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THE IMPACT OF FILLER THERMOMECHANICAL MODIFICATIONS ON STATIC AND DYNAMIC MECHANICAL PERFORMANCE OF FLEXIBLE FOAMED POLYURETHANE/GROUND TIRE RUBBER/ZINC BORATE COMPOSITES

The rapid development of the automotive industry is very beneficial to many aspects of human life, but it is also a very significant environmental burden. The most straightforward impact is related to the generation of exhaust, but the management of post-consumer car parts is also a major challenge. Among them, waste tires are very burdensome due to their enormous numbers. Therefore, it is essential to develop novel, environmentally friendly methods for their disposal, which would reduce their environmental impacts. One of the most promising approaches is shredding, resulting in the generation of ground tire rubber (GTR), which can be introduced into polymeric materials as a filler. The presented work is related to the thermomechanical treatment of GTR in a twin-screw extruder assisted by zinc borate (ZB), whose incorporation is aimed to increase interparticle friction within the extruder barrel. The impact of the treatment conditions on the particle size and surface development of the GTR/ZB compositions was evaluated. Modified GTR was introduced into flexible polyurethane (PU) foams, and the impact on the static and dynamic mechanical performance of the resulting composites was investigated. Increasing the treatment temperature occurred to have an adverse effect on the tensile performance of the composites due to the agglomeration of GTR particles limiting the efficiency of stress transfer, which was also confirmed by dynamic mechanical analysis. On the other hand, increasing the ZB share in the GTR/ZB compositions limited PU disruptions related to the reactivity of the GTR functional groups with isocyanates, which enhanced the mechanical performance of the composites. It was proven that the proposed method of GTR thermomechanical treatment assisted by ZB might benefit the performance of flexible PU foamed composites, which could broaden the application range of GTR and provide novel ways for its efficient utilization.

Keywords: ground tire rubber, polyurethane foams, filler modification, zinc borate, composites, recycling

INTRODUCTION

Ground tire rubber (GTR) is a product of the material recycling of post-consumer car tires [1]. It is generated by the shredding of tires and the removal of other non-rubber components. Due to the enormous number of car tires withdrawn from further use and forecasts indicating rapid growth of this number, the management of waste tires and the resulting GTR is a vital issue for the environment worldwide [2]. Currently, GTR is applied, e.g. as fuel for incineration or pyrolysis, an asphalt modifier, or infill material for artificial football fields [3]. Over the years, multiple research works have investigated its application as a filler for polymer composites, which seems very auspicious owing to the excellent mechanical performance of car tires [4]. GTR has been repeatedly incorporated into different polymer matrices including polyethylene [5], polypropylene [6],

poly(vinyl chloride) [7], polyamide [8], thermoplastic polyurethane (PU) [9], natural rubber [10], styrene-butadiene rubber [11], epoxy resins [12], flexible [13] and rigid PU foams [14]. However, to guarantee sufficient interfacial interactions between the polymer matrix and GTR applied as a filler, it is essential to apply a proper compatibilizer [15] or perform modification of the GTR particles aimed at surface development and/or the introduction of functional groups onto the surface [16, 17].

In recent years, multiple GTR treatments have been evaluated by various researchers [18-24]. Among them, one of the most promising methods is thermomechanical treatment using twin-screw extruders [25]. Such a process enables continuous modification of GTR with a relatively low energy input [25]. The combined

impact of temperature and shear forces provides optimal conditions for increasing the surface roughness of GTR particles and enhancing interfacial interactions in the final composites. Moreover, it provides the possibility of introducing additional modifiers, either reactive or non-reactive. The first group includes components inducing changes in the chemical structure of GTR, e.g. oxidizing agents [26] or peroxides [27]. On the other hand, non-reactive modifiers enable the physical character of GTR particles to be changed, e.g. by swelling [28] or encapsulation, e.g., with various elastomers [29].

Non-reactive modifications may also include the application of solid particles, which should increase the shear forces acting on the GTR particles during modifications. Therefore, in the presented work, inorganic zinc borate (ZB) particles were applied as modifiers for GTR during twin-screw extrusion treatment. The goal of applying ZB was to enhance the GTR particle size reduction and surface development, which yield friction. ZB was introduced in the amount of 20 or 40 parts per 100 parts by weight with respect to the GTR, and the compositions were extruded at varying temperatures (150 or 200°C) and screw speeds (80, 150, or 350 rpm). After characterization, the GTR/ZB compositions were applied as fillers for foamed flexible PU composites.

MATERIALS AND METHODS

Materials

The materials applied in the presented study are listed in Table 1.

TABLE 1. List of compounds used during manufacture of analyzed composites

Component	Trade name	Producer
Ground tire rubber (GTR)	---	Recykl S.A. (Poland)
Zinc borate (ZB)	Firebrake 500	U.S. Borax (USA)
Polyols	Rokopol® F3000	PCC Group (Poland)
	Rokopol® V700	PCC Group (Poland)
	Glycerol	Sigma Aldrich (Poland)
Diisocyanate	SPECFLEX NF 434	M. B. Market Ltd. (Poland)
Catalysts	PC CAT® TKA30	Performance Chemicals (UK)
	Dabco33LV	Air Products (USA)
	Dibutyltin dilaurate	Sigma Aldrich (Poland)
Blowing agent	Distilled water	---

Modification of ground tire rubber with zinc borate

The thermomechanical modification of GTR with zinc borate was performed in a co-rotating twin-screw

extruder EHP 2x20 Sline from Zamak Mercator (Poland). GTR was introduced into the extruder barrel with 20 or 40 parts per 100 parts by weight zinc borate. To investigate the impact of the processing parameters, the barrel temperature was set at 150 or 200°C, while the screw speed was 80, 150, or 350 rpm. For comparison, a premix without thermomechanical treatment was also prepared.

Preparation of composite foams

Composite foams were prepared by a single-step method with the isocyanate index of 1:1. A predetermined amount of GTR filler (20 wt.%) was mixed with the polyols (26.1 wt.% each) at 1000 rpm for 60 s to guarantee its proper distribution. Afterwards, all the components (0.6 wt.% glycerol, 0.5 wt.% dibutyltin dilaurate, 0.3 wt.% other catalysts and water, 25.8 wt.% isocyanate) were mixed for 10 s at 1800 rpm and poured into a closed aluminum mold with dimensions of 200 × 100 × 40 mm. After demolding, the samples were conditioned at room temperature for 24 h. All the foams were characterized by an apparent density of $187.5 \pm 2.5 \text{ kg/m}^3$.

Characterization techniques

The particle size distribution of the GTR/zinc borate compositions was determined using a laser particle sizer Fritsch Analysette 22 apparatus (Germany) operating in the range of 0.08–2000 μm. The microstructure of the applied GTR/ZB compositions was analyzed using a scanning electron microscope (SEM) MIRA3 (Tescan, Czech Republic). An approx. 20 nm carbon coating was deposited on the samples using a JEE 4B vacuum evaporator (Jeol USA, USA). After conditioning, the foamed polyurethane composites were cut into specimens, whose properties were later determined following the standard procedures.

The tensile strength of the foams was estimated following ISO 1798. The beam-shaped specimens with the dimensions 10 × 10 × 100 mm were measured with a slide caliper having an accuracy of 0.1 mm. The tensile test was performed on a Zwick/Roell tensile tester (Germany) at a 500 mm/min constant speed. The compressive strength of the foams was measured according to the ISO 604 standard using a Zwick/Roell Z020 tensile tester (Germany). Cylindrical specimens with dimensions of 20 × 20 mm (height and diameter) were employed. The test was conducted at a constant speed of 15%/min until reaching 70% deformation. Dynamical mechanical analysis (DMA) was performed using a Q800 DMA instrument (TA Instruments, USA) in a single cantilever mode at the heating rate of 4°C/min and a temperature range from –100 to 150°C. The specimens were rectangular with dimensions of 17 × 12 × 3 mm.

RESULTS AND DISCUSSION

Particle size distribution and surface development of GTR/zinc borate fillers

Figure 1 presents the impact of the thermomechanical treatment on the particle size distribution of the GTR/ZB compositions, while the SEM micrographs in Figure 2 provide more details about the surface of the applied fillers (compositions with 40 phr ZB). Prior to the treatment (Premix), the compositions were strongly heterogeneous and included two types of particles with sizes of 5-45 μm (ZB) and 100-1500 μm (GTR). Moreover, the SEM micrographs show that inorganic particles were only freely deposited on the surface of the GTR particles, which resulted from simple mechanical

mixing and potential electrostatic interactions. The extrusion of the compositions affected their particle size distribution and structure surface, which was attributed to the elevated temperatures, shear forces acting on the material, and interparticle friction. These factors caused two contradictory effects – grinding of the particles and their coalescence. The most significant changes were observed in the samples modified at the lowest screw speed of 80 rpm, implicating the longest residence time in the extruder and the highest degree of filling, which yielded strengthening of interparticle friction [30]. As a result, the inorganic ZB particles were partially compressed onto the GTR surface, reducing the share of the smallest particles, which can be seen in detail in Figure 2.

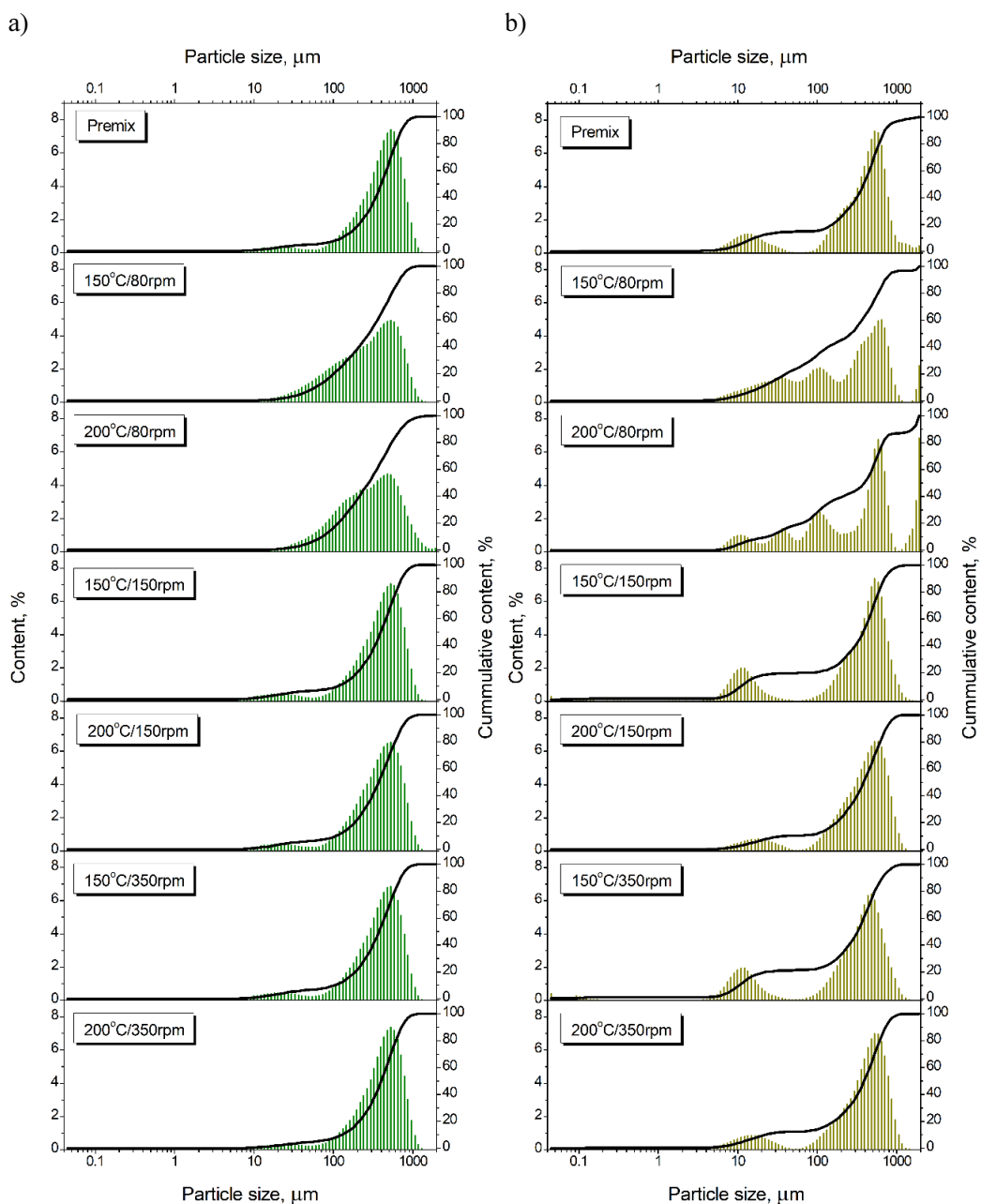


Fig. 1. Particle size distribution of filler compositions containing 20 phr (a) and 40 phr (b) zinc borate thermomechanically modified under different conditions

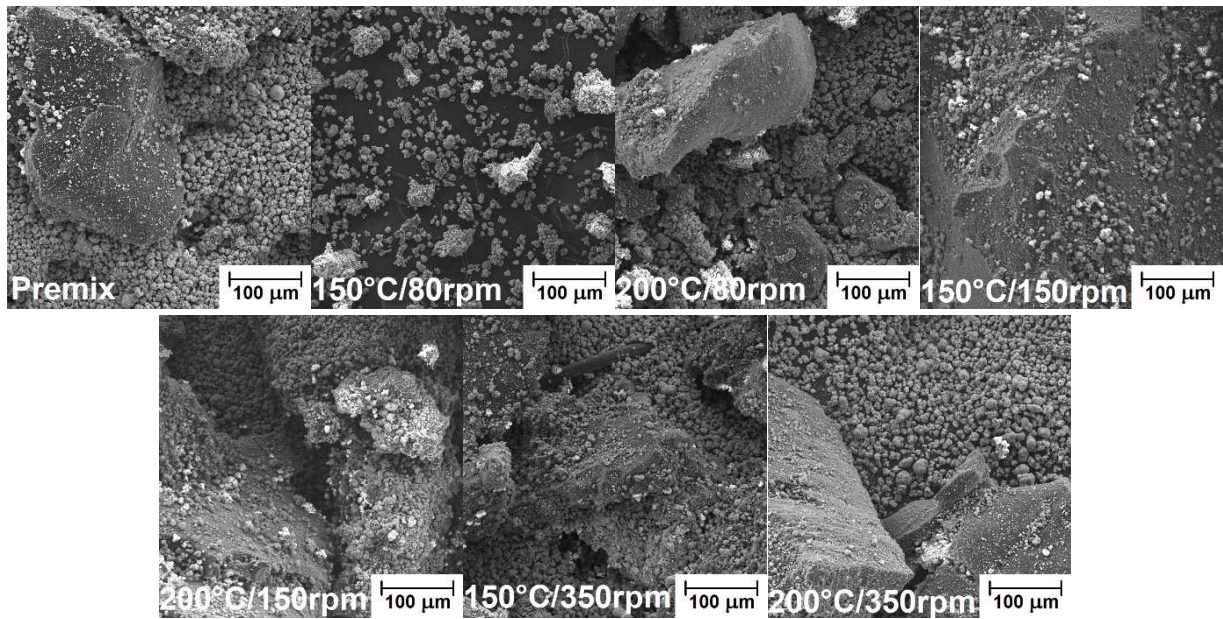


Fig. 2. Micrographs of GTR/zinc borate compositions obtained by SEM at magnification of 500x

As a result, the roughness of the GTR particles was noticeably enhanced. On the other hand, the content of the largest GTR particles was reduced due to their grinding. The lower ZB content (20 phr) resulted in a significant increase in particle size homogeneity, while the higher content (40 phr) caused the generation of several separate phases, whose particle size depended on the balance between the above-mentioned effects. When the GTR/ZB compositions were modified at higher screw speeds, the impact of treatment was not so strong owing to the shorter residence time and lower degree of filling of the extruder [31]. As a result, the GTR particles, especially in the case of the compositions modified at 350 rpm, had relatively smooth surfaces, similar to the Premix. In the case of the 150°C/150 rpm and 200°C/150 rpm samples, an increase in surface roughness can be noted due to the interparticle shear forces. Independent of the ZB content and applied screw speed, the rising treatment temperature increased the share of the largest particles, due to the agglomeration of GTR particles.

Static mechanical performance of composite foams

Table 2 summarizes the results of static tensile tests performed on the prepared composite foams. Moreover, for a deeper analysis of the impact of the applied fillers and their treatment on the tensile performance of the prepared composites, Table 3 provides values of the Pearson correlation coefficients (PCC), which express the strength of correlation between particular variables (Temp. – temperature; SS – screw speed; ZB phr – the ZB content in the GTR/ZB compositions) [32]. The values indicating strong (between 0.6 and 0.8) or very strong (between 0.8 and 1.0) correlations are in bold.

TABLE 2. Results of static tensile tests conducted on prepared composites (standard deviation in brackets)

GTR/ZB treatment conditions	Tensile strength [kPa]		Elongation at break [%]		Toughness [J/cm ³]	
	ZB content					
	20	40	20	40	20	40
150°C/80 rpm	87 (8)	91 (2)	98 (3)	128 (4)	4.14 (0.18)	4.87 (0.31)
200°C/80 rpm	70 (12)	90 (12)	110 (18)	112 (9)	3.78 (0.48)	4.69 (0.66)
150°C/150 rpm	84 (14)	96 (11)	118 (9)	130 (4)	4.69 (0.57)	5.12 (0.48)
200°C/150 rpm	51 (9)	60 (14)	82 (14)	105 (14)	1.95 (0.24)	2.89 (0.40)
150°C/350 rpm	82 (13)	86 (14)	115 (15)	112 (9)	4.50 (0.84)	4.63 (0.38)
200°C/350 rpm	57 (14)	76 (12)	99 (14)	105 (16)	2.70 (0.37)	3.93 (0.43)

It can be seen that the majority of foams have a relatively similar level of tensile strength (TS), except for the foams containing the PU/GTR compositions modified at 200°C and 150 or 350 rpm. Incorporation of the GTR/ZB compositions modified at 150°C resulted in a noticeably higher tensile strength than those modified at 200°C, which can be attributed to the coalescence and reduced surface roughness of the GTR particles owing to partial GTR decomposition, as suggested by the particle size distribution and SEM micrographs. The presented PCC values confirm the strong impact of the GTR/ZB treatment temperature on the tensile performance of the composites, especially on the tensile strength and toughness (TT).

TABLE 3. PCC values quantifying strength of relationships between applied GTR/ZB treatment parameters and tensile performance of prepared composites

Variable 1	Variable 2	PCC value	Variable 1	Variable 2	PCC value
All specimens			GTR/ZB modified at 150°C		
Temp.	TS	-0.72	SS	TS	-0.52
Temp.	Eb	-0.58	SS	Eb	-0.11
Temp.	TT	-0.70	SS	TT	-0.08
SS	TS	-0.19	ZB phr	TS	0.72
SS	Eb	-0.12	ZB phr	Eb	0.61
SS	TT	-0.11	ZB phr	TT	0.71
ZB phr	TS	0.40	GTR/ZB modified at 200°C		
ZB phr	Eb	0.46	SS	TS	-0.23
ZB phr	TT	0.38	SS	Eb	-0.19
GTR/ZB modified at 80 rpm			SS	TT	-0.21
Temp.	TS	-0.53	ZB phr	TS	0.61
Temp.	Eb	-0.09	ZB phr	Eb	0.52
Temp.	TT	-0.31	ZB phr	TT	0.57
ZB phr	TS	0.71	GTR with 20 phr ZB		
ZB phr	Eb	0.75	Temp.	TS	-0.91
ZB phr	TT	0.94	Temp.	Eb	-0.55
GTR/ZB modified at 150 rpm			Temp.	TT	-0.83
Temp.	TS	-0.96	SS	TS	-0.20
Temp.	Eb	-0.86	SS	Eb	0.15
Temp.	TT	-0.96	SS	TT	-0.08
ZB phr	TS	0.29	GTR with 40 phr ZB		
ZB phr	Eb	0.49	Temp.	TS	-0.65
ZB phr	TT	0.26	Temp.	Eb	-0.79
GTR/ZB modified at 350 rpm			Temp.	TT	-0.69
Temp.	TS	-0.79	SS	TS	-0.23
Temp.	Eb	-0.92	SS	Eb	-0.49
Temp.	TT	-0.82	SS	TT	-0.17
ZB phr	TS	0.52			
ZB phr	Eb	0.12			
ZB phr	TT	0.45			

Interestingly, the increase in the ZB content enhanced foams' tensile performance, expressed by higher values of all the determined parameters, including elongation at break (Eb). Such an effect can be associated with the reduced share of GTR particles in the final composite and limited disturbances during foaming. As reported in the literature [33-35], GTR particles, due to the presence of hydroxyl groups in their structure, can react with isocyanates present in the reacting system interfering with the stoichiometric balance of polyaddition leading to PU formation. The positive PCC values confirmed the beneficial impact of the ZB content.

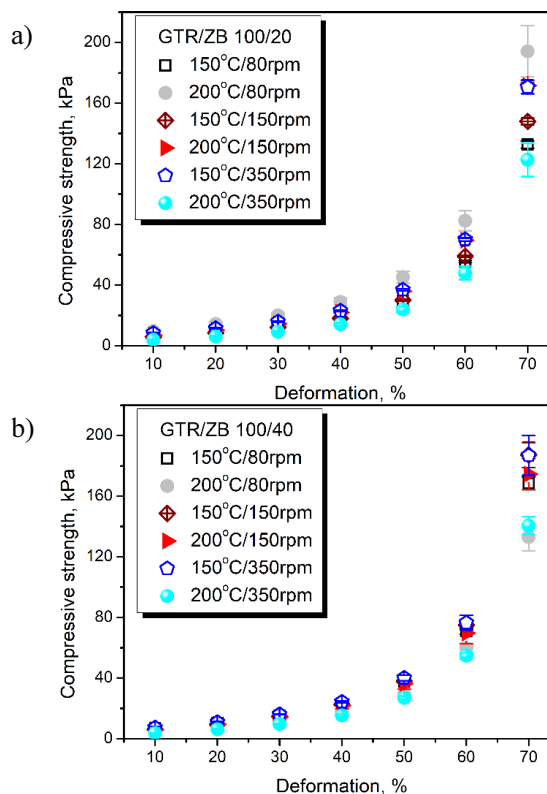


Fig. 3. Compressive strength of foams containing GTR/ZB compositions with: a) 20 phr ZB and b) 40 phr ZB

Figure 3 presents the impact of the applied GTR/ZB filler on the compressive performance of the foams. It can be seen that the produced materials exhibited typical behavior characteristic for cellular materials – a rapid rise in compressive strength related to densification of the structure with increasing deformation. For most of the specimens (except 200°C/80 rpm), increasing the ZB share from 20 to 40 phr resulted in a noticeable increase in the compressive strength, even up to 27%. Such an effect can be associated with reduced stoichiometric disruption during polyaddition, leading to a stronger PU structure. Nevertheless, all the produced materials exhibited relatively similar compressive strength, which can be associated with the similar level of apparent density of the composites, which plays a crucial role in the compressive performance of cellular materials [36].

Dynamic mechanical performance of composite foams

Based on the results of static mechanical tests, the specimens containing the GTR/ZB compositions with 40 phr ZB were selected for analysis of dynamic mechanical performance, whose results are presented in Figure 4. The provided storage modulus and loss tangent ($\tan \delta$) temperature plots show an appearance typical for flexible PU foams. The rapid and significant drop of storage modulus is associated with the glass transition inside the structure of the materials. At the ambient temperature at which the static mechanical tests were performed (25°C), the modulus of the com-

posites ranged from 140 to 872 kPa. Such a substantial variation is related to the differences in the structure of the GTR/ZB compositions visualized in Figure 2 and resulting in changes in the interfacial adhesion of the composites. Moreover, the closeness of the glass transition temperature (T_g) determined as the temperature position of the $\tan \delta$ peak significantly impacts the mechanical performance of the analyzed specimens [37]. Figure 4b shows that T_g varied from 13.0 to 14.8°C, which was affected by the stoichiometric changes induced by incorporating the GTR/ZB compositions [38]. Around the T_g region, a 1°C shift causes even a 20-25% drop in the storage modulus, as presented in Figure 4a. Considering the impact of GTR/ZB treatment, it can be seen that the increasing temperature reduced the storage modulus and resulted in a higher magnitude of $\tan \delta$ peaks. Such changes indicate inferior interfacial interactions and an enhanced structural ability to dissipate energy through molecular motions. They can be attributed to the agglomeration of GTR particles and reduced surface development, as suggested by Figures 1 and 2.

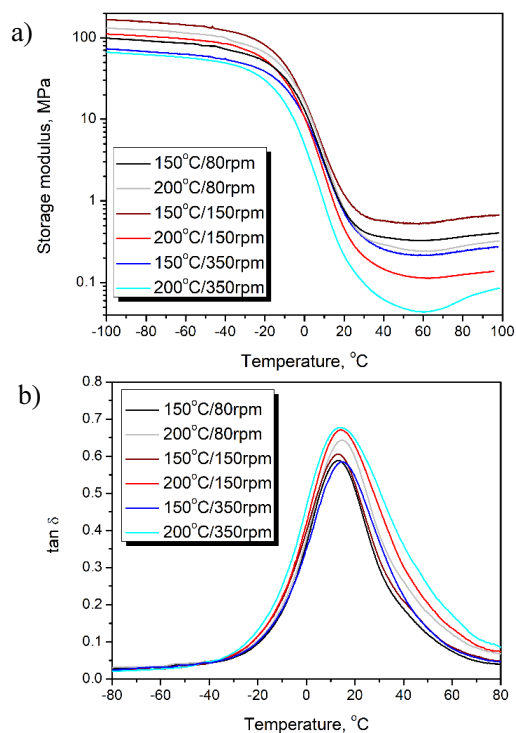


Fig. 4. Temperature plots of: a) storage modulus and b) loss tangent for prepared composites.

CONCLUSIONS

The presented work investigated the impact of the thermomechanical treatment parameters in a twin-screw extruder on the particle size and surface development of ground tire rubber/zinc borate compositions. The modified compositions were further incorporated into a flexible, foamed PU matrix, whose static and dynamic mechanical performance was analyzed. Increasing the GTR treatment temperature from 150 to 200°C reduced the tensile performance of the composites

owing to agglomeration of the GTR particles, hindering the stress transfer. These findings were confirmed by the increased magnitude of the $\tan \delta$ peaks, indicating weakened interfacial adhesion. Increasing the ZB share in the GTR/ZB compositions limited PU disruptions related to the interactions between the GTR functional groups and isocyanates, which typically result in an inferior cellular structure. Summarizing, the analyzed method of modifying GTR/ZB compositions in a twin-screw extruder and subsequent application of the obtained compositions in flexible PU foams poses an auspicious waste tire utilization method. Adjustment of the treatment conditions enables the manufacture of composite materials with varying static and dynamic mechanical performance.

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