Assessment of microstructure, physical and thermal properties of bitumen modified with LDPE/GTR/elastomer ternary blends

Krzysztof Formela\textsuperscript{a*}, Michał Sulkowski\textsuperscript{a}, Mohammad Reza Saeb\textsuperscript{b}, Xavier Colom\textsuperscript{c}, Józef T. Haponiuk\textsuperscript{a}

\textsuperscript{a}Department of Polymer Technology, Chemical Faculty, G. Narutowicza Str. 11/12, Gdańsk University of Technology, 80-233 Gdańsk, Poland
\textsuperscript{b}Department of Resin and Additives, Institute for Color Science and Technology, P.O. Box: 16765-654, Teheran, Iran
\textsuperscript{c}Department of Chemical Engineering, Universitat Politècnica de Catalunya Barcelona Tech, Terrassa, Spain

*Corresponded to: Krzysztof Formela, e-mail: krzysztof.formela@pg.gda.pl, kformela.ftp@gmail.com, Tel. No.: +48 58 347 2234/ Fax. No.: +48 58 347 2134

Abstract

LDPE/GTR/elastomer ternary blends with variable LDPE/GTR ratio and constant elastomer content were prepared via melt-compounding. Obtained LDPE/GTR/elastomer blends were applied as thermoplastic modifiers into bitumen. Microstructure, physical and thermal properties of the modified bitumen were determined. It was observed that chemical composition of LDPE/GTR/elastomer blends has significant influence on their density and rheological behavior, which are also main factors affecting the dispersion of LDPE/GTR/elastomer blends into bitumen matrix and interfacial interactions between used components. Microstructure and thermal behavior of modified bitumen confirmed that physical interactions between bitumen and LDPE/GTR/elastomer blends are limited with increasing content of GTR. This phenomenon is due to mainly cross-linked structure of GTR and its low flowability. The conducted investigations showed that interfacial interactions between of thermoplastic modifier and bitumen, therefore the conventional and thermal properties of modified bitumen can be improved and easily modified by changing composition of LDPE/GTR/elastomer blends.

Keywords: ground tire rubber; modified bitumen; recycling; thermoplastic blends; extrusion
1. Introduction

The estimated data demonstrates that more than 17 million tonnes of used car tires are discarded every year worldwide. One of the most important methods of used tires recycling is grinding [1], resulting in ground tire rubber (GTR) particles with desired shape and size. Typically, GTR is used as filler in rubber compounds [2, 3], thermoplastic composites [4, 5], thermoplastic elastomers [6, 7], polyurethanes [8] and epoxy resins [9]. Moreover, GTR can be applied in pyrolysis [10] and reclaiming/devulcanization [11, 12] of waste rubber. Among others applications at industrial scale, use of waste rubber in the construction and building materials should be mentioned. Most of researches in this area are focused on the modifications of cement, concrete [13, 14] and bitumen [15, 16].

Application of waste rubber and other polymeric wastes [17-19] as cheap polymeric modifiers of bitumen’s enhances their properties and extend their applicability in different branches of industry (e.g. road pavements, roofing applications, sealants, emulsions etc.). Results published by independent research centers over the last decades confirm that the use of GTR as modifier of bitumen improves the elasticity and resistance on permanent deformation of pavements. Road pavements based on bitumen modified with GTR show higher toughness and resistance to climatic factors, which increases their durability as well as keeps the costs of maintenance lower compared to pavements based on unmodified bitumen. Moreover, incorporation of GTR into the bitumen decreases the noise generated by car traffic and manifests the driving comfort and safety through the shortening of braking distance.

On the other hand, factors limiting the use of GTR-modified bitumen are higher costs of production arising from energy consumption of the process (long time of mixing at elevated temperatures) and necessity of modification of the devices currently used in the industry. Moreover, because of the cross-linked structure of waste rubber, bitumen modified with GTR shows low stability and high viscosity, which causes difficulties with their storage.
and further use. Comprehensive literature reviews of the research on the modifications of bitumen with ground tire rubber were recently presented in works of Lo Presti [20] or Shu and Huang [21].

Using of reclaimed/devulcanized waste rubber is one of methods of enhancement the stability of GTR-modified bitumen. Singh et al. [22] studied the effect of activated ground tire rubber on properties of bitumen. Activation of GTR was conducted via two-roll milling (strong shear forces) at 210-230°C in 2-3 hours’ time. During activation tar oil, elemental sulfur and gilsonite resin were used as reclaiming/devulcanization agents. Activation of GTR by reclaiming/devulcanization or controlled oxidation has beneficial effects on the homogeneity and stability of modified bitumen [23, 24]. Other possibilities to increase stability of GTR-modified bitumen is using of additives (e.g. waxes, plasticizers, thermoplastics), which may improve dispersing of cross-linked rubber particles in bitumen [25, 26].

Wang et al. [27, 28] proposed using of polyethylene and reclaimed rubber blends as modifiers of bitumen. Their findings suggest that blending of thermoplastics with reclaimed rubber via extrusion improves the storage stability of polyethylene/reclaimed rubber modified bitumen, which was related to dispersion level of modifiers throughout the bitumen. Similar observations were recently reported by Yan et al. [29], who studied the effect of GTR, recycled low density polyethylene and their combinations on the rheological properties of bitumen. In presented state of knowledge there is lack of information about effects of thermoplastics/GTR blends composition and its content in on properties of modified bitumen. These characteristics would be valuable data for evaluation and prediction of the interaction between GTR, thermoplastics and bitumen.

In the present work, interfacially modified LDPE/GTR blends with non-polar elastomers were used as bitumen modifiers in order to improve their performance and storage
stability. Thermoplastic composites based on LDPE/GTR/elastomer ternary blends were prepared using a co-rotating twin screw extruder. Advantages of extrusion are continuity of the process, short time, high efficiency of mixing and good quality of the obtained products. It is also worth mentioning that during the extrusion process partial reclaiming of GTR is possible [30, 31], which promote the interfacial interaction between polyethylene and bitumen.

In order to expand characterization of LDPE/GTR/elastomer blends, during present studies their density and rheological properties were evaluated. The influence of LDPE/GTR/elastomer ternary blends compositions and their content on microstructure, physical and thermal properties of the bitumen 160/220 were investigated. Physical properties of modified bitumens were evaluated by conventional tests (penetration, softening point and penetration index). Microstructure and thermal properties were determined using optical microscopy, dynamic mechanical analysis and thermogravimetric analysis.

2. Experimental

2.1. Materials

Ground tire rubber (GTR) produced by ambient grinding of used tires (about 50:50 %wt. mix of passenger and truck cars), was obtained from Grupa Recykl S.A. (Poland). Particle size distribution of the used GTR is presented in Figure 1.

Low density polyethylene (LDPE) Bralen VA 20-60 (density: 0.91 g/cm³, MFR190°C/2,16kg: 20 g/10 min) was received from Slovnaft (Slovakia).

During research two types of elastomers: styrene-butadiene block copolymer (SBS) or partially cross-linked butyl rubber, were used as compatibilizer of LDPE/GTR blend. Styrene-butadiene-styrene block copolymer Kraton 1102 (density: 0.94 g/cm³, MFR200°C/5kg: 8 g/10 min) from Kraton Polymers (Germany) is commercially used in industry as modifier of pavement bitumen or as substrate in production of sealants. For comparison, partially cross-
linked butyl rubber (IIR) Kalar 5215 (density: 1.07 g/cm\(^3\), Mooney viscosity: ML 1+3 (127°C): 47-57, filler content: 24.6 %wt.) from Ter Hell & Co (Germany) was applied.

Partially cross-linked butyl rubber is commonly used in the manufacture of sealants, caulks, roof coatings, construction adhesives etc. Both type of elastomers are sold as granules, which facilitates their metering for the extrusion process.

Bitumen 160/220 from Lotos Asfalt Sp. z o.o. (Poland) was characterized by the penetration at 25°C: 154 (1/10 mm) and softening point temperature: 38.7°C. The type of bitumen was picked based on content of oils and resins fraction, which are higher in comparison to other commercial available bitumen. These low molecular compounds present in bitumen could act like plasticizers, which improve reclaiming process of GTR and dispersion of GTR in the thermoplastic matrix [32].

2.2. Sample preparation

Step I: Preparation of thermoplastic modifiers

Five types of thermoplastic modifiers were used as bitumen modifiers; their composition is shown in Table 1. LDPE/GTR and LDPE/GTR/elastomer blends were prepared using a co-rotating twin screw extruder, type Leistritz ZSE 27HP (d=27, L/d=44) (Germany). Characteristics of screw configuration is presented in work [33]. During the extrusion barrel temperature was 180°C (80°C in hopper) and rotational speed of screws was 300 rpm. All components (LDPE, GTR, elastomer) were gravimetrically dosed directly into hopper with constant throughput (15 kg/h). During these studies gravimetric feeders from Brabender (Germany) were used. Interfacial interactions between the components in LDPE/GTR/elastomer blends were characterized in details in work [34].

Step II. Modification of bitumen

Bitumen 160/220 was modified with 2, 4, 6 and 12 parts by weight (pbw) of thermoplastic modifier for 100 parts of bitumen. Bitumen modification was performed at
180°C, using T 25 digital Ultra-Turrax® rotor-stator homogenizer from IKA (Germany).
Rotational speed of rotor was 15000 rpm. Bitumen modification was conducted until desired
homogeneity of material was obtained (around 30 minutes).

2.3. Measurements
Melt flow index of thermoplastic compositions was determined at 190°C, with load of
2.16, 5 and 10 kg, according to ISO 1133, using Mflow plastometer from Zwick. Tungsten
carbide capillary die having length of 8.000 ±0.025 mm and diameter of 2.095±0.005 was
applied for the measurements. Considering the average size of GTR particles shown in Figure
1, die diameter was about five times larger than the GTR particles.

Based on the methodology described by Jakubowska et al. [35] rheological
c characteristics of obtained thermoplastic compositions were determined. Viscosity of melt
(\( \eta_w \)) was calculated based on formula (1):

\[
\eta_w = \frac{\tau_w}{\dot{\gamma}_w} \quad (1)
\]

where: \( \tau_w \) - shear stress (Pa), \( \dot{\gamma}_w \) - shear rate after correction (s\(^{-1}\))

Shear stress were calculated according to formula (2):

\[
\tau_w = \frac{\Delta p \cdot R_c}{2 \cdot L_c} \quad (2)
\]

where: \( \Delta p \) - pressure drop (Pa), \( R_c \) - radius of capillary (m), \( L_c \) - length of capillary (m)

Weissenberg–Rabinowitsch corrected shear rate (\( \dot{\gamma}_w \)) was calculated based on formula (3):

\[
\dot{\gamma}_w = \frac{3n+1}{4n} \cdot \dot{\gamma}_a \quad (3)
\]

where \( n \) is slope in linear equation of straight line described as (4):

\[
\log(\tau_w) = f(\log(\dot{\gamma}_a)) \quad (4)
\]

Apparent shear rate was determined according to formula (5):

\[
\dot{\gamma}_a = \frac{4 \cdot Q}{\pi \cdot R_c^3} = \frac{4}{\pi \cdot R_c^3} \cdot \frac{m}{t \rho} \quad (5)
\]
where: $Q$ - the volume flow rate (m$^3$/s), $m$ - mass of sample (kg), $t$ - time of measurement (s),

$\rho$ - density of sample (kg/m$^3$)

Penetration measurements for analyzed samples were conducted according to PN-EN 1426 in 25°C. Softening point temperature of materials was determined with Ring and Ball method, according to PN-EN 1427. Penetration index (PI) was calculated in accordance to formulas (6) and (7):

$$PI = \frac{20(1 - 25A)}{1 + 50A}$$ (6)

$$A = \frac{\log \text{pen} T_{25^\circ C} - \log 800}{T_{\text{softening}} - T_{25^\circ C}}$$ (7)

The microstructure of modified bitumen was characterized using confocal microscope Horiba LabRAM ARAMIS. For sample preparation, a small quantity of bitumen was applied onto a glass slide, then the bitumen was heated to about 180°C and a second glass slide was placed onto the sample. Prepared sample was cooled to room temperature. During cooling constant load was put on sample, which allowed obtaining thin film of bitumen. After a short period of cooling, the morphology of samples was estimated.

Dynamic mechanical analysis was performed using DMA Q800 TA Instruments apparatus. Samples cut to the dimensions of 40 x 10 x 2 mm were loaded with a variable sinusoidal deformation force in the single cantilever bending mode at the frequency of 1 Hz under the temperature rising rate of $4^\circ C$/min within the temperature range between -40 and 40°C.

Thermogravimetric analysis (TGA) was performed on a Netzsch TG 209 apparatus. Samples (ca. 5 mg) were placed in a corundum dish. Measurements were conducted in a nitrogen atmosphere for the temperature range 25-550°C at a heating rate of 20°C/min.
3. Results and discussion

3.1. Density and melt viscosity of LDPE/GTR/elastomer blends

Density values of studied thermoplastic modifiers are shown in Table 1. This parameter gives some information about storage stability of modified bitumen during hot storage, which is related with significant changing of bitumen’s density during heating: from \(~1.02\) at \(25^\circ\text{C}\) to \(~0.91\) at \(190^\circ\text{C}\) [36]. It was observed that thermoplastic modifiers filled with 50 \%wt. of GTR possess slightly higher density than samples containing 50 \%wt. LDPE. Moreover, in comparison to styrene-butadiene-styrene block copolymer, using of butyl rubber as compatibilizer affects on increase of thermoplastic modifiers density, which is related with presence of inorganic filler in this type of elastomer (please see Materials section). Presented results suggest that, during hot storage stability test, in samples with 50 \%wt. of GTR, the GTR sediments to bottom, in contrary in samples with 50 \%wt. of LDPE, the LDPE migrates on top of modified bitumen.

The effect of LDPE/GTR/elastomer formulation on the characteristics of melt viscosity is presented in Figure 2. LDPE/GTR at ratio of 50:50 was used as reference sample. It was noticed, that replacement of LDPE or GTR with elastomer increased melt viscosity of obtained thermoplastic compositions. The exception was sample LDPE/GTR/SBS 50:25:25, which possess melt viscosity similar to reference sample (LDPE/GTR 50:50). This phenomenon suggests good compatibility of linear styrene-butadiene-styrene block copolymer with polyethylene matrix. Under tested conditions melt viscosity of LDPE/GTR/IIR 25:50:25 at low shear stress (2.16 kg load) could not be determined, which is due to high filler content in used IIR.

As could be expected, samples containing 50 \%wt. of GTR showed higher melt viscosity than samples comprising 50 \%wt. of LDPE, which is related with mainly cross-linked structure of ground tire rubber, decreasing it’s flowability. LDPE/GTR/elastomer melt
viscosity decreased with increasing shear rate. This behavior is characteristic for filled composites and confirm shear thinning phenomenon. Similar conclusions for PP/GTR and PP/GTR/(EPDM or EPR) blends were described recently by Prut et al. [37] and Lima et al. [38] respectively.

3.2. Physical properties of bitumen modified with LDPE/GTR/elastomer blends

The results of penetration and softening point of modified bitumen are presented in Figure 3. Addition of prepared thermoplastic modifiers has significant influence on physical properties of modified bitumens. It was observed that using of higher content of modifier caused decrease of penetration and proportionally increased the softening temperature of obtained bitumen. The ratio of LDPE/GTR obviously influences the conventional properties of bitumen. The highest content (75 % wt.) of LDPE and elastomer (SBS, IIR) led to lower values of penetration and higher softening point in comparison to samples with LDPE/GTR/elastomer in proportion 25:50:25 (only 50 % wt. of thermoplastic matrix). This result suggests higher interfacial interaction between thermoplastic components (LDPE, elastomer) and bitumen, than between bitumen and ground tire rubber, which is due to cross-linked structure of GTR. Three-dimensional cross-linked structure of the GTR limits its dissolution and dispersion in the bitumen phase, which corresponded with the results of penetration and softening point. Moreover, it was noticed that addition of 12 pbw LDPE/GTR/IIR 50:25:25 modifier cause deterioration of physical parameters of such modified bitumen in comparison to modification with thermoplastic blends of composition LDPE/GTR 50:50 or LDPE/GTR/SBS 50:25:25. This phenomenon suggests decrease of solubility of this type of modifier in bitumen, which may be related with limited interfacial interactions between IIR elastomer and other components (GTR, LDPE and bitumen).

Penetration index (PI) describes bitumen temperature susceptibility at relatively small range of temperatures. Penetration index values are presented in Figure 4. Temperature
susceptibility is defined as the change in the consistency parameter as a function of temperature. It is well known, that low value of PI parameter corresponds with higher temperature susceptibility of bitumen. It was observed that higher content of modifiers in bitumen 160/220 increases penetration index values. These results suggest that the modified bitumen is more resistant to low temperature cracking and permanent deformation [39].

3.3. Microstructure of bitumen modified with LDPE/GTR/elastomer blend

Figure 5 presents microstructure of pure bitumen 160/220 and bitumen 160/220 with 12 pbw modifier content. It was noticed that using of 12 pbw LDPE/GTR/elastomer blend as modifier did not affect on bitumen/polymer phase inversion. Continuous (dominant) phase was bitumen and dispersed phase was LDPE/GTR/elastomer blend. Presented results indicate that the ratio of LDPE to GTR has significant effect on dispersion of modifier in bitumen. It was observed that lower content of GTR affects on better dispersion of thermoplastic phase (LDPE and elastomer phase). It was noticed that better dispersion of thermoplastic modifier in bitumen phase was observed for LDPE/GTR/SBS modifier, as presented in Figures 5C and 5E. Better dispersion of this modifier is due to lower melt viscosity of LDPE/GTR/SBS modifier (see Figure 2). For comparison, morphology of bitumen with 12 pbw LDPE/GTR/IIR modifier shows aggregates of thermoplastic phase (Figures 5D and 5F). This phenomenon is related with cross-linked structure of GTR and different compatibility between used components. The largest thermoplastic phase agglomerates were presented in bitumen modified with using LDPE/GTR/IIR 25:50:25, which is due to poor compatibility between butyl rubber and styrene-butadiene rubber, butadiene rubber or natural rubber (main components of car tires) [40] and only partial compatibility with polyethylene matrix [41]. In comparison to slightly cross-linked butyl rubber (IIR), using of styrene-butadiene-styrene (SBS) block copolymer as modifier of LDPE/GTR blend reduces the melt viscosity and
improves interfacial interactions between LDPE matrix and ground tire rubber [30, 42]. This phenomenon has dominant influence on interactions between bitumen and LDPE/GTR/elastomer blends. Based on presented results further studies were limited to LDPE/GTR and LDPE/GTR/SBS blends.

3.4. Dynamic mechanical analysis of bitumen modified with LDPE/GTR/elastomer blends

As could be noticed in previous paragraph (see Figure 3), pure bitumen and bitumen modified with 2 pbw of thermoplastic composition are characterized by very low softening point (~ 40°C), which could cause small size deformation during placement of samples to DMA apparatus. It is well known that inaccuracies in dimension of samples cause remarkable deviations of storage and loss modulus values. Therefore, to prevent mistakes during analysis of DMA results, dimension independent loss tangent (tan δ) values were evaluated. The results of dynamic mechanical analysis are shown in Figure 6.

According to literature [43, 44], the temperature at maximum value of the loss tangent (tan δ) is related to the change in colloidal structure of bitumen due to collapse of the structure formed by asphaltene phase, immersed in a maltene phase. It was observed that higher content of LDPE/GTR/elastomer blend used as thermoplastic modifier causes shift of the maximum value of the loss tangent (tan δ) to higher temperatures. This indicates that the modified bitumen becomes harder, which correspond also with the results of bitumen penetration (see Figure 3). This phenomenon is related to the interfacial interactions between the polymer modifier (LDPE/GTR/elastomer blend) and the saturate oils, which causes change in the maltene phase and stabilized asphaltene phase. Furthermore, short-term aging (e.g. oxidation, volatilization of low molecular compounds, etc.) during bitumen modification causes partial transformation of the maltene phase into the asphaltene phase, which could also affect the
maximum value of the loss tangent ($\tan \delta$). It was noticed that addition of thermoplastic modifiers not only shifts the position of the $\tan \delta$ peak towards higher temperatures, but also lowers the peak magnitude. These results confirm the changes in the stiffness of the modified bitumen due to increasing viscosity of bitumen during modification with thermoplastic modifiers, which is related to partial swelling of used modifiers [45]. Bitumen modification conducted at elevated temperature with non-polar low-molecular weight compounds causes swelling of LDPE and non-polar elastomer, while aromatic compound should interact with GTR due to polarity of used components.

The transition temperature associated with the loss tangent peak ($\tan \delta$ maximum) and values of $\tan \delta$ at -30°C are presented in Table 2. As mentioned above, the transition temperature at $\tan \delta$ maximum is related to the change in the colloidal structure of bitumen. It could be surprising that thermoplastic modifier composition had a small impact on transition temperature at $\tan \delta$ maximum determined for modified bitumen. This phenomenon confirms weak interactions between bitumen phase and ground tire rubber, due to the cross-linked structure of GTR. These results correspond also with increasing values of penetration and softening point determined for modified bitumen. Furthermore, it was noticed that the presence of SBS in LDPE/GTR blends causes decrease of transition temperature at $\tan \delta$ maximum, comparing to LDPE/GTR blend. This observation suggests stronger interactions between bitumen phase and SBS copolymer, which affect also on thermal properties presented in next section (see Figure 7).

The results of $\tan \delta$ at -30°C provides information about mechanical response of road pavement in winter conditions. It was observed that higher content of thermoplastic modifier in bitumen caused higher losses comparing to pure bitumen, which indicate their lower stiffness and enhanced flexibility at low temperature [43]. An exception was the bitumen sample modified with 12 pbw LDPE/GTR 50:50 due to the highest content of polyethylene.
According to the literature, application of polyethylene as bitumen modifier improves high-temperature performance of bitumen and at the same time deteriorate its low-temperature properties [46, 47].

3.5. Thermal properties of bitumen modified with LDPE/GTR/elastomer blends

Thermogravimetric analysis of pure bitumen, LDPE, GTR, SBS and their blends was conducted in nitrogen atmosphere and obtained results are presented in Table 3. $T_{2\%, 5\%}$, $T_{10\%}$ and $T_{50\%}$ represent temperatures for which the samples have lost the indexed amount of their initial mass, respectively. $T_{\text{max}}$ is temperature at which the rate of thermal decomposition of the sample is at its peak, as estimated from the derivative thermogravimetry (DTG). Additionally, the char residue at 550°C is given. For better illustration of thermal behavior of selected samples obtained results are presented as TGA curves in the Figure 7.

It was observed that, regardless of thermoplastic modifier type and its content used during bitumen modification, bitumen modified with LDPE/GTR/elastomer blend showed lower thermal stability in comparison to pure bitumen. This phenomenon is related with two main factors. First of them is obviously lower thermal stability of used thermoplastic modifiers. Second factor affecting on thermal stability of modified bitumen are interfacial interactions between bitumen and LDPE/GTR/elastomer, due to swelling/plasticization of thermoplastic matrix (LDPE, elastomer) and partial reclaiming/devulcanization of GTR. It was noticed that bitumen modified with LDPE/GTR and LDPE/GTR/elastomer blends were characterized by lower char residue values in comparison to pure bitumen or pure thermoplastic modifiers. This effect was observed especially in case of bitumen modified with 12 pbw LDPE/SBS/GTR blend in ratio 50:25:25 % wt.. It should be mentioned, that this sample was characterized by the highest content of thermoplastic matrix. Presented TGA results suggest swelling, plasticization and partial solubility of thermoplastic matrix (LDPE,
SBS), which cause higher mobility of polymer chains in bitumen. Similar observations were described by Zhang et al. [48], who used bitumen as compatibilizer during processing of thermoplastic elastomers containing GTR.

Furthermore, elevated temperature and high shear forces applied during modification of bitumen cause swelling and partial reclaiming/devulcanization of GTR, which simultaneously release the low molecular weight compounds [49]. Higher content of low molecular weight products generated during thermo-mechanical degradation of GTR contributed to higher mass loss at lower temperatures before reaching the highest rate of thermal decomposition and to lower content of char residue at 550°C.

For better characterization of interfacial interactions between bitumen and LDPE/GTR/elastomer blends, theoretical and experimental values of weight loss determined for modified bitumens have been compared. Theoretical results of weight loss at different temperatures were calculated from the data for pure bitumen and pure blends components (LDPE, GTR, SBS) assuming the additivity principle and lack of interactions. Calculated theoretical results are compared with experimental thermal degradation measurements, as presented in the Table 4. It was observed that experimental results of weight loss at different temperatures were generally higher than calculated values. This indicates better compatibility between the bitumen and GTR particles. Swelling and partial reclaiming/devulcanization of GTR particles during bitumen modification, cause components exchange between bitumen phase and GTR phase, which facilitated release of the volatile rubber degradation products to bitumen phase and diffusion of some bitumen compounds into GTR phase [50, 51].

Furthermore, it was noticed that at 300°C, experimental values of weight loss were lower than calculated theoretical values only for bitumen modified with LDPE/GTR/SBS in ratio 25:50:25 % wt. At higher content (12 pbw) of modifier LDPE/GTR/SBS 25:50:25 % wt. this effect was observed also at 350°C. These results suggest weak interfacial interactions
between bitumen and LDPE/GTR/SBS in ratio 25:50:25 % wt. in comparison to other used modifiers (LDPE/GTR 50:50 % wt. and LDPE/GTR/SBS 50:25:25 % wt.). This phenomenon may be related with the higher melt viscosity of modifier LDPE/GTR/SBS 25:50:25 % wt. (see Figure 2). Weak interfacial interactions between bitumen and LDPE/GTR/SBS 25:50:25 % wt. were also confirmed by measurements of penetration and softening point. Based on presented above assumptions schematic diagram of physical interactions between bitumen and LDPE/GTR/elastomer blend is presented in Figure 8.

4. Conclusions

Application of LDPE/GTR/elastomer blends as potential bitumen modifiers was evaluated. LDPE/GTR/elastomer blends were prepared via melt compounding using a co-rotating twin screw extruder. It was found that LDPE/GTR ratio and type of used elastomer have significant influence on density and rheological properties of obtained blends. LDPE/GTR/SBS blends was characterized by significantly lower density and melt viscosity in comparison to LDPE/GTR/IIR blends. Chemical composition, density and rheological properties of LDPE/GTR/elastomer are also crucial factors affecting on processing and storage stability of modified bitumen, which is related with dispersion of thermoplastic modifier into bitumen matrix and interfacial interactions between these components.

Maximum tan δ value of modified bitumen shifted to higher temperatures comparing to pure bitumen in result of swelling of the LDPE/GTR/elastomer blend and physical interactions on phase boundary. The maximum loss tangent value shift was predominantly influenced by the LDPE/GTR/elastomer blend content and only slightly by its composition. Furthermore, dynamic mechanical analysis confirmed that addition of thermoplastic modifiers to bitumen improves stiffness and enhances the flexibility at low temperature.
Thermal stability of the modified bitumen was lower comparing to pure bitumen due to interaction between bitumen phase and LDPE/GTR/elastomer phase. This phenomenon was related with plasticization of thermoplastic matrix (LDPE, elastomer) and partial reclaiming/devulcanization of GTR. It was found that interfacial interactions between bitumen and LDPE/GTR/elastomer blends are limited with increasing content of GTR, which is due to its mainly cross-linked structure and its limited flowability. The conducted investigations indicate that bitumen performances can be improved by addition of LDPE/GTR/elastomer blends.

References


Tables captions

Table 1. Composition of thermoplastic modifiers

Table 2. Comparison of temperature at maximum tangent and tanδ at -30°C determined for modified bitumen

Table 3. Decomposition temperatures as function of weight losses, different maximum peak and char residue determined for pure components and modified bitumen

Table 4. Comparison between theoretical and experimental results of weight loss at different temperatures determined by TGA

Figures captions

Figure 1. Particle size distribution of GTR

Figure 2. Melt viscosity of LDPE/GTR/elastomer blend measured at 190°C

Figure 3. Penetration (at 25 °C) and softening point of bitumen modified with LDPE/GTR/elastomer blend

Figure 4. Penetration index (PI) of bitumen modified with LDPE/GTR/elastomer blend


Figure 6. Loss tangent as a function of temperature plotted for bitumen with: A - 2 pbw thermoplastic modifier; B - 12 pbw thermoplastic modifier

Figure 7. TGA curves determined for used components and selected modified bitumens: A - normal view, B - magnification of curves for 400-550°C temperature range

Figure 8. Schematic diagram of physical interactions between bitumen and LDPE/GTR/elastomer blend
### Table 1. Composition of thermoplastic modifiers

<table>
<thead>
<tr>
<th>Composition</th>
<th>Density at 25°C (g/cm³)</th>
<th>Density at 190°C * (g/cm³)</th>
<th>MFI190°C/2.16kg</th>
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<tbody>
<tr>
<td>LDPE</td>
<td>GTR</td>
<td>SBS</td>
<td>IIR</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>-</td>
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</table>

* determined as MFR/MVR from MFI measurements

### Table 2. Comparison of temperature at maximum tangent and tanδ at -30°C determined for modified bitumen

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>Transition temperature at tanδ max (°C)</th>
<th>Damping factor (tanδ) at -30°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bitumen 160/220</td>
<td>23.8</td>
<td>0.056</td>
</tr>
<tr>
<td>+ 2 pbw LDPE/GTR 50:50</td>
<td>33.3</td>
<td>0.093</td>
</tr>
<tr>
<td>Bitumen 160/220 + 12 pbw LDPE/GTR 50:50</td>
<td>37.7</td>
<td>0.058</td>
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<td>Bitumen 160/220 + 2 pbw LDPE/GTR/SBS 50:25:25</td>
<td>27.5</td>
<td>0.063</td>
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<td>35.0</td>
<td>0.109</td>
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<tr>
<td>Bitumen 160/220 + 2 pbw LDPE/GTR/SBS 25:50:25</td>
<td>30.7</td>
<td>0.072</td>
</tr>
<tr>
<td>Bitumen 160/220 + 12 pbw LDPE/GTR/SBS 25:50:25</td>
<td>34.2</td>
<td>0.089</td>
</tr>
</tbody>
</table>
Table 3. Decomposition temperatures as function of weight losses, different maximum peak and char residue determined for neat components and modified bitumen

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>T_{2%} (°C)</th>
<th>T_{5%} (°C)</th>
<th>T_{10%} (°C)</th>
<th>T_{50%} (°C)</th>
<th>Char residue at 550°C (%)</th>
<th>T_{\text{max}} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bitumen 160/220</td>
<td>371.4</td>
<td>402.0</td>
<td>424.0</td>
<td>471.4</td>
<td>18.1</td>
<td>472.5</td>
</tr>
<tr>
<td>LDPE</td>
<td>425.1</td>
<td>441.8</td>
<td>452.2</td>
<td>477.7</td>
<td>0.03</td>
<td>480.2</td>
</tr>
<tr>
<td>GTR</td>
<td>255.7</td>
<td>302.6</td>
<td>348.1</td>
<td>453.1</td>
<td>41.6</td>
<td>388.8/435.2</td>
</tr>
<tr>
<td>SBS</td>
<td>313.3</td>
<td>391.2</td>
<td>414.5</td>
<td>463.9</td>
<td>0.3</td>
<td>471.2</td>
</tr>
<tr>
<td>LDPE/GTR 50:50</td>
<td>307.9</td>
<td>358.7</td>
<td>384.0</td>
<td>479.9</td>
<td>18.3</td>
<td>486.8</td>
</tr>
<tr>
<td>LDPE/GTR/SBS 50:25:25</td>
<td>361.5</td>
<td>388.8</td>
<td>411.8</td>
<td>476.1</td>
<td>9.0</td>
<td>486.2</td>
</tr>
<tr>
<td>LDPE/GTR/SBS 25:50:25</td>
<td>314.7</td>
<td>362.2</td>
<td>386.7</td>
<td>472.6</td>
<td>19.6</td>
<td>484.1</td>
</tr>
<tr>
<td>Bitumen 160/220 + 2 pbw LDPE/GTR 50:50</td>
<td>354.0</td>
<td>383.5</td>
<td>405.9</td>
<td>461.2</td>
<td>14.2</td>
<td>464.7</td>
</tr>
<tr>
<td>Bitumen 160/220 + 12 pbw LDPE/GTR 50:50</td>
<td>347.3</td>
<td>382.0</td>
<td>407.0</td>
<td>466.1</td>
<td>13.9</td>
<td>471.3</td>
</tr>
<tr>
<td>Bitumen 160/220 + 2 pbw LDPE/GTR/SBS 50:25:25</td>
<td>363.7</td>
<td>394.8</td>
<td>418.2</td>
<td>468.4</td>
<td>14.2</td>
<td>472.9</td>
</tr>
<tr>
<td>Bitumen 160/220 + 12 pbw LDPE/GTR/SBS 50:25:25</td>
<td>344.1</td>
<td>375.7</td>
<td>399.2</td>
<td>459.6</td>
<td>6.7</td>
<td>469.7</td>
</tr>
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<td>467.1</td>
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<td>467.6</td>
<td>14.9</td>
<td>466.3</td>
</tr>
</tbody>
</table>
Table 4. Comparison between theoretical and experimental results of weight loss at different temperatures determined by TGA

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>Weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300°C</td>
</tr>
<tr>
<td>Bitumen 160/220</td>
<td>theo.</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
</tr>
<tr>
<td>LDPE</td>
<td>theo.</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
</tr>
<tr>
<td>GTR</td>
<td>theo.</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
</tr>
<tr>
<td>SBS</td>
<td>theo.</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
</tr>
<tr>
<td>Bitumen 160/220 + 12 pbw LDPE/GTR 50:50</td>
<td>theo.</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
</tr>
<tr>
<td>Bitumen 160/220 + 2 pbw LDPE/GTR/SBS 50:25:25</td>
<td>theo.</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
</tr>
<tr>
<td>Bitumen 160/220 + 12 pbw LDPE/GTR/SBS 50:25:25</td>
<td>theo.</td>
</tr>
<tr>
<td></td>
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<td>Bitumen 160/220 + 2 pbw LDPE/GTR/SBS 25:50:25</td>
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<td>Bitumen 160/220 + 12 pbw LDPE/GTR/SBS 25:50:25</td>
<td>theo.</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
</tr>
</tbody>
</table>
Figure 1. Particle size distribution of GTR
Click here to download high resolution image
Figure 2. Melt viscosity of LDPE/GTR/elastomer blend measured at...
Figure 3. Penetration (at 25 °C) and softening point of bitumen
Click here to download high resolution image
Figure 3. Penetration (at 25 °C) and softening point of bitumen
Figure 4. Penetration index (PI) of bitumen modified with LDPE/G
Figure 5. Microstructure of: A - bitumen 160/220; bitumen with 1
Figure 5. Microstructure of: A - bitumen 160/220; bitumen with 1

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Figure 5. Microstructure of: A - bitumen 160/220; bitumen with 1
Figure 5. Microstructure of: A - bitumen 160/220; bitumen with 1
Figure 5. Microstructure of: A - bitumen 160/220; bitumen with 1
Figure 5. Microstructure of: A - bitumen 160/220; bitumen with 1
Figure 6. Loss tangent as a function of temperature plotted for:

- Bitumen 160/220
- + 2 pbw LDPE/GTR 50:50
- Bitumen 160/220
- + 2 pbw LDPE/GTR/SBS 25:50:25
- Bitumen 160/220
- + 2 pbw LDPE/GTR/SBS 50:25:25
Figure 6. Loss tangent as a function of temperature plotted for:

- Bitumen 160/220
- Bitumen 160/220 + 12 pbw LDPE/GTR 50:50
- Bitumen 160/220 + 12 pbw LDPE/GTR/SBS 50:25:25
Figure 7. TGA curves determined for used components and selected:

- LDPE
- Bitumen 160/220
- 2 pbw LDPE/GTR 50:50
- 12 pbw LDPE/GTR 50:50
- LDPE/GTR 50:50
- LDPE/GTR/SBS 50:25:25
- SBS
Figure 7. TGA curves determined for used components and selected blends. The graph shows the weight loss (%) against temperature (°C) for various samples, including Bitumen 160/220, LDPE, LDPE/GTR 50:50, LDPE/GTR/SBS 50:25:25, and SBS.
Figure 8. Schematic diagram of physical interactions between bitumen and tire rubber. The process involves mixing a thermoplastic phase, an elastomer phase, and ground tire rubber (GTR) to create a thermoplastic/GTR composition. This mixture then interacts with bitumen, leading to swelling of the modifier. High shear forces and temperature and time are applied to facilitate physical interaction on the phase boundary, resulting in modified bitumen.