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OIL-ASSISTED THERMO-MECHANICAL RECLAMATION OF GROUND TIRE RUBBER

Abstract. *Nowadays, it is crucial to seek for the methods of by-products and waste utilization, considering both environmental and economic factors. The example of waste material generated in the massive amounts, which requires the attention is ground tire rubber generated during recycling of post-consumer car tires. It can be applied as a filler into different polymer matrices, but to enhance its effectivity proper modifications should be performed. In the presented paper, we investigated the oil-assisted thermo-mechanical treatment of ground tire rubber in twin-screw extruder. Changes in the chemical structure were determined by the measurement of hydroxyl numbers of modified rubber. Moreover, application of oils enhanced thermal stability of treated ground tire rubber.*

Keywords: *Ground tire rubber; recycling; rubber modification; oil; thermo-mechanical treatment*

Introduction

Ground tire rubber (GTR) is a waste material, generated currently in the enormous amounts and lacking the proper industrial applications which could provide its utilization on higher scale. This material could be efficiently introduced into different polymer matrices as a filler, but it should be properly modified. One of the potential methods of modification, and the promising one, is the reactive extrusion. This process is economically and ecologically beneficial alternative for the conventional methods of rubber modifications. Moreover, it provides the possibility for the incorporation of various modifiers, and is generally very flexible process. In the presented paper we investigated the oil-assisted thermo-mechanical treatment of ground tire rubber in twin-screw extruder and the impact of oil type (fresh or waste rapeseed oil), oil content (20 or 40 parts per hundred rubber) and screw speed (50, 150 or 350 rpm) on the structure and thermal stability of modified ground tire rubber particles.

Materials and methods

Ground tire rubber obtained by ambient grinding of used tires (a combina-tion 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. (Srem, Poland).

Two types of rapeseed oil were applied as modifiers for ground tire rubber. Fresh rapeseed oil was acquired from Lidl (Poland), while waste oil was obtained from a local restaurant (Gdańsk, Poland).

Thermo-mechanical treatment of GTR was described in our previous work [1]. Briefly, treatment was performed with EHP 2x20 Sline co-rotating twin-screw extruder from Zamak Mercator (Poland). Ground tire rubber was premixed with 20 or 40 phr (parts per hundred of rubber) of oil before treatment and then was dosed into the extruder by a volumetric feeder with a constant throughput of 2 kg/h. The screw speed was set at 50, 150, or 350 rpm. The value of 50 rpm was selected as a minimum screw speed, which could be applied to process the ground tire rubber effectively. For samples containing 40 phr of oils, minimum screw speed had to be increased to 150 rpm to enable the extrusion without clogging in the dosing section. Barrel temperature in all zones was set at 200 °C. For each set of parameters, extrusion was carried out for at least 5 minutes after stabilizing the extruder's motor load, indicating the stabilization process.

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 [2]. The 0.5 g samples of GTR were put in a glass flask with 0.5 g of toluene diisocyanate and 20 cm^3 of acetone. Mixtures were thor-oughly mixed, sealed and stored at room temperature for 24 h. Then, 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 changed 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. Such evaluation is essential for the potential application of modified GTR as a filler for polyurethane materials.

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

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

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 these values, the assumed hydroxyl numbers (L_{OH}) of GTR were calculated. During calculations, it was assumed that all of the consumed isocyanate groups reacted with the GTR particles. Another assumption was that all of the functional groups present on the surface of GTR were hydroxyls. Considering these assumptions, the number of hydroxyl groups, which took part in reactions was calculated following the Equation (2):

$$X_{OH} = X_{NCO} = ((\%_{NCO-TDI} - \%_{NCO}) \cdot m_{TDI} \cdot 2)/(M_{TDI} \cdot 100) \quad (2)$$

where: $\%_{NCO-TDI}$ – free isocyanate content in TDI, equal to 42.7%; M_{TDI} – the molar mass of TDI, equal to 174.2 g/mol.

Then, the hydroxyl number of GTR was calculated from the Formula (3):

$$L_{OH} = 56100 \cdot X_{NCO} / m_{GTR} \quad (3)$$

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

The thermogravimetric (TGA) analysis of GTR and composites was performed using the TG 209 F3 apparatus from Netzsch (Germany). Samples of composites weighing approx. 10 mg were placed in a ceramic dish. The study was conducted in an inert gas atmosphere - nitrogen in the range from 30 to 900 °C with a temperature increase rate of 10 °C/min.

Results and discussion

In Figure 1, there are presented values of the hydroxyl number for prepared GTR samples, as reported in our previous paper [1]. This Figure indicates the significant changes in the chemical structure of rubber particles. Hydroxyl number is associated with the amount of -OH groups present on the surface of GTR particles. Their presence is very important for the potential application of GTR as filler in polymer composites, because hydroxyl groups changes the surface polarity. They are generated during thermo-mechanical treatment as a result of partial oxidation of rubber. Moreover, their presence can be also associated to the addition of oils, especially the waste one, which could be partially decomposed during primary use in restaurant. Its stability was lower, which resulted in burning during processing. According to the literature data, the rapeseed oil smoke point may vary in the range of 180-220 °C [3]. Therefore, oil with previous thermal history could be easily oxidized and degraded during processing, which resulted in the generation of lower-molecular weight compounds with functional groups during processing.

Table 1 presents the results of thermogravimetric analysis of thermo-mechanically reclaimed ground tire rubber. It can be seen that applied treatment caused the enhancement of GTR thermal stability.

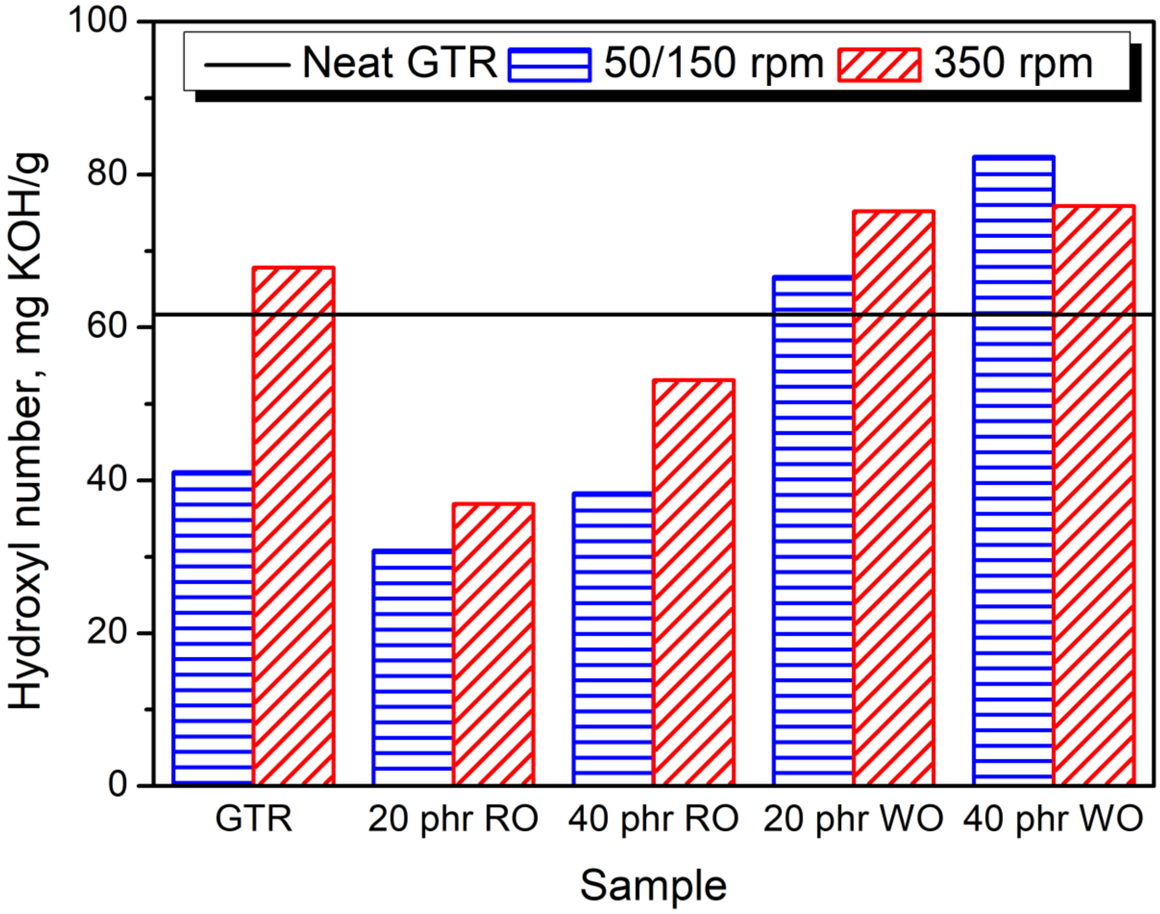

Fig. 1. The values of TVOC parameter for analyzed recycled LDPE streams.

Such an effect could be associated with the partial decomposition of rubber and oxidation of surface suggested by the changes in the hydroxyl number. Incorporation of oils caused the enhancement of GTR thermal stability, which could be associated with their relatively good stability [4]. For fresh rapeseed oil, the onset of GTR thermal decomposition, expressed by the 2 wt% mass loss was shifted from 256.6 to 269.3-283.7 °C, and the effect was more pronounced for higher oil content. Smaller enhancement was noted for waste oil, which could be associated with its partial decomposition during its primary use in restaurants. Therefore, modification with rapeseed oil may be applied to ihibit thermal decomposition of ground tire rubber. Nevertheless, despite the shift of degradation onset, drop of char residue was noted. Such an effect is attributed to the course of rapeseed oil thermal degradation. Literature data, indicate that for neat rapeseed oil, the char residue is around 10 wt%, which points to the “more complete” decomposition than for GTR [4].

Table 1

Results of TGA analysis of prepared samples of GTR

Sample	Oil content, phr	Screw speed, rpm	$T_{-2\%}$, °C	$T_{-5\%}$, °C	$T_{-10\%}$, °C	$T_{-50\%}$, °C	Char residue at 800 °C, wt%	T_{max1}, °C	T_{max2}, °C
Neat GTR	-	-	256.6	307.2	347.9	444.7	37.51	379.0	431.2
GTR	-	50	260.0	308.5	347.4	443.9	37.48	377.9	436.6
		350	261.1	310.2	348.9	444.4	37.40	378.2	431.8
Rapeseed oil	20	50	269.3	315.7	346.2	427.0	32.24	382.1	441.6
		350	269.5	316.6	347.2	429.3	32.37	382.4	442.9
	40	150	280.2	323.3	349.8	417.5	28.30	389.1	441.6
		350	283.7	325.0	350.3	417.4	27.72	389.2	441.6
Waste oil	20	50	263.0	305.6	339.8	426.6	32.53	381.5	440.6
		350	259.9	305.1	340.4	427.0	32.32	381.9	440.6
	40	150	265.5	307.5	339.6	415.6	28.22	386.1	440.6
		350	267.1	308.8	340.4	415.3	27.94	386.3	440.6

Two characteristic peaks related to the two main components of GTR were noticed at approx. 377.9–389.1 °C (T_{max1}) and at approx. 431.2–442.9 (T_{max2}). These peaks are associated with the thermal decomposition of of natural rubber and styrene-butadiene rubber [5], which proves that used material originated from used post-consumer tires. Samples subjected to thermo-mechanical treatment without addition of oil were characterized by very similar values of T_{max1} and T_{max2}. Addition of oils caused the shift of these values towards higher temperatures, which was associated with thermal stability of rapeseed oil [4]. Lower shifts for waste oil point to its partial decomposition during its primary use in restaurants.

Conclusions

Generally, presented results indicated that ground tire rubber could be efficiently modified with fresh and recycled rapeseed oil. Such treatment could be considered an effective method for utilization of waste oils. Moreover, except for the economical advantage, applied oil-assisted thermo-mechanical treatment enhanced thermal stability of GTR particles and shifted the onset of thermal decomposition by even 27.1 °C, which may broaden the potential range of applications for modified GTR in the future.

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