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FINAL REPORT

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Title:

Novel thermoplastic dynamic vulcanizates (TDV) with enhanced wear resistance based on in situ produced polyurethane matrix

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1. Introduction

The successful adoption of thermoplastics in the market is primarily attributed to their use in blends. By combining two or more different polymers through melt blending, it becomes possible to create materials with novel or improved properties. Blending can enhance attributes like mechanical performance, especially toughness, resistance to thermal degradation, processability, and cost efficiency, and even introduces novel characteristics. One notable category of polymer blends on the rise is thermoplastic dynamic vulcanizates (TDVs). These TDVs consist of a continuous thermoplastic phase wherein dynamically cured rubber is dispersed, effectively merging rubber's elasticity with the ease of processing and recyclability offered by thermoplastics.

The term "dynamic" pertains to the fact that the curing of the rubber component occurs simultaneously with its dispersion in the molten thermoplastic resin, thanks to intense mixing and kneading. This technique achieves a fine dispersion of the rubber phase in the thermoplastic matrix, often referred to as a "sea-island" structure with submicron to micron-sized rubber "islands" within the thermoplastic matrix "sea." This structure combines the advantageous properties of both components, namely the elastic behavior of rubbers and the straightforward processing (as well as potential reprocessing) of thermoplastic polymers.

The origins of TDV development trace back to research aimed at enhancing the impact properties of thermoplastics, particularly rubber-modified isotactic polypropylenes (iPP). These studies revealed that incorporating uncured saturated or unsaturated ethylene-propylene-based rubbers significantly improved the impact resistance of iPP homopolymers. This enhancement was especially noticeable below the glass transition temperature range of iPP and depended on the dispersion state of the rubber phase. However, the dispersibility of the rubber phase was hindered by the recurring agglomeration and coalescence of rubber particles during compounding. As a solution, partial curing of the rubber phase was proposed and pursued. The breakthrough occurred in the late 1970s and early 1980s when several patents were filed, and the first commercially available TDV, known as Santoprene®, combining iPP and ethylene-propylene-diene terpolymer rubber (EPDM), was introduced by Monsanto.

Based on extensive research, the optimal mechanical performance requirements for TDVs were determined and can be summarized as follows: minimal interfacial tension between the constituents (similar surface free energy for rubber and thermoplastic), high crosslink density in the rubber phase, semicrystalline matrix polymer.

Polyurethanes (PUs) offer a wide range of application possibilities due to the structural diversity of their constituents, including isocyanates, polyols, and chain extenders. These components can be bifunctional or polyfunctional, allowing for the creation of linear and crosslinked molecular structures. By selecting precursor properties such as chain polarity, mechanical, thermal, and optical behavior can be tailored, and reactive moieties can be introduced into the final chain.

Numerous studies have explored blending PUs with rubbers, particularly NBR rubbers, due to their similar polar character. These studies typically focus on solution and high-temperature melt blending techniques, which are less economical as they consume more time and energy. Dynamic curing is rarely, if ever, employed. Some research reports show improved quasi-static and dynamic mechanical properties (sometimes surpassing neat PU) in these blends. However, the reinforcing effect is limited by the melting of the PU phase at higher temperatures and the breakdown of secondary structures between PU and NBR at higher strain amplitudes. Similar reinforcing effects are observed in blends produced using the solution method. An increase in the acrylonitrile content of the NBR leads to better compatibility between the PU and NBR phases.

In summary, blending thermoplastic polymers with rubbers holds promise for creating materials with novel performance characteristics. This potential can be amplified by utilizing thermoplastic polyurethanes as matrix materials as received or in situ synthesized from the components. The dynamic curing technique introduced earlier also offers additional advantages.

2. Development of TDVs with polyurethane matrix

This chapter is dedicated to the discussion of the results we gathered during our research.

2.1. TDVs with in-situ one-step bulk polymerized polyurethane matrix

We began this research project with the clarification and acquisition of the base materials. The selection of the materials was made based on the literary background of the materials, and the most deeply characterized ones were chosen to ensure that our research is based on the most stable basis. The related results are presented hereby.

Materials

Selected materials, their manufacturers, types, and basic properties of the materials are listed in Table 1.

Material	Manufacturer	Main properties
MDI 4,4′-methylenebis(phenyl isocyanate)	Sigma Aldrich Darmstadt, Germany	molecular mass 250.25 g/mol
BD 1,4-butanediol	Sigma Aldrich Darmstadt, Germany	molecular mass 90.12 g/mol
PTHF poly(tetrahydrofuran)	Sigma Aldrich Darmstadt, Germany	molecular mass 1000 g/mol, functionality: 2.0
NBR acrylonitrile-butadiene rubber	Lanxess Cologne, Germany	Perbunan 3445F Mooney viscosity (ML, 1 + 4, 100 °C): 45 ± 5, bound acrylonitrile content: 34 ± 1 wt%
XNBR carboxylated acrylonitrile-butadiene	Lanxess Cologne, Germany	Krynac X146 Mooney viscosity (ML, 1 + 4, 100 °C): 45 ± 5, bound acrylonitrile content: 32.5 ± 1.5 wt%
ENR epoxidized natural rubber	Muang Mai Guthrie Company Limited Rasada Muang, Thailand	Dynathai Epoxyprene 50 Mooney viscosity (ML, 1 + 4, 100 °C): 70–90, level of epoxidation is 50 ± 2%

Table 1. Types and producers of raw materials

Results

The initial stage of our polyurethane synthesis experiment began in a Brabender internal mixer, with processing parameters derived from existing literature. During this initial phase, we investigated how various processing conditions, such as temperature, rotor speed, and processing time, as well as different types and quantities of polyols, influenced the characteristics of the resulting polyurethanes. We utilized two types of polyols: polytetrahydrofuran (PTHF) and hydroxyl-terminated polybutadiene (HTPB). PTHF is a commonly used polyether polyol in polyurethane production, while our interest in exploring the suitability of HTPB stemmed from the possibility of creating polyurethanes with polybutadiene chain segments. This could potentially offer advantages in subsequent thermoplastic dynamic vulcanizate (TDV) production experiments, including improved compatibility between polyurethane and polybutadiene or polybutadiene copolymer-based rubbers, which are cost-effective and commonly employed in traditional crosslinked rubbers. However, unfortunately, the synthetization trials of HTPB-based polyurethanes were unsuccessful because at lower temperatures, the resulting material was solid-powder-like and when we tried to elevate the temperature above its melting temperature, the material started to smoke and turned brown immediately. The development of TDVs based on these in-situ synthesized polyurethanes entailed not only advancing the polyurethane phase but also enhancing the rubber phase. In our experiments, we initially worked with polar rubbers, specifically acrylonitrile butadiene rubber (NBR), carboxylated acrylonitrile butadiene rubber (XNBR), and epoxidized natural rubber (ENR). The selection of these rubbers was based on existing literature and their mutual polarity, which is beneficial for promoting interfacial adhesion and, consequently, the overall performance of the resulting TDVs. Our initial trials focused on rubbers with minimalistic formulations, consisting solely of rubber and peroxidic curatives. This simplicity was deliberate, as we aimed to evaluate the influence of different base rubbers while excluding potential side effects from other rubber components such as oils or reinforcing fillers. These model rubbers were characterized, and model TDVs were created. During our work, we investigated the chemical structure of the produced thermoplastic polyurethanes (TPU) and the interactions between TPU and the rubber phase using a Fourier-transform infrared (FTIR) spectrometer purchased within the project. We have successfully employed this technique several times in our research. We also investigated the phase structure of the samples using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Our findings revealed that during dynamic vulcanization, we successfully created micron-sized rubber domains within the TPU matrix. Our initial experiments yielded promising results, with the fundamental mechanical properties (e.g., hardness, tensile properties) of the produced TDVs proving comparable to those of commercially available TDVs based on polypropylene-ethylene propylene-diene monomer (PP-EPDM). These results are particularly encouraging, given that the current mechanical performance of the rubber phase is somewhat lacking. We believe that enhancing the mechanical properties of the rubber phase, which currently suffers due to the absence of reinforcing fillers, will lead to an overall improved performance of the TDV system.

2.2. Reproducibility issues

We initiated the second phase of the project by investigating the reproducibility of TPU synthesis. In each series of experiments, we also generated a reference TPU sample. This reference sample had a specific isocyanate-to-hydroxyl group ratio (NCO/OH) of 1.05, and the ratio of polyol hydroxyl groups to all hydroxyl groups in the reaction mixture (polyOH/OH) was set at 0.5. The initial settings for the internal mixer were a temperature of 125 °C, a rotational speed of 50 revolutions per minute (rpm), and a mixing time of 30 min. Subsequently, we examined these samples produced under the same conditions but at different times. We compared the torque and temperature curves recorded by the internal mixer and observed variations. This is significant because torque is directly related to the material's viscosity, which, in turn, depends on its molecular weight. Therefore, changes in torque can serve as a reliable indicator of alterations in molecular weight when all other parameters remain constant. Furthermore, these samples displayed notably distinct mechanical properties, with some instances where we could not form a thermoplastic vulcanizate (TPV) at all, as the material remained liquid even after 30 min. It is worth noting that polytetrahydrofuran and 1,4-butanediol are hydrophilic, meaning they can absorb water even from the air. The presence of water in these components can lead to undesired side reactions when reacting with the diisocyanate, thus necessitating thorough drying of the components. Consequently, we subjected the alcohols to vacuum drying at 90 °C overnight before their use in each case. We found that the mentioned adverse reactions often occurred when the 1,4-butanediol bottle was repeatedly opened. To address this issue, we sought advice from several experts who explained that the diol could absorb moisture from the air upon bottle opening, and this moisture could not be entirely eliminated through subsequent vacuum drying or simple drying methods. To mitigate this problem, we converted one of the vacuum drying chambers in the department into a glove chamber. With this setup, we exclusively opened newly purchased bottles of 1,4-butanediol in an inert argon atmosphere. We then transferred the butanediol into smaller bottles within this inert atmosphere and added zeolite to absorb any potential trace amounts of water. Subsequently, we sealed these smaller bottles and the originally opened bottle with parafilm and stored them in a desiccator containing phosphorus pentoxide.

2.3. TDVs with polyurethane matrix produced via a two-step prepolymer method, effect of various curing systems, and compatibilization

In addition to the previously mentioned single-step method, we explored the two-step or prepolymer approach for manufacturing thermoplastic polyurethanes. This method offers several notable advantages, one of the most significant being its reduced impact on health. Consequently, it has become the primary method employed in industrial-scale production. Another substantial benefit of this approach is its capacity to produce polyurethane materials with a more consistent structure. Furthermore, this system is less sensitive to moisture, which allows for a more stable synthesis.

In our research, we examined four different prepolymers with varying isocyanate contents (8%, 10%, 15%, and 19%). In addition to the chain extender 1,4-butanediol, we also experimented with 1,6-hexanediol. We conducted a series of tests on the resulting TPU samples and observed that an increase in isocyanate content in the prepolymer led to greater rigidity, increased tensile strength, and reduced elongation at break in the samples.

Notably, we found that 1,6-hexanediol produced superior results compared to the same prepolymer. Due to the limited material volume generated in the small chamber of the internal mixer (55 cm^3), we could only conduct basic tests. To address this limitation, we increased the chamber size to the larger 370 cm^3 chamber, which brought about some unexpected technological challenges, primarily related to dosing. However, these issues were successfully resolved. We also investigated the reproducibility of thermoplastic polyurethanes produced in the large chamber, which holds great significance for TDV production. This expansion allows for a more extensive array of tests on these samples. After overcoming the challenges associated with upscaling production, we created dynamic vulcanizates (TDVs) with thermoplastic polyurethane in the large chamber of the internal mixer. In this process, the synthesis of the thermoplastic polyurethane matrix was carried out using the prepolymer method, which includes the prepolymer (with 10% free isocyanate) and the chain extender (1,6-hexanediol) selected in the previous research phase. In the large chamber, we produced the reference TPU matrix, the rubber blends for TDVs, and the TDVs themselves. Throughout the experiment, we investigated the impact of different vulcanization systems on the properties of the resulting TDVs. For the dispersed phases in the TDVs, we used acrylonitrile butadiene rubber (NBR) based blends with peroxide and sulfur vulcanization systems containing different accelerators. Various mechanical and morphological tests were conducted on the TDV samples, revealing that the applied dicumyl peroxide can form chemical bonds not only within the rubber phase but also between the two phases, thereby enhancing the mechanical properties of the produced TDVs. Among the various rubber blends featuring different sulfur vulcanization systems, the one with the longest scorch time was found to produce the dynamic vulcanizate with the best mechanical properties. This extended scorch time allowed the rubber phase to be fragmented and evenly distributed in the TPU matrix before vulcanization commenced, a conclusion supported by scanning electron microscope (SEM) images. By combining peroxide and sulfur vulcanization systems with a delayed-action accelerator, we further improved the mechanical properties of the fabricated TDVs.

In the following phase of our project, our objective was to enhance the compatibility between the thermoplastic polyurethane matrix and the rubber phase. We undertook a comparative analysis of different methods for achieving this compatibility. Firstly, we explored the feasibility of in-situ TPU matrix production during compounding. The results demonstrated the positive impact of in-situ polymerization on compatibility. This was evident not only in the increased tensile strength and elongation at break of the samples but also in the reduced standard deviation of results. The material exhibited a more uniform structure compared to conventionally produced TDVs. Subsequently, we examined the influence of the polarity of the applied acrylonitrile-butadiene rubber (NBR). Different acrylonitrile (AN) content rubbers, ranging from 18%, 34% and 40% AN content, were utilized in our experiment. Our study revealed that the mechanical properties measured at room temperature were not significantly affected by the acrylonitrile content in the NBR. However, dynamic mechanical analysis (DMA) indicated that as the AN content in the rubber phase increased, the cold resistance of the resulting TDV diminished. In the third step, we investigated the impact of incorporating various ethylene-vinyl acetate (EVA) copolymers containing different levels of vinyl acetate (18%, 28%, and 50%). Unfortunately, the addition of EVA led to a deterioration in the mechanical properties of the TDVs. Scanning electron microscope (SEM) images of the cryo-fractured surface of the samples revealed that EVA introduced a third phase within the TDVs rather than effectively compatibilizing the two phases. This had the unintended effect of weakening the TDVs by creating an additional defect site.

2.4. TDVs with recycled ground tyre rubber (GTR)

Introduction

In alignment with the principles of the circular economy, during the final phase of the project, our focus shifted towards the utilization of recycled materials in the development of thermoplastic vulcanizates (TDVs) with a thermoplastic polyurethane matrix. We attempted to source commercially available recycled TPU, but regrettably, we could not find a suitable supplier.

Globally, approximately 1.5 billion scrap tyres are generated each year, with over 40% of their weight comprising various synthetic and natural rubber components. Despite the large volume of waste, not all is being effectively recycled. Material recycling, in the form of regrind from which steel and textile reinforcing structures have been removed, is possible but is currently utilized in relatively small quantities for the production of new goods. Our research indicated that the rubber regrind obtained in this manner could potentially replace some or all of the rubbers typically used in the rubber phase of our thermoplastic vulcanizates. These findings align with the results of our preliminary experiments conducted in previous studies. In our preliminary experiments, we initially produced various TPU-based blends with different ground tire rubber modifications using an internal mixer and later an intermeshing co-rotating twin-screw extruder. During the experiments, we worked with both in-situ synthesized TPU and commercially available TPU. Adapting the in-situ polyaddition process to the co-rotating twin-screw extruder posed challenges related to the moisture content of the raw materials. Unfortunately, the equipment available in our laboratory did not allow for a closed system to control and exclude the moisture content during the processing. As a result, we decided to use commercially available TPU for the experiments conducted with the intermeshing co-rotating twin-screw extruder. It is worth noting that the literature suggests that there have not been many prior studies on this particular material pairing, indicating the potential for new scientific discoveries in this field.

Building on our previous results, we explored the optimization of two devulcanization methods: high-pressure water jet grinding and microwave-aided thermomechanical devulcanization of ground tyre rubber (GTR) extracted from truck tyre treads. Regarding productivity, the thermomechanical method was far more beneficial; therefore, we continued our work with this method.

During the work prepared blends of thermoplastic polyurethane (TPU) with ground tyre rubber (GTR) and its devulcanized version (dGTR). Our main objective was to create thermoplastic elastomers in which thermoplastic polyurethane is partially "replaced" with GTR sourced from a secondary raw material, thus forming a blend with a good cost-performance ratio.

Materials and methods

In the first series of experiments, we chose Elastollan C 78 A 15 supplied by BASF (Düsseldorf, Germany), a polyester-polyol-based thermoplastic polyurethane, as the matrix polymer. The TPU was combined with WJET GTR, a high-pressure water-jet ground tyre rubber produced by Aquajet Zrt. (Budapest, Hungary) from truck tyre tread (200 - 400 μm). The composition of the ground tyre rubber, determined by thermogravimetric analysis, was as follows: 4-6 phr oil, 50-55 phr natural rubber, 45-50 phr synthetic rubber, 33-37 phr carbon black, and 7-8 phr other additives. During the experiment, the GTR and dGTR content in the blends varied from 0 to 50 wt% and we investigated the effects of the composition on their mechanical properties.

In the course of this work, we attempted the dynamic vulcanization of dGTR during the blending process, thus producing thermoplastic dynamic vulcanizates (TDVs). The materials used in the vulcanization system are summarized in Table 2.

Material	Manufacturer	Trademark	Function
ZnO Zinc oxide	Werco Metal (Zlatna, Romania)	-	Activator
Stearic acid	Oleon (Ertvelde, Belgium)	Radiacid 0154	
CBS N-Cyclohexyl-2-benzothiazolesulfenamide	Rhein Chemie (Mannheim, Germany	Rhenogran CBS-80	Accelerator
Sulfur	Ningbo Actmix Polymer (Zhejiang, China)	ACTMIX S-80	Curing agent

Table 2. Types, producers, trademarks and functions of the raw materials used as curatives in the rubber phase of the TDVs

The thermomechanical devulcanization of ground tyre rubber (GTR) was made using a Labtech Scientific LTE 26-44 (Labtech Engineering Co., Ltd., Samutprakarn, Thailand), corotating twin-screw extruder. Based on our previous research results, all heating zones of the equipment were set to 190 °C, and the screw speed was 60 rpm. According to the Horikx analysis, these settings closely approximate the theoretical curve associated with selective network scission.

Due to their hydrophilic nature, the thermoplastic polyurethanes were dried at 80 °C for 4 hours under vacuum as per the technical datasheet before processing. We used a vacuum drying cabinet, Binder VD 53, equipped with a Vacuubrand MZ 2 NT vacuum pump (Vacuubrand GmbH, Wertheim, Germany) for this purpose. The ground tyre rubber was also dried under the abovementioned conditions before blending.

We prepared the rubber compound of the thermoplastic dynamic vulcanizate (TDV) rubber phase in a Brabender Plasti-Corder (Brabender GmbH, Duisburg, Germany) intermix type mixer with a 350 cm³ chamber (350 SX). The chamber temperature was set to 50 °C, and the applied formulation is presented in Table 3.

Material	Amount [phr]
dGTR	100
ZnO	5
Stearic acid	1
CBS	1.5
Sulfur	1.5

Table 3. Formulation of the dGTR-based rubber phase of the TDV ($dGTR_{CBS}$)

Besides the TDV, we prepared blends with various compositions of TPU and (d)GTR. The compositions of the prepared blends are listed in Table 4. In our work, we transitioned from internal mixers to using a twin-screw extruder. This technique offers several advantages that batch internal mixers cannot provide, such as the ability to control temperature profiles, manipulate shear profiles essential for chemical reactions and component mixing. Additionally, the scalability of this method promotes potential industrial-scale manufacturing. During our preliminary experiments, we examined the effects of screw speed and the chosen temperature profile on the properties of the produced materials. Subsequently, we selected the parameters based on these findings for our further experiments. The temperature profile during extrusion (from the feed zone to the tool) was 185-185-190-190-195-195-200-200-205-205-205 °C, and the screw speed was 120 rpm.

Sample	Amount [wt%]			
	TPU	GTR	dGTR	$dGTR_{CBS}$
TPU	100	-	-	-
$TPU/GTR_{90/10}$	90	10	-	-
$TPU/GTR_{80/20}$	80	20	-	-
$TPU/GTR_{70/30}$	70	30	-	-
$TPU/GTR_{60/40}$	60	40	-	-
$TPU/GTR_{50/50}$	50	50	-	-
$TPU/dGTR_{90/10}$	90	-	10	-
$TPU/dGTR_{80/20}$	80	-	20	-
$TPU/dGTR_{70/30}$	70	-	30	-
$TPU/dGTR_{60/40}$	60	-	40	-
$TPU/dGTR_{50/50}$	50	-	50	-
$TPU/dGTR_{CBS\_50/50}$	50	-	-	50

Table 4. Formulation of the (d)GTR-TPU blends and the TDV

80 x 80 mm square-shaped specimens having 2 mm of thickness from the compounds were produced by injection molding using an Arburg Allrounder Advance 270S 400-170 (Arburg GmbH, Lossburg, Germany) machine. The injection molding parameters employed during sample production are summarized in Table 5. The test specimens required for the tests were prepared from these plates.

Property	Value
Melt temperature	210 °C
Injection speed	50 cm^3/s
Mold tempereture	30 °C
Holding pressure	450 bar
Holding time	10.2 s
Remaining cooling time	50 s

Table 5. Injection molding parameters

Vulcanization properties of the rubber compounds were tested using a MonTech D-RPA 3000 (MonTech GmbH, Buchen, Germany) device under isothermal (185 and 205 °C) and anisothermal conditions (185→205 °C, 10 °C/min) with a frequency of 1.67 Hz and an amplitude of 1°.

The mechanical properties of the produced samples were determined using a tensile testing machine equipped with a 5 kN force sensor (Zwick Z005, Zwick GmbH, Ulm, Germany). Tensile tests were conducted at room temperature with a crosshead speed of 500 mm/min using type 2 test specimens as per MSZ ISO 37:2003, applying a gauge length of 45 mm. The specified mechanical properties are averages from 5 measurements.

We conducted instrumented falling weight impact testing on the plate specimens of the samples using a Ceast Fractovis 9350 (Instron, Massachusetts, USA) instrumented falling weight impact tester. The total weight of the dart was 20.036 kg, the drop height was 1 m, the impact energy was 196.5 J, the radius of the semi-spherical dart tip was 20 mm, and the diameter of the supporting ring was 40 mm. The specified mechanical properties are averages from 10 measurements.

The Shore A hardness of the injection-molded plates was determined according to ISO 7619-1:2010 using a hardness tester (Zwick H04.3150.000, Zwick GmbH, Ulm, Germany). 10 points for each sample were measured and averaged. The thickness of the tested samples was approximately 6 mm (3 plates stacked on top of each other), and the waiting time was 3 seconds.

We determined the compression set of the samples according to ISO 815-1, "Method A." We compressed the cylindrical type B test specimens (diameter 13 mm, thickness 6 mm) by 25% and held them for 24 hours in a 70 °C drying cabinet (Baxter DN-63, Baxter International, Deerfield, USA). Afterward, the compression device was removed from the drying cabinet and after relieving the pressure, the samples were placed on a flat surface. After a 30-minute recovery period, we measured the thickness of the samples. The specified compression set values are averages from 5 samples.

The morphology of the produced samples was investigated using a scanning electron microscope (SEM) JEOL JSM 6380LA (Jeol Ltd., Tokyo, Japan). Based on previous experience, it is not always possible to clearly distinguish the two phases in the cryo-fractured surface images. Therefore, we studied the cross-sections of broken test specimens during the examination. Before the analysis, the surfaces were coated with a thin layer of gold.

Results

Isothermal and anisothermal curing curves of the compound used in the dynamic vulcanizate were recorded. Based on the results (Figure 1, Table 6), it can be concluded that the induction phase of the blend (t_{10}) is extremely short, which was indicated in our previous work. This has a negative impact on the properties of the resulting TDVs. Regarding vulcanization time (t_{90}), it can be stated that the vulcanization of the blend is completed during the sample residence time (approximately 2 min). However, based on the torque curves, the high temperature caused significant reversion in the compound.

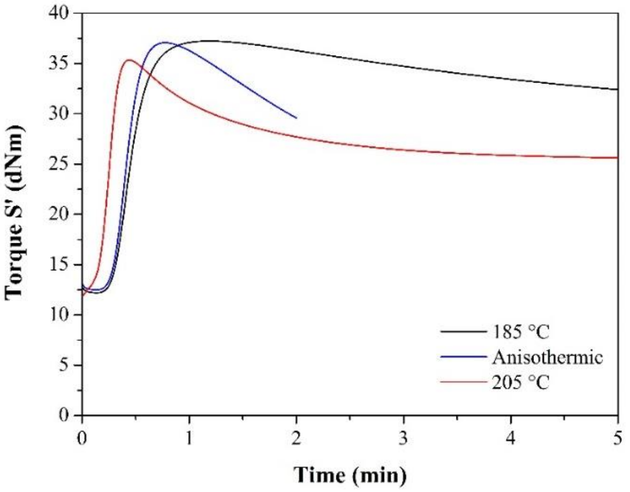


Figure 1. Curing curves of the rubber compound of the TDV (dGTR$_{CBS}$)

Compounds	Temperature [°C]	S'$_{min}$ [dNm]	S'$_{max}$ [dNm]	t$_{10}$ [min]	t$_{90}$ [min]
dGTR$_{CBS}$	185	12.2	37.2	0.3	0.7
	185→205 (2 min)	12.5	37.1	0.3	0.6
	205	13.4	35.3	0.2	0.3

Table 6. Curing parameters of the rubber compound of the TDV (dGTR$_{CBS}$)

The results of the tensile tests are provided in Table 7, and characteristic stress-strain curves are presented in Figure 2. The table includes the tensile strength, elongation at break, and the corresponding stress values for each relative strain. In the case of elastomers, stress values at the specified relative strains are typically provided instead of the traditional modulus. M50, M100, and M300 represent the stress values corresponding to 50%, 100%, and 300% relative strain, respectively.

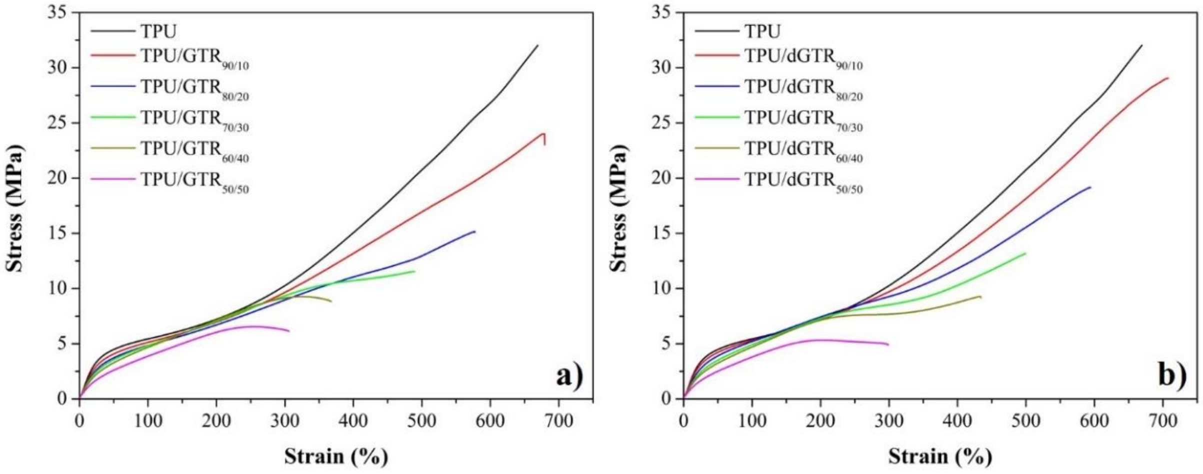


Figure 2. Characteristic tensile curves of the compounds

Sample	Tensile strength [MPa]	Strain at break [%]	M50 [MPa]	M100 [MPa]	M300 [MPa]
TPU	33.0 ± 0.8	670 ± 21	4.5 ± 0.0	5.5 ± 0.0	10.5 ± 0.2
dGTR$_{CBS}$	5.9 ± 0.6	101 ± 8	3.1 ± 0.0	6.6 ± 0.1	—
TPU/GTR$_{90/10}$	24.2 ± 0.9	681 ± 16	4.1 ± 0.0	5.2 ± 0.0	9.6 ± 0.1
TPU/GTR$_{80/20}$	15.3 ± 0.7	572 ± 18	3.8 ± 0.0	5.0 ± 0.1	9.3 ± 0.2
TPU/GTR$_{70/30}$	11.2 ± 0.5	485 ± 23	3.6 ± 0.1	4.9 ± 0.1	9.4 ± 0.1
TPU/GTR$_{60/40}$	9.2 ± 0.2	367 ± 13	3.3 ± 0.0	4.6 ± 0.0	9.1 ± 0.1
TPU/GTR$_{50/50}$	6.8 ± 0.2	304 ± 17	2.7 ± 0.0	4.0 ± 0.1	6.5 ± 0.3
TPU/dGTR$_{90/10}$	29.1 ± 1.1	714 ± 18	4.2 ± 0.0	5.3 ± 0.0	9.6 ± 0.1
TPU/dGTR$_{80/20}$	19.5 ± 0.8	600 ± 24	3.8 ± 0.1	5.1 ± 0.1	9.2 ± 0.2
TPU/dGTR$_{70/30}$	13.1 ± 0.3	500 ± 11	3.5 ±0.0	4.9 ± 0.0	8.6 ± 0.1
TPU/dGTR$_{60/40}$	9.4 ± 0.9	442 ± 28	3.2 ± 0.1	4.6 ± 0.1	7.4 ± 0.3
TPU/dGTR$_{50/50}$	5.4 ± 0.1	305 ± 31	2.6 ± 0.0	3.9 ± 0.1	5.1 ± 0.2
TPU/dGTR$_{CBS\_50/50}$	5.1 ± 0.5	365 ± 42	3.0 ± 0.0	4.2 ± 0.1	4.8 ± 0.2

Table 7. Tensile results of the compounds

Based on the results, it can be concluded that the presence of ground tyre rubber (GTR) led to a reduction in the tensile strength and the stress values at specified strains (modulus-like characteristics) of the samples.

Conversely, with the addition of 10% by weight of GTR, the elongation at break of the samples increased slightly, but further increasing the quantity resulted in a decrease in this value.

Figure 3 clearly illustrates that both the tensile strength and the elongation at break were higher for the samples containing devulcanized ground tyre rubber. This can be attributed to the fact that during devulcanization, some of the cross-links in the rubber was broken. As a result, polymer chains became more mobile and could deform to a greater extent under stress, making them less prone to act as defect sites. The mechanical compatibility between the two phases improved due to devulcanization.

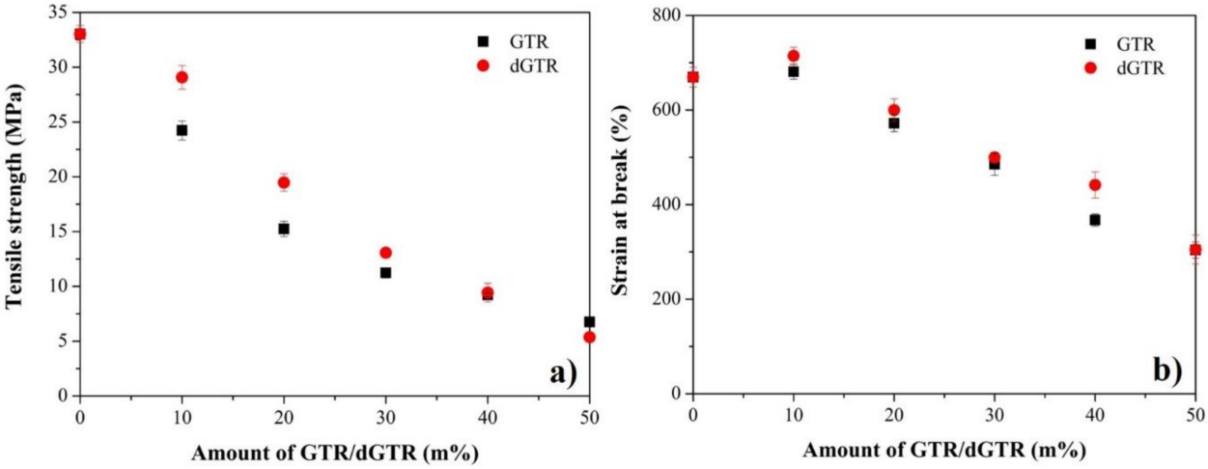


Figure 3. Tensile strength (a) and strain at break (b) values of the compounds as a function of (d)GTR content

As a result of the vulcanizing agent, the elongation at break of the TPU/dGTR$_{CBS, 50/50}$ dynamic vulcanizate increased, while its tensile strength showed a slight decrease (Table 7, Figure 4). It is also evident that the presence of the vulcanizing agent altered the shape of the stress-strain curve. The flattening of the curve became even more pronounced in the samples containing dGTR.

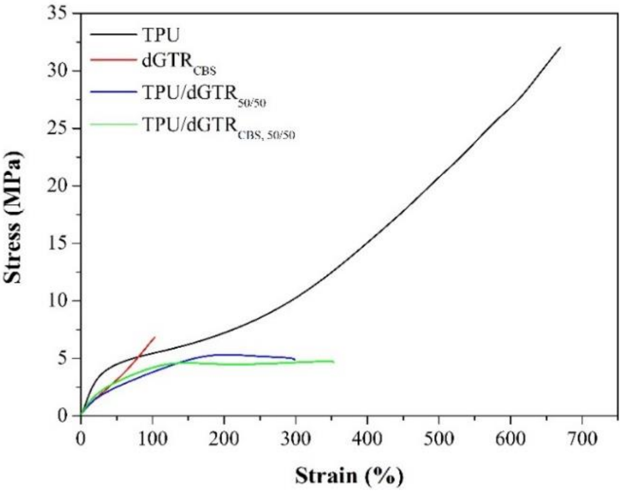


Figure 4. Characteristic tensile curves of the TPU, the rubber phase and one of the compounds

The results of the instrumented falling weight impact (IFWI) testing are provided in Table 8, and characteristic force-displacement curves are presented in Figure 5.

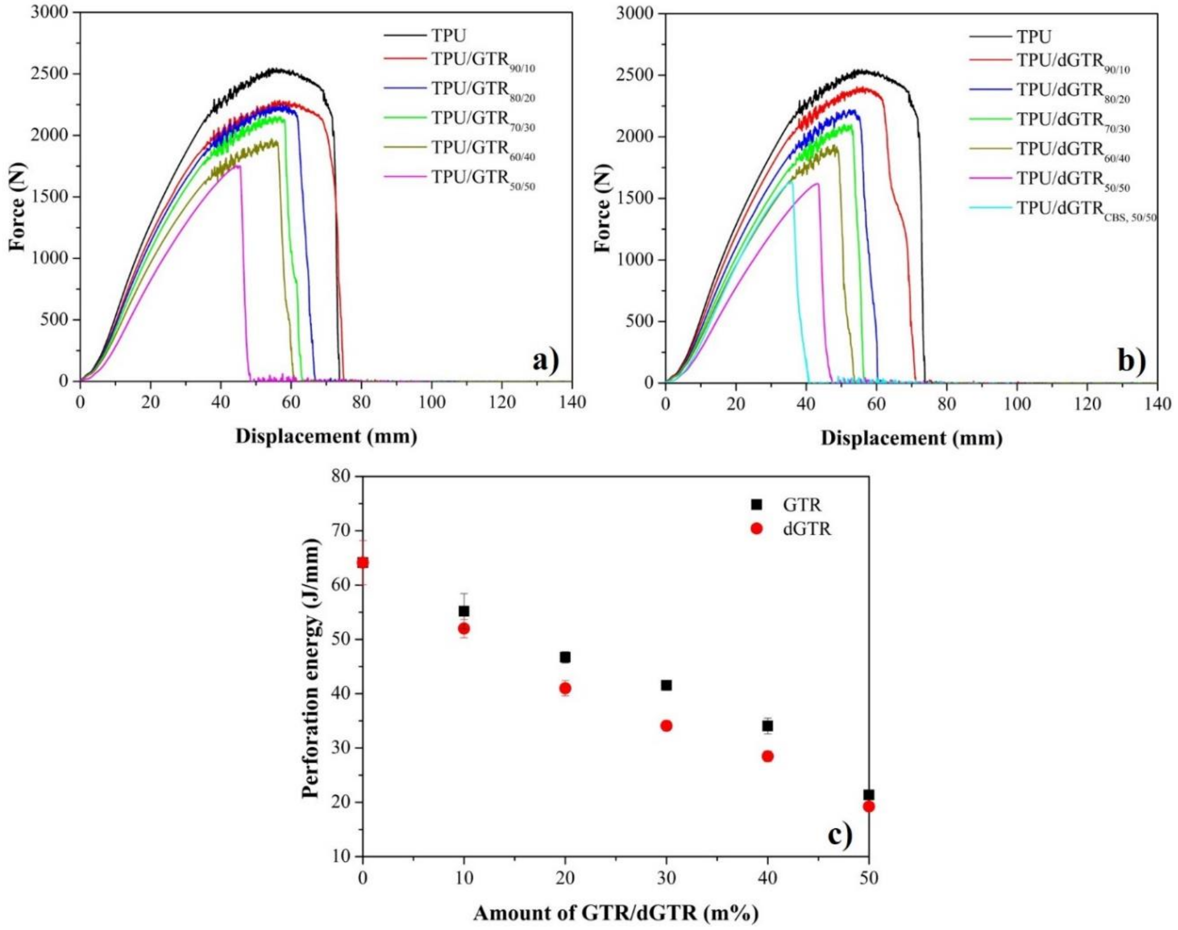


Figure 5. The force-displacement curves recorded during IFWI testing of the samples are as follows: a) TPU/GTR, b) TPU/dGTR c) Perforation energy as a function of the quantity of ground tyre rubber (GTR) in the samples.

Using the IFWI test, we investigated the behavior of the samples under dynamic loading. In all cases, the dart punctured the 2 mm thick injection-molded plates. Based on the results, it can be concluded that increasing the amount of ground tyre rubber (GTR) in the blends reduced the energy required for their perforation. As shown in Figure 5, this change is in line with variations in the maximum force recorded during the test and the displacement measured during sample rupture.

It is evident that dynamic vulcanization further decreased the energy required for perforation of the samples, and the nature of the force-displacement curve also changed.

Sample	**Perforation energy [J/mm]**
TPU	64.1 ± 4.1
TPU/GTR$_{90/10}$	55.2 ± 3.3
TPU/GTR$_{80/20}$	46.7 ± 1.0
TPU/GTR$_{70/30}$	41.5 ± 0.9
TPU/GTR$_{60/40}$	34.1 ± 1.4
TPU/GTR$_{50/50}$	21.4 ± 0.7
TPU/dGTR$_{90/10}$	52.0 ± 1.7
TPU/dGTR$_{80/20}$	41.0 ± 1.4
TPU/dGTR$_{70/30}$	34.1 ± 0.9
TPU/dGTR$_{60/40}$	28.5 ± 1.0
TPU/dGTR$_{50/50}$	19.2 ± 0.7
TPU/dGTR$_{CBS\_50/50}$	15.7 ± 0.3

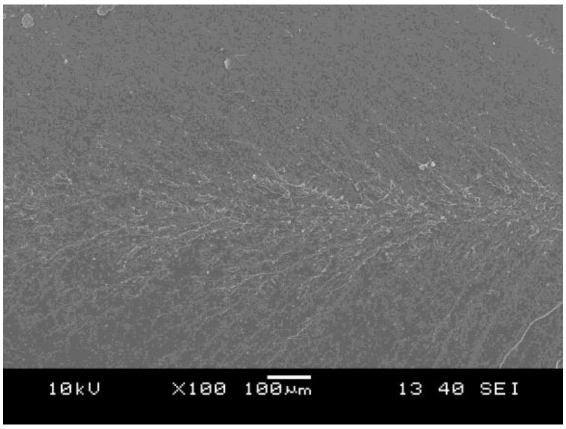
Table 8. Perforation energy of the compounds

The Shore A hardness of the samples (Table 9) decreased with an increase in the quantity of ground tyre rubber (GTR) compared to the matrix thermoplastic polyurethane. Furthermore, it can be observed that the devulcanization of GTR did not influence the hardness of the blends. We investigated the compression set of the samples at an elevated temperature. Regarding the values of the compression set, there were no significant changes with the presence of devulcanized ground tyre rubber (dGTR). However, the "untreated" ground tyre rubber led to an increase in the compression set of the samples by nearly 20%. The material structural reason for this effect is still under investigation.

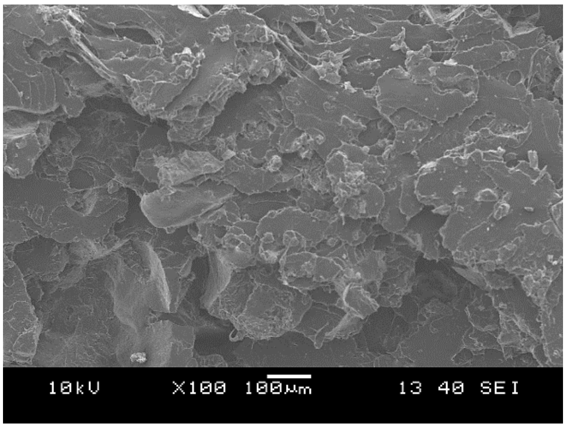
Sample	**Shore A hardness** [Sh A°]	**Compression set (70 °C, 24 h)** [%]
TPU	85.7 ± 0.3	57 ± 1.8
TPU/GTR$_{90/10}$	70.6 ± 0.5	35 ± 1.4
TPU/GTR$_{80/20}$	83.6 ± 0.4	67 ± 1.2
TPU/GTR$_{70/30}$	81.8 ± 0.4	67 ± 2.5
TPU/GTR$_{60/40}$	80.0 ± 0.6	70 ± 1.4
TPU/GTR$_{50/50}$	77.8 ± 0.5	67 ± 2.2
TPU/dGTR$_{90/10}$	71.4 ± 0.4	75 ± 0.6
TPU/dGTR$_{80/20}$	83.5 ± 0.3	56 ± 2.0
TPU/dGTR$_{70/30}$	81.3 ± 07	61 ± 1.4
TPU/dGTR$_{60/40}$	79.1 ± 0.7	62 ± 1.3
TPU/dGTR$_{50/50}$	77.1 ± 0.6	59 ± 2.0
TPU/dGTR$_{CBS\_50/50}$	70.2 ± 0.7	70 ± 1.6

Table 9. Shore A hardness and compression set of the compounds

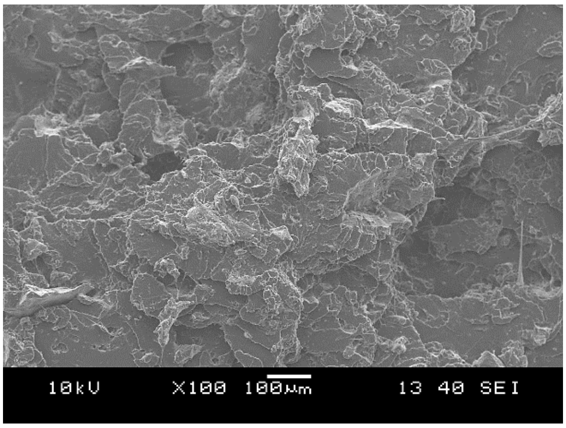
We studied the fracture surfaces of the samples using a scanning electron microscope. The prepared images are visible in Figure 6. The presence of ground tyre rubber (GTR) resulted in a more textured surface of the samples. As the quantity of GTR in the blend increased, more and larger particles were observed in the images. In general, sharper particle boundaries can be observed in the samples containing GTR compared to those containing devulcanized GTR. Based on this, we concluded that devulcanization led to a stronger connection between the two phases (TPU and GTR), with the matrix more effectively surrounding the particles. This is in line with the results of the tensile testing. The dynamic vulcanization resulted in large particles with sharp boundaries on the fracture surfaces, which explains its poor performance.



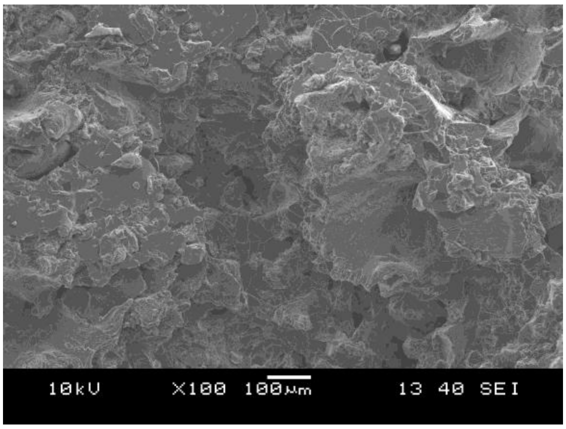
TPU



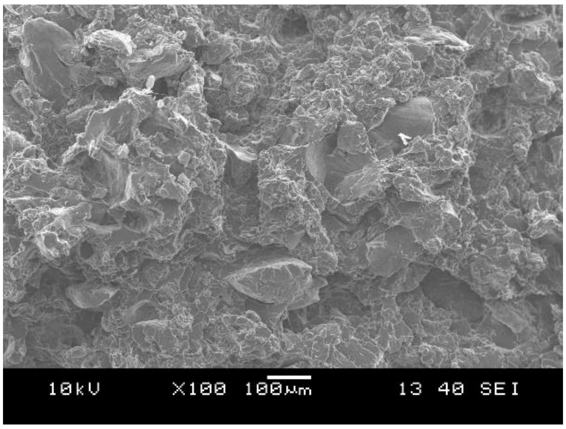
TPU/GTR$_{90/10}$



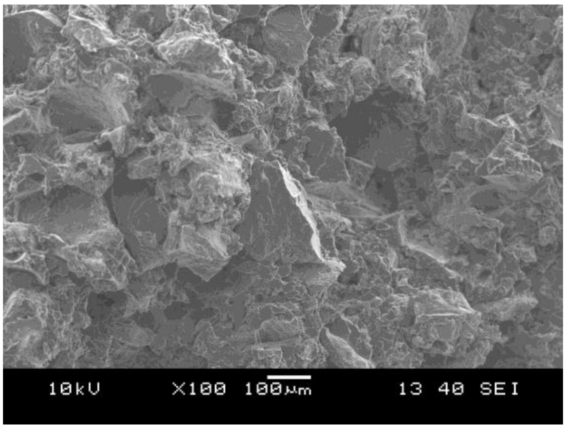
TPU/dGTR$_{90/10}$



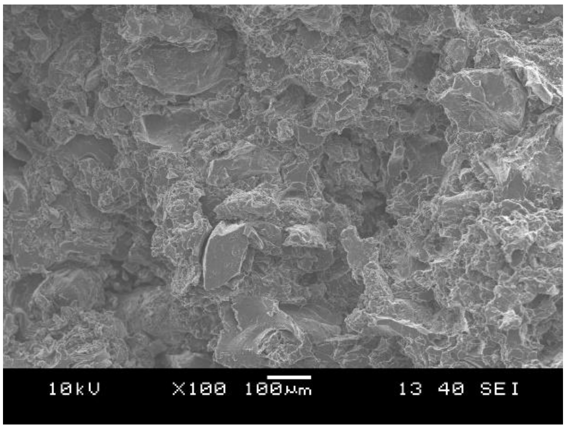
TPU/GTR$_{80/20}$



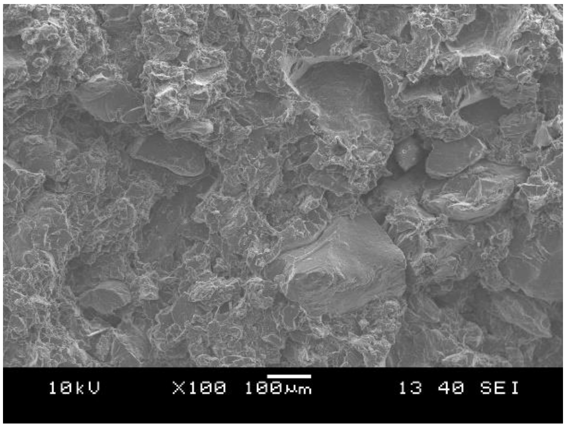
TPU/dGTR$_{80/20}$



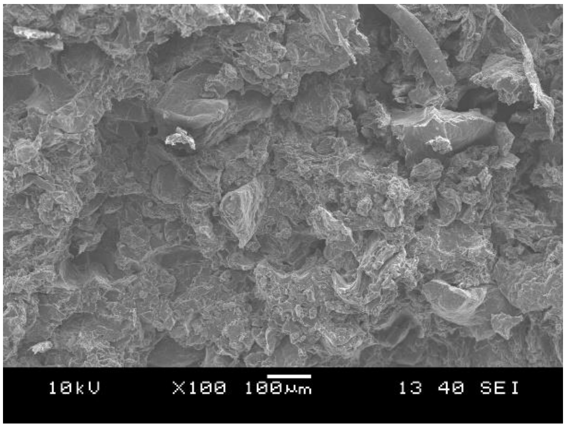
TPU/GTR$_{70/30}$



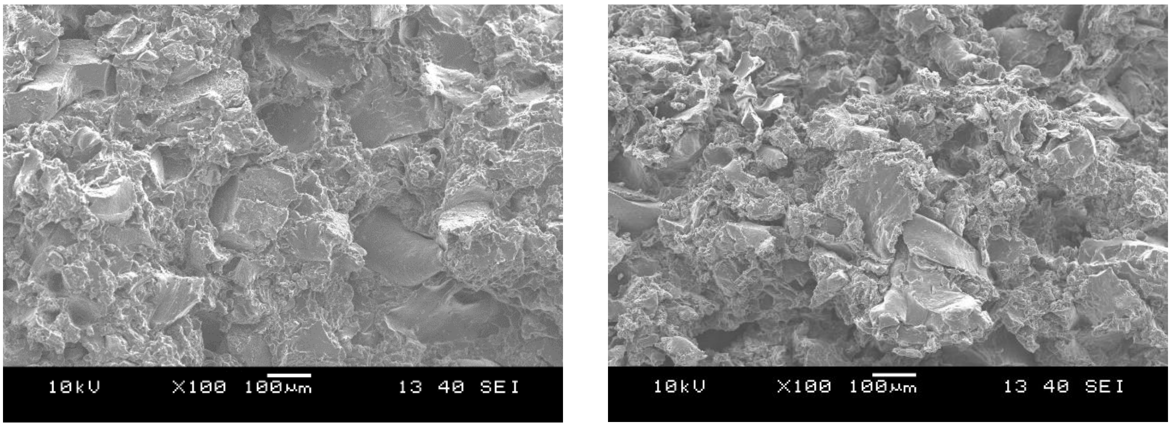
TPU/dGTR$_{70/30}$



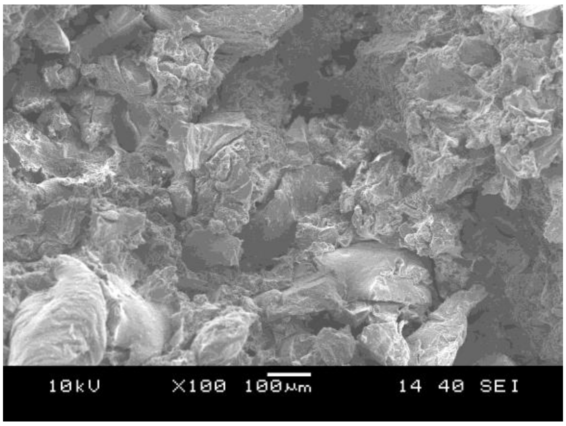
TPU/GTR$_{60/40}$



TPU/dGTR$_{60/40}$



TPU/GTR$_{50/50}$ TPU/dGTR$_{50/50}$



TPU/dGTR$_{CBS,\ 50/50}$

Figure 6. SEM images of the fractured surfaces of the samples

2.5. TDVs with commercially available dGTR

In the meantime, due to unfortunate economic circumstances, the source of our water-jet ground GTR ceased; therefore, we had to look for another opportunity. Keeping in mind the future utilization of the results and the possible commercialization of TDVs based on this current research, we opted to use a dGTR, which is already available on the market and may be purchased easily in large quantities.

Materials and methods

In this series, we again used Elastollan 1170 A 10 000 supplied by BASF (Düsseldorf, Germany), a polyether-polyol-based thermoplastic polyurethane, as the matrix polymer, as in the preliminary experiments. The reason for the change was that, based on our experience and the literature, the zinc oxide and other additives in the ground tyre rubber are able to catalyse the hydrolysis of ester bonds in polyester polyol-based TPU. The TPU was combined with a new type of dGTR, a truck tyre tread-based devulcanizate produced by Tyromer Inc. (Waterloo, Canada). We also obtained the base GTR from which this dGTR is made in order to be able to measure the devulcanization rate in the process used by Tyromer. The particle size distribution of the base GTR is depicted in Figure 7.

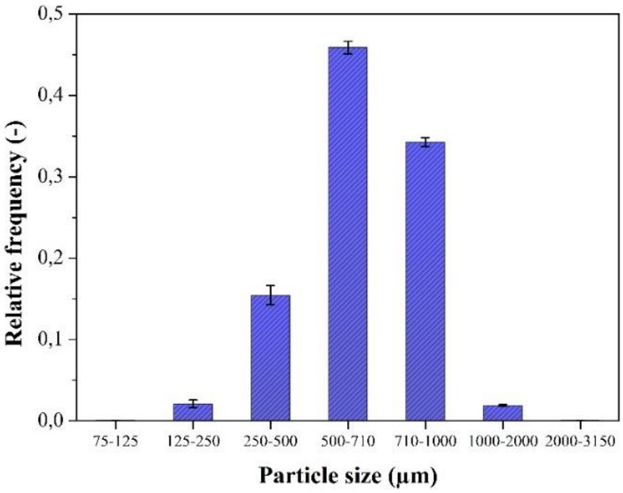


Figure 7. Particle size distribution of the GTR used in the production of blends

In the course of this work, we attempted the dynamic vulcanization of dGTR during the blending process, thus producing thermoplastic dynamic vulcanizates (TDVs). The materials used in the vulcanization system are summarized in Table 10.

Material	Manufacturer	Trademark	Function
ZnO Zinc oxide	Werco Metal (Zlatna, Romania)	-	Activator
Stearic acid	Oleon (Ertvelde, Belgium)	Radiacid 0154	
CBS N-Cyclohexyl-2-benzothiazolesulfenamide	Rhein Chemie (Mannheim, Germany	Rhenogran CBS-80	Accelerator
TMTD Tetramethylthiuram disulfide	Lanxess (Mannheim, Germany)	Rhenogran TMTD-70	Accelerator
Sulfur	Ningbo Actmix Polymer (Zhejiang, China)	ACTMIX S-80	Curing agent
DIPP (Di-(2-tert.-butyl-peroxyisopropyl)-benzene)	Nouryon (Pergan GmbH (Bocholt, Germany)	Peroxan BIB-40 EV-G	Curing agent
BDMA (1,4-Butanediol dimethacrylate)	Lanxess (Mannheim, Germany)	Rhenofit BDMA/S	Coagent

Table 10. Types, producers, trademarks, and functions of raw materials used as curatives in the rubber phase of the TDVs

Due to their hydrophilic nature, the thermoplastic polyurethane was dried, as described before in Chapter 2.4.

We prepared the rubber compound of the thermoplastic dynamic vulcanizate (TDV) rubber phase as described before in Chapter 2.4 and the applied formulation is presented in Table 11.

Material	**Amount (phr)**	
	$dGTR_{sulfur}$	**$dGTR_{peroxide}$**
dGTR	167	167
ZnO	5	—
Stearic acid	2	—
CBS	1.5	—
TMTD	0.5	—
Sulfur	1	—
DIPP	—	2.5
BDMA	—	1

Table 11. Formulation of the dGTR-based rubber phase of the TDV ($dGTR_{CBS}$)

Besides the TDV, we prepared blends with various compositions of TPU and (d)GTR. The compositions of the prepared blends and TDVs are listed in Table 12. The production of the TPU/(d)GTR blends and the TDVs were made using the twin-screw extruder as described above. The temperature profile during extrusion (from the feed zone to the tool) was 185-185-155-155-160-160-165-170-175-180-185-190-190 °C, and the screw speed was 120 rpm.

80 x 80 mm square-shaped specimens having 2 mm of thickness from the compounds were produced by injection molding using the exact same machine and parameters as in the previous series.

Vulcanization properties of the rubber compounds were tested using a MonTech D-RPA 3000 (MonTech GmbH, Buchen, Germany) device under isothermal (180 °C) and anisothermal conditions (155→190 °C, 17.5 °C/min) with a frequency of 1.67 Hz and an amplitude of 1°.

The mechanical properties, Shore A hardness and the impact resistance of the produced samples were determined with the same machine and the same parameters as described before in Chapter 2.4.

Sample	**Amount [wt%]**				
	TPU	**GTR**	**dGTR**	**$dGTR_{sulfur}$**	**$dGTR_{peroxide}$**
TPU	100	—	—	—	—
$TPU/GTR_{70/30}$	70	30	—	—	—
$TPU/GTR_{60/40}$	60	40	—	—	—
$TPU/GTR_{50/50}$	50	50	—	—	—
$TPU/GTR_{40/60}$	40	60	—	—	—
$TPU/dGTR_{70/30}$	70	—	30	—	—
$TPU/dGTR_{60/40}$	60	—	40	—	—
$TPU/dGTR_{50/50}$	50	—	50	—	—
$TPU/dGTR_{40/60}$	40	—	60	—	—
$TPU/dGTR_{sulfur\_70/30}$	70	—	—	30	—
$TPU/dGTR_{sulfur\_60/40}$	60	—	—	40	—
$TPU/dGTR_{sulfur\_50/50}$	50	—	—	50	—
$TPU/dGTR_{sulfur\_40/60}$*	40	—	—	60	—
$TPU/dGTR_{peroxide\_70/30}$	70	—	—	—	30
$TPU/dGTR_{peroxide\_60/40}$	60	—	—	—	40
$TPU/dGTR_{peroxide\_50/50}$	50	—	—	—	50
$TPU/dGTR_{peroxide\_40/60}$*	40	—	—	—	60

* can not be produced

Table 12. Formulation of the (d)GTR-TPU blends and the TDVs

We determined the compression set of the samples according to ISO 815-1, "Method A." We compressed the cylindrical type B test specimens (diameter 13 mm, thickness 6 mm) by 25% and held them for 72 hours at 25 °C. After the 72 hours we relieved the pressure, the samples were placed on a flat surface. After a 30-min recovery period, we measured the thickness of the samples. The specified compression set values are averages from 5 samples.

The dynamic mechanical properties of the produced samples were measured using a TA Q800 DMA device (TA Instruments Ltd., New Castle, DE, USA). The nominal dimensions of the samples cut from the injection-molded plates were 2.0 x 2.5 x 10 mm (thickness x width x gauge length). The tests were conducted between -80 °C and +150 °C with a heating rate of 3 °C/minute, a frequency of 10 Hz, a strain amplitude of 0.1%, and a preload force of 0.01 N, all under tensile loading. For the Payne effect investigation we used the same DMA equipment in tensile mode at room temperature with a 10 Hz frequency. The pre-load was set at 0.01 N, and the examined deformation range was 0.01-10%. The nominal dimensions of the samples cut from the injection-molded sheets were 2.0 x 2.5 x 10 mm (thickness x width x grip length) in both cases.

Results

We started our investigation with the Horikx analysis of the dGTR to get some insight into the quality of the devulcanization. Results showed that the soluble content of the GTR was 7.3%, and 30.2% at the dGTR. The decrease in the crosslink density was 63.1%. The results are depicted in Figure 8.

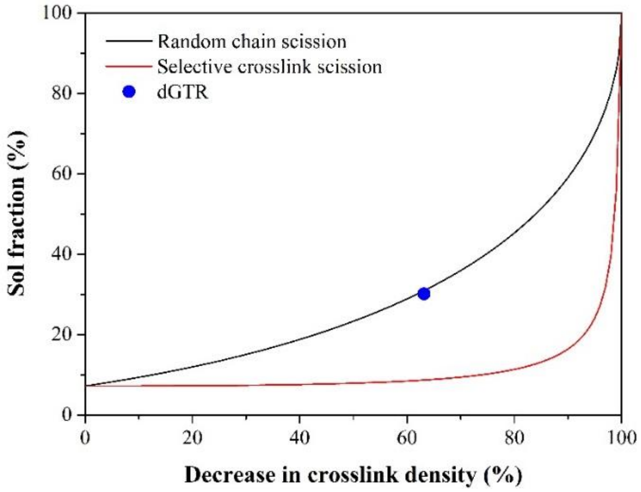


Figure 8. Horikx plot of the Tyromer dGTR

The vulcanization properties of the rubber compounds used in the dynamic vulcanizates were tested at 180 °C, as well as under anisothermal conditions. The latter aimed to closely approximate the temperature profile developed in the extruder during dynamic vulcanization, thereby investigating the processes taking place. Based on the results (Figure 9, Table 13), it can be stated that for both compounds, sufficient time was available for vulcanization to commence significantly (t_{10}) for the dispersion of the blends.

According to the anisothermal curves, within the available residence time (~2 min), the sulfur-containing blend ($dGTR_{sulfur}$) is completely vulcanized without or with only minimal reversion. In contrast, the peroxide-cured-blend's torque curve did not reach saturation within this time, indicating incomplete vulcanization. However, the higher temperature used during injection molding allows this process to take place during sample production.

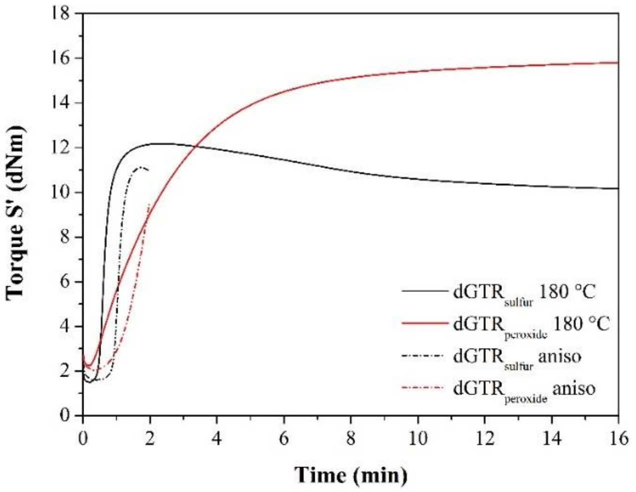


Figure 9. Curing curves of the rubber compounds based on Tyromer dGTR

Compounds	Temperature [°C]	S'$_{min}$ [dNm]	S'$_{max}$ [dNm]	t_{10} [min]	t_{90} [min]
dGTR$_{sulfur}$	180	1.5	12.2	0.5	1.0
	155→190 (2 min)	1.6	11.1	0.9	1.3
dGTR$_{peroxide}$	180	2.2	16.2	0.6	6.8
	155→190 (2 min)	2.0	9.6	-	-

Table 13. Curing parameters of the compounds based on Tyromer dGTR

The results of the tensile tests are presented in Table 14, and characteristic stress-strain curves are shown in Figure 10. The table includes the tensile strength, elongation at break, and the corresponding stress values at specific relative strains. In the case of elastomers, stress values at certain relative strains are typically used instead of the traditional modulus. M50, M100, and M300 represent the stress values at 50%, 100%, and 300% relative strains, respectively.

Based on the results, it can be concluded that GTR and dGTR reduced the tensile strength, elongation at break, and stress values at specific strains (modulus-like properties) of the samples. When comparing the effect of GTR and dGTR, dGTR up to 40 wt% softened the blends, reducing their strength and modulus while increasing their elongation at break. This contradicts the results of the samples containing 50 and 60 wt% dGTR. In these cases, a dual continuous structure may have first formed, and by further increasing the dGTR content, the devulcanizate became the continuous phase. This may also explain why the production of TPVs with 60 wt% dGTR "rubber blends" was unfeasible during the DV process.
As for TPVs, the samples made with peroxide exhibited better performance, with higher tensile strength and elongation at break. This is consistent with our previous findings since peroxide can potentially form bonds not only in the rubber phase but also at the interface between the two phases, creating a better connection.

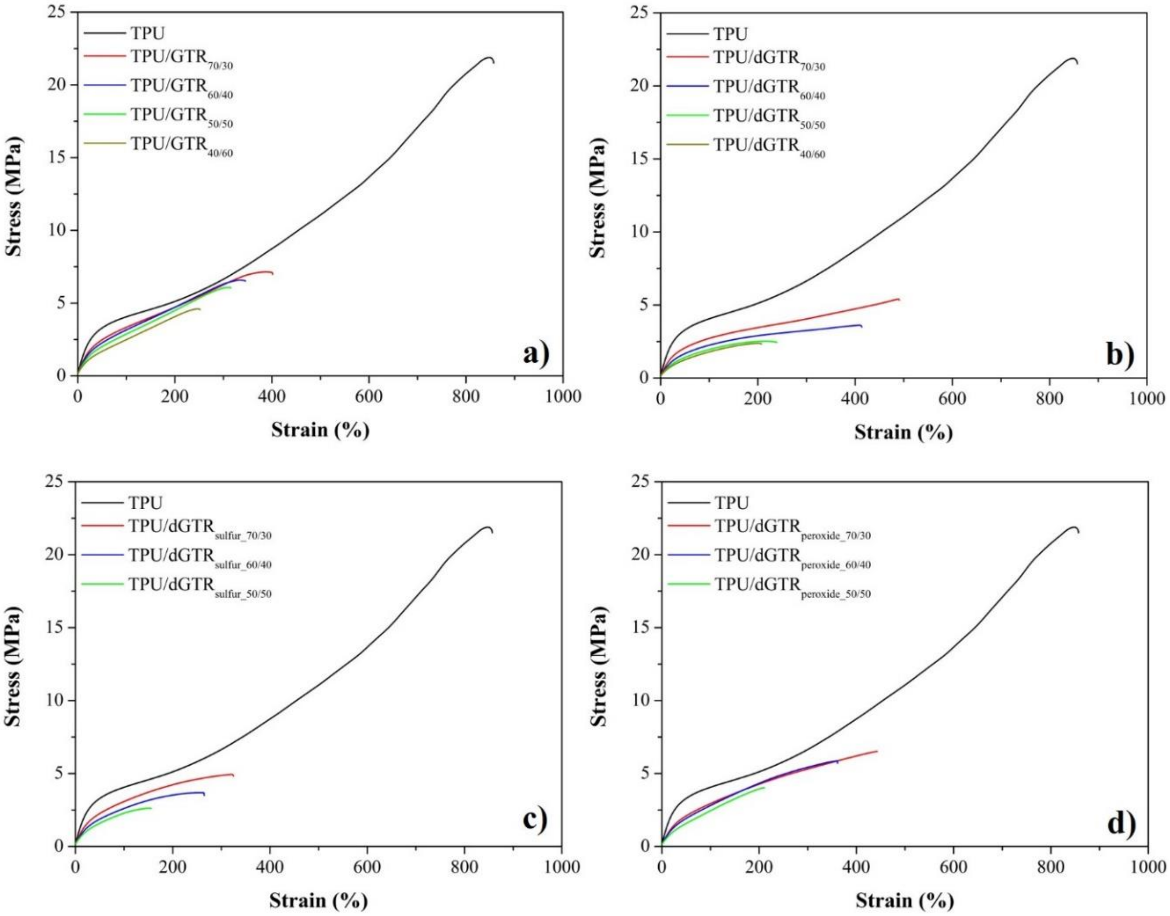


Figure 10. Characteristic tensile curves of the compounds, a) TPU/GTR, b) TPU/dGTR, c) TPU/dGTR$_{sulfur}$, d) TPU/dGTR$_{peroxide}$

Sample	**Tensile strength [MPa]**	**Strain at break [%]**	**M50 [MPa]**	**M100 [MPa]**	**M300 [MPa]**
TPU	21.99 ± 0.68	889.6 ± 31.8	3.24 ± 0.06	4.00 ± 0.07	6.60 ± 0.11
TPU/GTR$_{70/30}$	7.15 ± 0.19	400.4 ± 16.0	2.48 ± 0.06	3.34 ± 0.08	6.27 ± 0.14
TPU/GTR$_{60/40}$	6.51 ± 0.20	341.2 ± 6.7	2.32 ± 0.06	3.21 ± 0.08	6.26 ± 0.16
TPU/GTR$_{50/50}$	6.04 ± 0.12	313.8 ± 4.2	2.03 ± 0.05	2.90 ± 0.06	6.01 ± 0.11
TPU/GTR$_{40/60}$	4.66 ± 0.18	254.7 ± 8.7	1.71 ± 0.06	2.52 ± 0.09	—
TPU/dGTR$_{70/30}$	5.37 ± 0.48	508.5 ± 32.4	2.11 ± 0.06	2.76 ± 0.08	4.02 ± 0.13
TPU/dGTR$_{60/40}$	3.79 ± 0.23	419.7 ± 30.0	1.74 ± 0.04	2.34 ± 0.06	3.38 ± 0.09
TPU/dGTR$_{50/50}$	2.74 ± 0.13	242.2 ± 25.4	1.49 ± 0.06	2.07 ± 0.09	—
TPU/dGTR$_{40/60}$	2.37 ± 0.08	201.6 ± 11.8	1.28 ± 0.03	1.83 ± 0.04	—
TPU/dGTR$_{sulfur\_70/30}$	4.84 ± 0.16	338.9 ± 12.1	2.22 ± 0.07	3.02 ± 0.09	4.76 ± 0.16
TPU/dGTR$_{sulfur\_60/40}$	3.76 ± 0.10	252.1 ± 13.2	1.90 ± 0.03	2.64 ± 0.05	—
TPU/dGTR$_{sulfur\_50/50}$	2.70 ± 0.10	155.7 ± 8.8	1.59 ± 0.02	2.31 ± 0.04	—
TPU/dGTR$_{sulfur\_40/60}$	—	—	—	—	—
TPU/dGTR$_{peroxide\_70/30}$	6.44 ± 0.21	444.3 ± 10.2	2.07 ± 0.04	2.90 ± 0.05	5.25 ± 0.09
TPU/dGTR$_{peroxide\_60/40}$	5.67 ± 0.29	347.7 ± 32.5	1.92 ± 0.01	2.80 ± 0.02	5.37 ± 0.07
TPU/dGTR$_{peroxide\_50/50}$	4.05 ± 0.09	217.8 ± 5.8	1.57 ± 0.01	2.45 ± 0.02	—
TPU/dGTR$_{peroxide\_40/60}$	—	—	—	—	—

Table 14. Tensile results of the compounds

The results of the IFWI test are provided in Table 15, and characteristic force-displacement curves are shown in Figure 11.

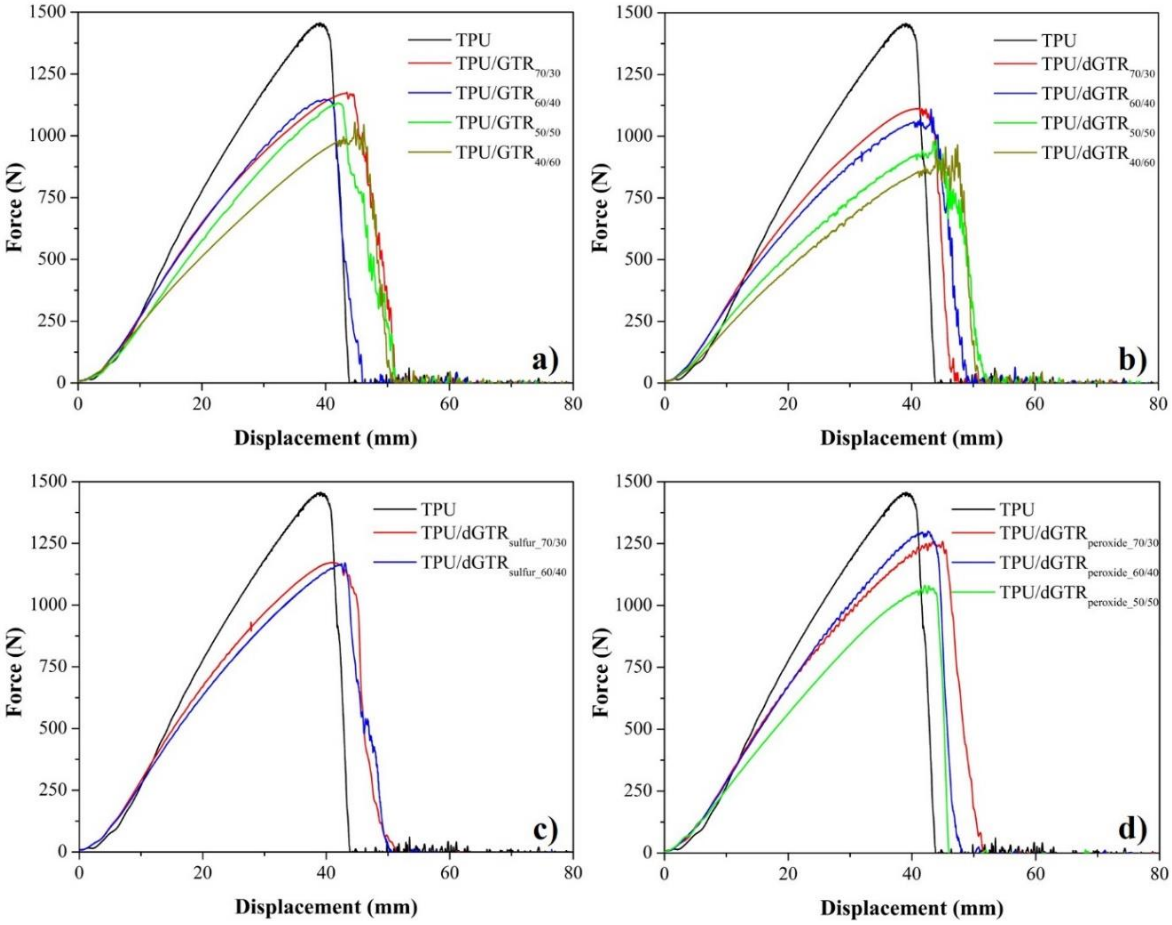


Figure 11. The force-displacement curves recorded during IFWI testing of the samples are as follows: a) TPU/GTR, b) TPU/dGTR, c) TPU/dGTR$_{sulfur}$, d) TPU/dGTR$_{peroxide}$

Sample	**Perforation energy [J/mm]**
TPU	17.86 ± 2.32
TPU/GTR$_{70/30}$	17.39 ± 1.13
TPU/GTR$_{60/40}$	14.16 ± 0.76
TPU/GTR$_{50/50}$	15.01 ± 0.36
TPU/GTR$_{40/60}$	14.39 ± 0.68
TPU/dGTR$_{70/30}$	15.32 ± 0.55
TPU/dGTR$_{60/40}$	15.21 ± 0.60
TPU/dGTR$_{50/50}$	13.63 ± 1.05
TPU/dGTR$_{40/60}$	13.03 ± 0.94
TPU/dGTR$_{sulfur\_70/30}$	16.65 ± 0.70
TPU/dGTR$_{sulfur\_60/40}$	15.88 ± 0.44
TPU/dGTR$_{sulfur\_50/50}$	—
TPU/dGTR$_{sulfur\_40/60}$	—
TPU/dGTR$_{peroxide\_70/30}$	17.92 ± 1.43
TPU/dGTR$_{peroxide\_60/40}$	16.91 ± 0.76
TPU/dGTR$_{peroxide\_50/50}$	13.38 ± 0.95
TPU/dGTR$_{peroxide\_40/60}$	—

Table 15. Perforation energy of the compounds

We investigated the behavior of the samples under dynamic loading using the IFWI test. In each case, the dart penetrated through the 2 mm thick injection-molded plaques. The presence of the rubber phase reduced the energy required for the perforation of the samples (the area under the curve), which can be attributed to the weak interaction between the phases. However, it is worth noting that the presence of the rubber phase altered the force-displacement curves of the samples. In all cases, the maximum deformation increased, but the detected maximum force decreased, indicating a more elastic behavior of the material.

The highest perforation energy and maximum force values were measured for the samples containing the peroxide mixture ($dGTR_{peroxide}$), which can be attributed to the better interaction between the phases, as previously demonstrated in the tensile test results.

The Shore A hardness of the samples (see Table 16) decreased as the quantity of different rubber phases increased compared to the TPU matrix. Since devulcanization (dGTR) reduced the cross-link density in the rubber phase (as mentioned earlier), the samples containing dGTR also exhibited lower hardness. With the dynamic vulcanization of the rubber phase, we increased the number of cross-links, thereby approaching the Shore A hardness of the rubber particle-filled samples in the TDVs.

Additionally, we investigated the compression set of the samples at room temperature (Table 16). It is evident that the residual deformation of the samples increased with a decrease in their hardness and with the increasing amount of GTR or dGTR. Curing the rubber phase with either a sulfuric or a peroxidic curing system had a stabilizing effect on the compression set, the increasing tendency of the compression set as a function of dGTR content disappeared at the samples which contained cured rubber phase.

Sample	**Shore A hardness [Sh A°]**	**Compression set (25 °C 72 hours) [%]**
TPU	76.7 ± 0.3	12 ± 1.7
$TPU/GTR_{70/30}$	69.7 ± 0.4	15 ± 2.6
$TPU/GTR_{60/40}$	66.9 ± 1.4	18 ± 2.7
$TPU/GTR_{50/50}$	63.5 ± 1.5	18 ± 3.0
$TPU/GTR_{40/60}$	58.7 ± 1.5	18 ± 1.6
$TPU/dGTR_{70/30}$	65.1 ± 0.3	20 ± 2.0
$TPU/dGTR_{60/40}$	62.2 ± 0.6	35 ± 0.8
$TPU/dGTR_{50/50}$	55.7 ± 0.3	37 ± 0.4
$TPU/dGTR_{40/60}$	51.9 ± 0.4	37 ± 0.7
$TPU/dGTR_{sulfur\_70/30}$	68.3 ± 0.4	30 ± 1.5
$TPU/dGTR_{sulfur\_60/40}$	64.8 ± 0.6	31 ± 1.3
$TPU/dGTR_{sulfur\_50/50}$	61.5 ± 0.7	31 ± 1.0
$TPU/dGTR_{sulfur\_40/60}$	—	—
$TPU/dGTR_{peroxide\_70/30}$	66.4 ± 0.7	28 ± 0.7
$TPU/dGTR_{peroxide\_60/40}$	64.4 ± 0.3	29 ± 1.9
$TPU/dGTR_{peroxide\_50/50}$	59.4 ± 0.2	28 ± 1.4
$TPU/dGTR_{peroxide\_40/60}$	—	—

Table 16. Shore A hardness and compression set of the compounds

Observing the DMA curves of the compounds led to the recognition that in the storage modulus and tanδ curves of the thermoplastic polyurethane, a sharp glass transition can be observed, which belongs to the soft phase of the matrix polymer. Similar transitions are also observed in the blends and TPVs. This is due to the overlapping glass transition temperature ranges of the TPU's soft phase and the rubber phase. Increasing the quantity of different rubber variants in the samples lowers the T_g, increasing the mobility of polymer chains in the material. Along with this change, the maximum of the tanδ peak also increases, which is attributed to an increase in the number of molecules participating in the transition. The damping properties of elastomers are often associated with this peak maximum. Therefore, the presence of rubber powder increased the damping capacity of the samples.

Looking at the storage modulus of the samples at room temperature (20 ℃), it can be observed that its value decreases due to the influence of various rubber powder modifications, which is consistent with the results of the tensile tests.

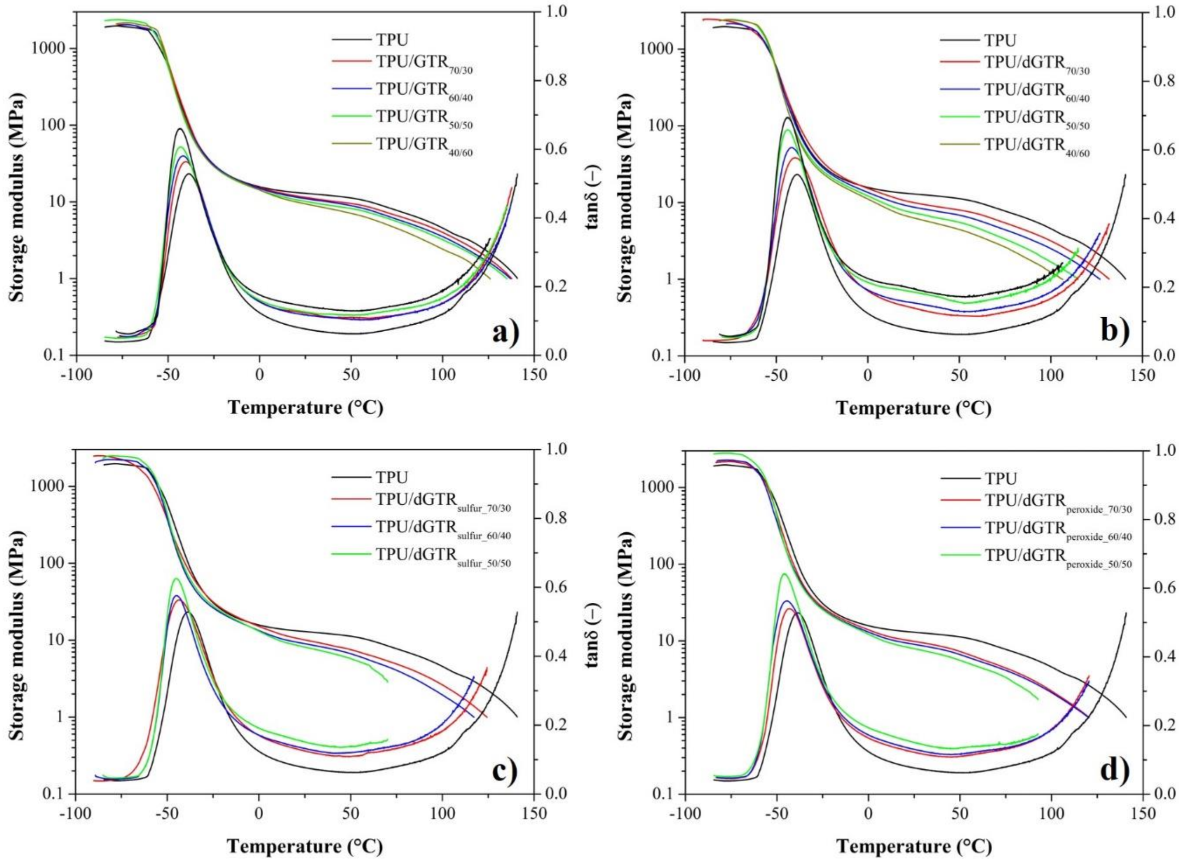


Figure 12. The DMA curves of the samples are as follows: a) TPU/GTR, b) TPU/dGTR, c) TPU/dGTR$_{sulfur}$, d) TPU/dGTR$_{peroxide}$

For products made of elastomers, such as shoe soles, it is crucial to consider their traction on icy and wet surfaces. This is typically characterized by the tanδ curve values at -20 and 0 ℃. Based on the results, it can be noted that we were able to improve the samples' adhesion on icy and wet surfaces with different GTR modifications. The tanδ value measured at 60 ℃ is associated with the energy dissipated during the dynamic loading of the rubber, which is related to their rolling resistance.

Sample	**T$_g$** (°C)	**tanδ$_{max}$** (-)	**tanδ$_{-20\,°C}$** ice traction (-)	**tanδ$_{0\,°C}$** wet grip (-)	**tanδ$_{60\,°C}$** rolling resistance (-)	**Payne effect E'$_{Payne}$** (M$_{0.01}$-M$_{10}$) (MPa)
TPU	-38.7	0.528	0.271	0.124	0.066	4.488
TPU/GTR$_{70/30}$	-40.2	0.564	0.282	0.157	0.108	4.237
TPU/GTR$_{60/40}$	-41.9	0.581	0.286	0.156	0.104	4.234
TPU/GTR$_{50/50}$	-43.2	0.607	0.279	0.161	0.121	4.403
TPU/GTR$_{40/60}$	-43.7	0.661	0.283	0.176	0.132	4.290
TPU/dGTR$_{70/30}$	-39.8	0.577	0.336	0.190	0.116	3.408
TPU/dGTR$_{60/40}$	-41.6	0.607	0.313	0.192	0.131	3.160
TPU/dGTR$_{50/50}$	-43.7	0.658	0.312	0.214	0.157	3.577
TPU/dGTR$_{40/60}$	-43.9	0.695	0.322	0.226	0.175	3.184
TPU/dGTR$_{sulfur\_70/30}$	-43.4	0.563	0.283	0.170	0.120	4.549
TPU/dGTR$_{sulfur\_60/40}$	-44.8	0.576	0.260	0.171	0.127	4.717
TPU/dGTR$_{sulfur\_50/50}$	-45.1	0.626	0.281	0.192	0.148	4.588
TPU/dGTR$_{sulfur\_40/60}$	—	—	—	—	—	—
TPU/dGTR$_{peroxide\_70/30}$	-43.1	0.540	0.262	0.164	0.118	3.729
TPU/dGTR$_{peroxide\_60/40}$	-44.7	0.563	0.271	0.173	0.125	3.796
TPU/dGTR$_{peroxide\_50/50}$	-46.1	0.643	0.282	0.193	0.140	3.748
TPU/dGTR$_{peroxide\_40/60}$	—	—	—	—	—	—

Table 17. Dynamic mechanical parameters of the compounds derived from the DMA curves

3. Summary

In our research, we aimed at the development of thermoplastic polyurethane-based thermoplastic dynamic vulcanizates (TPU-TDVs). The conclusions of our work can be summarized in the following points:

- We demonstrated that the in situ synthesis of thermoplastic polyurethanes (TPUs) from their precursors (polyol, isocyanate, and chain extender) and the production of thermoplastic dynamic vulcanizates is possible.
- We showed that the properties of the resulting material are highly dependent on the initial moisture content of the 1,4-butanediol chain extender. Even traces of moisture can destabilize the synthesis and deteriorate the properties of the resulting material.
- We proved that the synthesis is also feasible with the so-called prepolymer route, which has lower health-related risks and grants the opportunity for a more stable production of the TPU.
- Based on the results from the first part of the research, it can be stated that production of a TPU based TDVs can be achieved with less technological complexity when a commercially available TPU is used; therefore, we continued our work with this kind of TPUs.
- In accordance with recent trends focusing on ecological aspects of materials, we involved recycled ground tyre rubber (GTR) in the research as the rubber phase of the TDV.
- Our results showed that the mechanical performance of the neat TPU decreases with the addition of various forms of GTR, which significantly lowers the compounds' price. Moreover, the mechanical performance of the compounds is still good enough to make them viable for many applications.
- Thus, usability is accompanied by the economical benefits of lower price and ecological benefits of the utilization of recycled material, which makes these materials a desirable candidate on the market of thermoplastic elastomers.

4. Main results and outcomes of the project

The main result of this project is the successful development of TPU and recycled rubber-based thermoplastic vulcanizates. The mechanical performance of the TPUs used in the experiments was unfortunately deteriorated by the addition of any forms of rubbers but stayed well in the usable range. Considering the enormous gap between the prices of GTR/dGTR and TPU (~0.5-1.0 EUR/kg vs. 8-10 EUR/kg) one can see that with the addition of GTR into a TPU matrix the overall price of the material can significantly be reduced. This means that the results of our research showed that the production and market penetration of a TPU and GTR-based thermoplastic elastomer is a viable option that has great ecological benefits in terms of using recycled material.

5. Project related project papers, BSc, MSc theses, PhD dissertations

Project related project papers:

Bence Boldizsár Szederkényi, Andor Magyar, Patrik Fónagy: Development of thermoplastic polyurethane/ ground tyre rubber-based blends (2021)

Ngo Ha Trang, Réka Miklós, Éva Takách: Development of thermoplastic polyurethane elastomer–based foams (2022)

Project related BSc theses:

Benedek Levente Tajti: Effect of compounding parameters on the properties of thermoplastic dynamic vulcanizates with in situ produced polyurethane matrix (2019)

András Simon: Development of thermoplastic dynamic vulcanizates with rubber oligomer based polyurethane matrix (2019)

András Somogyi: Tribology of thermoplastic dynamic vulcanizates with in situ polyurethane matrix (2020)

Bence Attila Horváth: The effect of composition on the properties of thermoplastic polyurethanes (2022)

Project related MSc theses:

Szabó Nikoletta Kata: Development of thermoplastic dynamic vulcanizates (TDV) with in situ produced matrix (2019)

Péter Pandur: Effect of different rubber compounds on the properties of thermoplastic dynamic vulcanizates with in situ produced polyurethane matrix. (2019)

László Herpai: Compatibilization of thermoplastic polyurethane (TPU) and rubber phase in thermoplastic dynamic vulcanizates (TDV) (2021)

Project related PhD dissertations:

Andrea Kohári: Novel thermoplastic dynamic vulcanizates (TDV) with enhanced wear resistance based on in situ produced polyurethane matrix (in progress) 2019-

6. Project-related papers, conference abstract

1. Kohári A., Halász I. Z., Bárány T.: Thermoplastic dynamic vulcanizates with in situ synthesized segmented polyurethane matrix, Polymers 11: (10) 1663, 2019
2. Kohári A., Halász I., Bárány T.: In situ előállított, poliuretán alapú termoplasztikus elasztomerek fejlesztése, Polimerek 5: (7-8) 622-625, 2019
3. Kohári A., Bárány T.: In situ–produced polyurethane-based thermoplastic elastomers: the effect of the acrylonitrile content of the rubber phase, IOP Conference Series: Materials Science and Engineering, 1246: 012001, 2022

4. Kohári A., Bárány T.: Development of thermoplastic vulcanizates based on in situ synthesized thermoplastic polyurethane and acrylonitrile-butadiene rubber: the influence of the curing system, Journal of Polymer Research 29: 361, 2022
5. Simon D. Á., Bárány T.: Microwave devulcanization of ground tyre rubber and its improved utilization in natural rubber compounds, ACS Sustainable Chemistry & Engineering, 11, 1797-1808, 2023
6. Kohári A., Bárány T..: Termoplasztikus poliuretán alapú elasztomer fejlesztése újrahasznosított gumiőrlet társításával. Műanyag- és Gumiipari Évkönyv, 21, 94-98, 2023
7. Kohári A., Görbe Á., Halász-Kutasi I., Bárány T.: Eco friendly thermoplastic elastomers based on thermoplastic polyurethanes and devulcanized ground tyre rubber, Journal of Applied Polymer Science, under submission
8. Görbe Á., Kohári A., Halász-Kutasi I., Bárány T.: Rubber compounds from devulcanized ground tyre rubber: Recipe formulation and characterization, Polymer Testing, under submission
9. Kohári A., Görbe Á., Halász-Kutasi I., Bárány T.: Thermoplastic vulcanizates based on thermoplastic polyurethane and devulcanized ground tyre rubber, Journal of Cleaner Production, under submission