzed sample, ml;  $N_{HCl}$  – molarity of HCl, M;  $m_{TDI}$  – the mass of TDI placed in the flask, g.

Based on the  $\%_{NCO}$  values, the assumed hydroxyl numbers ( $L_{OH}$ ) of GTR were calculated. During calculations, it was assumed that the functional groups present on the surface of GTR particles consumed all isocyanate groups in the system. Another assumption was that all of the functional groups present on the surface of GTR were hydroxyls. The total amount of free isocyanate groups present in the system ( $A_{NCO}$ ) was calculated based on the mass of TDI placed in the flask by the equation (2):

$$A_{NCO} = \frac{2 \cdot m_{TDI}}{M_{TDI}} \quad (2)$$

where:  $M_{TDI}$  – the molar mass of TDI, equal to 174.2 g/mol.

The number of the free isocyanate groups that reacted with GTR ( $R_{NCO}$ ) was calculated following the formula (3):

$$R_{NCO} = \frac{\Delta_{NCO}}{100} \cdot A_{NCO} \quad (3)$$

where:  $\Delta_{NCO}$  – difference between free isocyanate content in TDI, equal to 42.7% and  $\%_{NCO}$  of particular sample.

Considering the above mentioned assumptions, the number of hydroxyl groups, which took part in reactions ( $R_{OH}$ ) is equal to  $R_{NCO}$ .

Then, the mass of GTR accounting for the 1 mol of hydroxyl groups ( $Eq_{OH}$ ) was calculated using the equation (4):

$$Eq_{OH} = \frac{m_{GTR}}{R_{OH}} \quad (4)$$

where:  $m_{GTR}$  – the mass of GTR placed in the flask, g.

Finally, the hydroxyl number of GTR was calculated from the formula (5):

$$L_{OH} = \frac{56100}{Eq_{OH}} \quad (5)$$



## Results and discussion

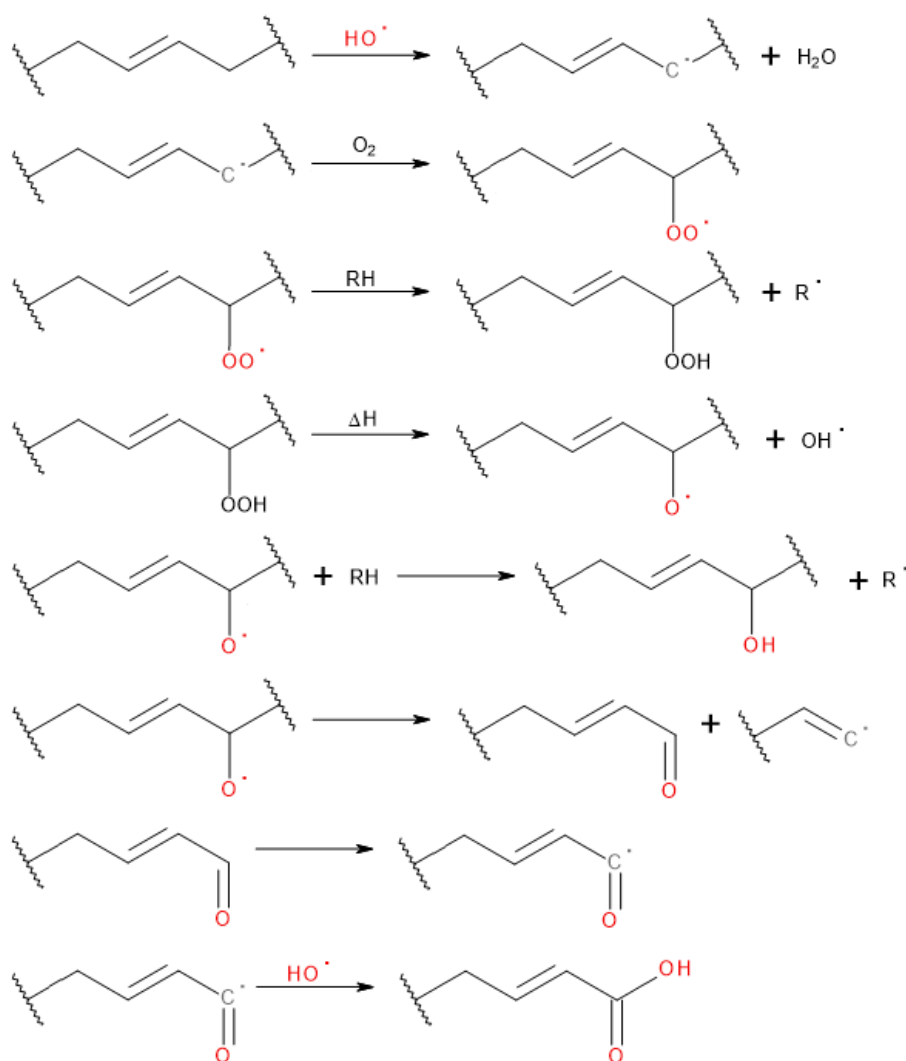
Table 1 presents the impact of the applied ground tire rubber treatment on the free isocyanate contents of GTR/TDI mixtures and calculated hydroxyl numbers of GTR.

**Table 1**

**Results of the free isocyanate content determination and calculations of hydroxyl number of GTR samples**

	Sample	%NCO, %	$\Delta$ NCO, %	RNCO, mmol	EqOH, g/mol	LOH, mg KOH/g
	Neat GTR	$33.3 \pm 1.1$	$9.4 \pm 1.1$	$0.55 \pm 0.07$	$920 \pm 119$	$61.7 \pm 3.0$
Oxidation	GTR:H <sub>2</sub> O <sub>2</sub> 2:1	$37.0 \pm 0.3$	$5.7 \pm 0.3$	$0.32 \pm 0.02$	$1542 \pm 68$	$36.4 \pm 1.6$
	GTR:H <sub>2</sub> O <sub>2</sub> 1:1	$37.3 \pm 1.1$	$5.4 \pm 1.1$	$0.31 \pm 0.06$	$1676 \pm 154$	$34.5 \pm 2.4$
	GTR:H <sub>2</sub> O <sub>2</sub> 1:2	$37.9 \pm 1.1$	$4.8 \pm 1.1$	$0.29 \pm 0.06$	$1790 \pm 220$	$32.1 \pm 2.3$
	GTR:KMnO <sub>4</sub> 2:1	$12.1 \pm 0.5$	$30.6 \pm 0.5$	$1.84 \pm 0.18$	$274 \pm 25$	$205.9 \pm 9.9$
	GTR:KMnO <sub>4</sub> 1:1	$7.4 \pm 0.5$	$35.3 \pm 0.5$	$2.02 \pm 0.04$	$248 \pm 7$	$226.3 \pm 6.2$
	GTR:KMnO <sub>4</sub> 1:2	$3.7 \pm 0.2$	$39.0 \pm 0.2$	$2.36 \pm 0.13$	$213 \pm 11$	$248.9 \pm 3.3$
Oil treatment in the extruder	GTR50	$36.3 \pm 0.4$	$6.4 \pm 0.4$	$0.37 \pm 0.03$	$1371 \pm 126$	$41.1 \pm 3.6$
	GTR350	$32.1 \pm 0.1$	$10.6 \pm 0.1$	$0.61 \pm 0.01$	$827 \pm 16$	$67.8 \pm 1.3$
	GTR/20FO/50	$37.9 \pm 0.5$	$4.8 \pm 0.5$	$0.28 \pm 0.03$	$1834 \pm 180$	$30.8 \pm 3.2$
	GTR/20FO/350	$33.8 \pm 0.3$	$8.9 \pm 0.3$	$0.51 \pm 0.02$	$987 \pm 40$	$56.9 \pm 2.4$
	GTR/40FO/150	$36.7 \pm 0.2$	$6.0 \pm 0.2$	$0.34 \pm 0.01$	$1467 \pm 48$	$38.3 \pm 1.2$
	GTR/40FO/350	$34.5 \pm 0.1$	$8.2 \pm 0.1$	$0.47 \pm 0.01$	$1057 \pm 21$	$53.1 \pm 1.0$
	GTR/20WO/50	$32.4 \pm 0.1$	$10.3 \pm 0.1$	$0.60 \pm 0.01$	$841 \pm 12$	$66.6 \pm 0.9$
	GTR/20WO/350	$30.9 \pm 0.5$	$11.8 \pm 0.5$	$0.67 \pm 0.03$	$746 \pm 35$	$75.2 \pm 3.5$
	GTR/40WO/150	$29.9 \pm 0.5$	$12.8 \pm 0.5$	$0.74 \pm 0.02$	$682 \pm 26$	$82.3 \pm 3.2$
	GTR/40WO/350	$30.9 \pm 1.0$	$11.8 \pm 1.0$	$0.68 \pm 0.06$	$742 \pm 65$	$75.9 \pm 0.9$

It can be seen that performed modifications of GTR resulted in the significant changes in the %NCO, and calculated hydroxyl number. These changes are in line with the theoretical assumptions. The oxidation of rubber with hydrogen peroxide caused the drop of hydroxyl number of GTR. Previous reports indicated rubber surface activation by creating carboxylic sites [5]. Hydrogen peroxide causes the generation of carbonium ions on the surface, which are converted into carboxylic sites, which hardly influence the calculated hydroxyl number due to the lower reactivity with isocyanates. Potential reactions are presented in Figure 2.



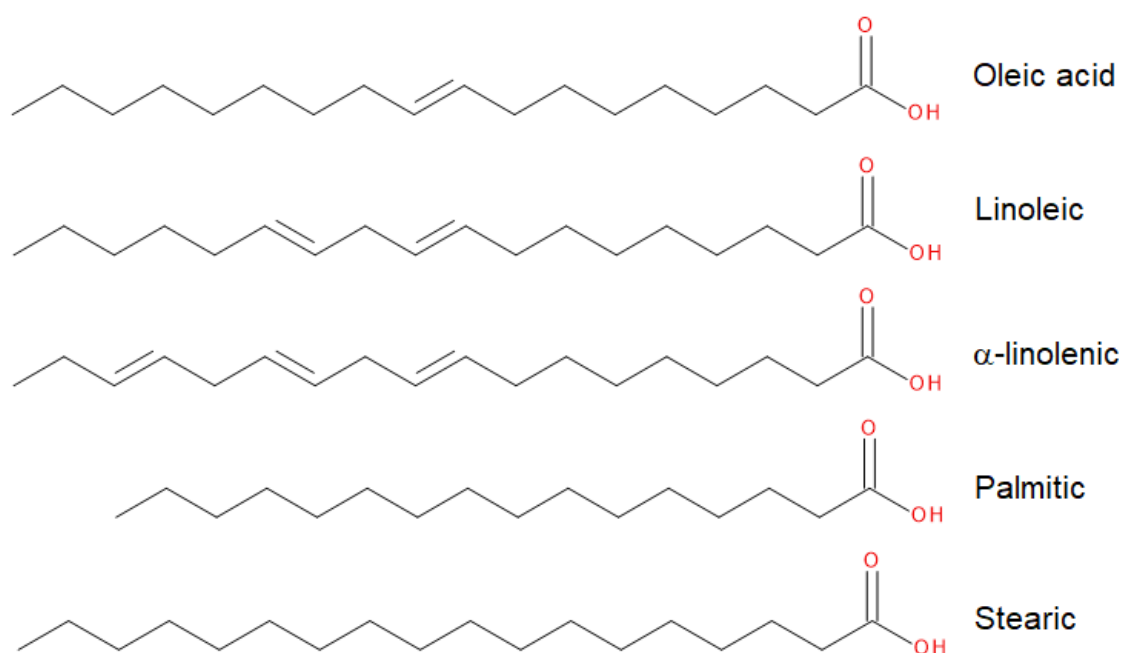
**Fig. 2. Potential reactions during GTR oxidation with  $\text{H}_2\text{O}_2$**

On the other hand, oxidation with potassium permanganate drastically increased the amount of consumed free isocyanate groups and enhanced the calculated values of hydroxyl number. Such an effect is associated with the generation of four hydroxyl groups during reduction of  $\text{KMnO}_4$  in the neutral solution [6]. As a result, the number of functional groups able to react with isocyanates is significantly boosted.

Considering the modification with oils, significantly different values of hydroxyl numbers were noted for fresh and waste oils. When the fresh oil was applied, the  $L_{OH}$  was decreased, which is resulted to the chemical structure of rapeseed oil, especially contents of oleic, linoleic,  $\alpha$ -linolenic, palmitic and stearic acids, whose structures are presented in Figure 3. It can be seen that these acids do not contain hydroxyl groups in the structure, so they are not contributing to the hydroxyl number [1]. As a result, they are only swelling



rubber particles. Nevertheless, after frying, the chemical structure of oils is changing due to the hydrolysis, oxidation and polymerization of oil. The first two groups of reactions may enhance the hydroxyl number. Hydrolysis results in formation of mono- and diglycerols, as well as free fatty acids, sometimes even glycerol. These compounds show significantly higher hydroxyl numbers, so they can increase its value for modified GTR. Oxidation of oils may result in generation of carbonyl groups, noticeably less often hydroxyls. Nevertheless, it may also increase the hydroxyl number of oil [7].



**Fig. 3. The main fatty acids present in the rapeseed oil**

Considering the theoretical knowledge about the GTR modification and physical, as well as chemical changes occurring during different treatments, proposed method for the determination of hydroxyl number of modified GTR should be considered valid. In the future works, the influence of obtained values on the structure and performance of polyurethane/ground tire rubber composites would be evaluated.

### Acknowledgments

This work was supported by The National Centre for Research and Development (NCBR, Poland) in the frame of LIDER/3/0013/L-10/18/NCBR/2019 project – *Development of technology for the manufacturing of foamed polyurethane-rubber composites for the use as damping materials.*



**References:**

1. Vilar WD (1998): *Química e Tecnologia dos Poliuretanos*, 2nd. ed. Vilar Consultoria Técnica Ltda.: Rio de Janeiro, Brazil.
2. Hejna A, Kosmela P (2020): *Insights into Compatibilization of Poly( $\epsilon$ -caprolactone)-based Biocomposites with Diisocyanates as Modifiers of Cellulose Fillers*. Mindanao Journal of Science and Technology, 18, 221-241.
3. Formela K, Klein M, Colom X, et al. (2016): *Investigating the combined impact of plasticizer and shear force on the efficiency of low temperature reclaiming of ground tire rubber (GTR)*. Polymer Degradation and Stability, 125, 1–11.
4. Zedler Ł, Kosmela P, Olszewski A, et al. (2020): *Recycling of Waste Rubber by Thermo-Mechanical Treatment in a Twin-Screw Extruder*. The First International Conference on “Green” Polymer Materials 2020, Online, 05-25.11.2020.
5. Shatanawi KM, Biro S, Naser M, et al. (2013): *Improving the rheological properties of crumb rubber modified binder using hydrogen peroxide*. Road Materials and Pavement Design, 14(3), 723–734.
6. Dash S, Patel S, Mishra BK (2009): *Oxidation by permanganate: synthetic and mechanistic aspects*. Tetrahedron, 65(4), 707–739.
7. Choe E, Min D (2007): *Chemistry of Deep-Fat Frying Oils*. Journal of Food Science, 72, R77-R86.