Petroleum and Coal

Article **Open Access**

Bitumen Modified with Virgin and Waste Low-Density Polyethylene

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Received July 27, 2022; Accepted February 22, 2023

Abstract

The changes in the asphalt pavement technology have resulted in new technology, new highly improved products, but also in development of a new analytical tools and testing procedures. To improve the properties of asphalt mixtures the modification of bitumen is usually adopted as one of the most attractive strategies to achieve the desired properties of the used materials. The present study focused on the understanding the feasibility of adding the various polymer and/or by inorganic particles modified polymer to net bitumen. Physical tests, including penetration, softening point, and kinematic viscosity have been carried out to prove the effectiveness of modification on the binder properties. The effectiveness of blending process and the appropriate concentration of additives leads to a homogeneous polymer-modified bitumen without any aggregates in the structure. However, the most important result of this research article is the modification of bitumen using regranulated waste low-density polyethylene. The results of the work clearly demonstrate that, with properly selected reaction conditions, it is possible to incorporate recycled low density polyethylene into bitumen, which afterwards can be used in asphalt mixtures forming road structures. Such approach may lead to the meaningful use of waste plastics into new materials in the future.

Keywords*: Bitumen, Virgin and waste low-density polyethylene (PE-LD), Standard method, Microscopy technique, Blending process, Bitumen modification.*

1. Introduction

According to European Asphalt Pavement Association (EAPA) data, 90% of the more than 5 million roads in Europe are made from asphalt [1]. The main reason is that asphalt pavements have: great suitability for high traffic volumes, no impact for the subsoil, all-purpose and easy application in the inner city as well as on bridges, independence of the technology from the weather, lower noise level of the surface of new pavements made of asphalt, low cost of local and continuous repairs and last but not least higher number of contractors. However, in addition to the above mentioned advantages, asphalt surfaced roads have some undesirable characteristics. By far the most significant of these is the risk of permanent deformation (rutting). This is caused by the change in the properties of asphalt, which is the binder in asphalt mixtures, due to constantly increasing ambient temperatures. The combination of the effects of high ambient temperatures and high volumes of heavy traffic can significantly impair the serviceability of the road and thus road safety within a few days. The sensitivity of asphalt mixtures to surroundings temperatures (both plus and minus - frost cracking) is well known, and options for eliminating are constantly being sought.

It should be pointed out, that the term asphalt is often mistakenly used to describe bitumen. Asphalt is a mixture of aggregates, binder and fillers, used for constructing and maintaining roads, parking areas, ports, airport runways, bicycle lanes, sidewalks and also playgrounds and sport areas. It is produced in a plant that heats, dries and mixes initial materials (aggregate, sand and bitumen) into a composite mixture. Bitumen is the liquid binder that holds components together in the asphalt mixture. According to the historical notes, bitumen has been widely used from the earlier civilizations, such as Sumers and Assyrians. The beginning of the modern bitumen industry can be attributed to 1712 when bituminous stones were discovered in France [2]. At that time the preparation and layering technique was very simple, and the roads fell apart over time. Moreover, during the last decades, the number of vehicles as well as the traffic load has dramatically increased. All these factors can lead to the shortening the lifetime of pavements and increasing the cost of maintenance and risks to users. In order to decrease above mentioned effects it is necessary to improve the quality and performance of pavements. These concepts should be done by modification of the binder, which is bitumen. There are several chemical additives which can modify the binder and thus improved the physical-chemical properties of the binder. The most used additives are polymers. By accompanying the polymer molecules to the structure of bitumen we should prepare a so-called polymer-modified bitumen (PMB). The first bitumen reformation dates back to 1843. In the 1930s, experimental bitumen refinement project experiments were carried out in Europe, and in the 1950s, the use of Neoprene Latex, as bitumen modifier in North America, was begun [3]. In 1963, the first experimentally modified bitumen roads in France were made in order to understand the behavior of modified bitumen with various types of natural and synthetic rubbers [4]. Since their introduction PMBs´ have gained in importance and now they play a fundamental role in the field of road paving.

1.1. Chemistry of bitumen

According to the European specification (EN 12597) [5], bitumen is a practically non-volatile, adhesive and waterproof material obtained from petroleum or present in natural asphalt, which is completely or almost completely soluble in toluene and it is very viscous, or almost solid at ambient temperature [5]. Elemental analysis shows that the properties of the bitumen binder are primarily determined depending on the source of oil, properties of crude oil and distillation refining process, respectively.

Based on the Strategic Highway Research Special Report (SHRP) studies, the main elements are carbon, which ranges from 80 to 88 % by volume and hydrogen from 8 to 11% by volume. In addition, bitumen contains heteroatoms - sulfur, nitrogen and oxygen - and transition metal atoms, mainly vanadium (up to 2000 ppm) and nickel (up to 200 ppm) [6]. From a chemical point of view, bitumen is a complex mixture of approximately 300 to 2000 chemical compounds. The most and important are two groups of species: asphaltenes and maltenes [7].

Asphaltenes are amorphous brown, and/or black solids which contain oxygen, sulfur and transition metal atoms in the form of porphyrin rings of different length of aliphatic chains, pyrrole and pyridine rings. These large aromatic systems form large agglomerates / aggregates that are connected by intermolecular forces and π - π interactions. The resulting molecular aggregates form the so-called sandwich clusters and cause lower mobility of asphaltene molecules and thus significantly affect the viscoelastic properties and especially flexibility of bitumen. The proportion of asphaltenes in the bitumen ranges from 5 % to 25 % [8]. Due to the permanent electric charge and the presence of polar groups, together with polycyclic aromatic rings and metal complexes, asphaltenes contribute to the surface activity and adhesion of bitumen to aggregates.

Maltenes, which are responsible for adhesive properties, flexibility, and stiffness, form the second important fraction of bitumen structure. They contain lower molecular weight compounds, including resins, aromatic oils, saturated paraffins, respectively. Maltenes are soluble in low molecular n-alkane (n-pentane, n-heptane) [7].

1.2. Mixing of bitumen with polymer – principle of compatibility

An important parameter affecting the physical-chemical properties of bitumen is temperature. It has been proven that the effect of high temperatures and increasing traffic intensity can significantly impair the roadworthiness of a road in a few hours, and traffic safety consequently. From all the facts mentioned above follows that the main carrier of important mechanical properties in asphaltenous mixtures is bitumen. If we want to improve the condition of the roads, we clearly need to improve the properties of the asphalt binder, e.g. bitumen. There is a synergistic effect between the chemical structure - rheological properties - mechanical properties - usability of bitumen. Based on this synergy it is obvious that knowledge of the chemical structure is the base for understanding and the possibility of interactions with other components.

One of possibilities for improving the properties of bitumen and improving the adhesion of bitumen to aggregates and consequently to asphalt mixtures, is mixing with the polymer molecules. Since the introduction of polymer-modified-asphalts in the paving industry, researchers have attempted to use almost all available polymers as asphalt modifiers, including thermoplastics and reactoplastics [8]. On the other hand, the prepared and used PMBs should satisfy a number of requirements including mechanical properties, storage stability, high-temperature viscosity. The reasonable cost and environmental effect are the most important, respectively. From the huge amount of available polymers only a minor part of them are used for modification of bitumen and for industry applications. The most widely used is styrene-butadiene-styrene block copolymer (SBS) [9]. On the other hand, the polyethylene, and the high-, and low-density polyethylene blends are also very common additives in bitumen [8,10-13]. The polymers used in bitumen modification have a common characteristic: ability to form a physical network, which usually originates from the simultaneous presence of both crystalline - rigid and amorphous - flexible segments in their backbone. If the network is swelled by the asphalt molecules during the mixing phase without losing its main structure, it will become a determining factor for the binder properties. This is the main principle of the polymer modification of bitumen.

However, the use of chemically prepared, virgin and commercially available polymers raises another very important question. This aspect is related to the environment. The preparation and use of commercially available polymers increase the production of polymers and thus production of waste. Moreover, the price of the used virgin polymer is an another very important aspect. For this reason, the development in this field is moving towards the use of waste plastics. The use of recycled plastics instead of primary materials should help in easing landfill pressures, protecting environment and minimizing the consumption of original resources [14-18].

The main objective of our research work was to study the incorporation of virgin and recycled low-density polyethylene into the structure of bitumen and thus prepared the polymer-modified bitumen which should be used for preparation of asphalt mixture with polymers. The study focuses on analyzing the main properties of the prepared modified bitumen samples and on the morphology of the samples. Moreover, the studied virgin polymers were modified with inorganic particles (bentonites, zeolites and calcium carbonate) to improve the mechanical, physical-chemical properties of polymers and thus improve the properties of bitumen after mixing. The standard techniques together with special microscopy techniques were used to characterize the prepared polymer-modified bitumens. Our main idea is to find the appropriate reaction condition for the preparation of virgin and regranulated LDPE modified bitumen with enhanced properties.

2. Experimental

2.1. Materials

The neat bitumen and a polymer-modified bitumen meeting specification for performance grade (AC 50-70) and (PMB 45/80-70) were used in this study as a reference blank sample. The two bitumen samples from MOL group Hungary were obtained. These two bitumen samples represent the most common used bitumen in Slovakia as the main component of road construction material.

A commercially available low-density polyethylene (LDPE) from SLOVNAFT, a. s. Slovakia was obtained, modified with fillers or regranulated and used as a modifying agent.

For the preparation of modified PE-LD samples with inorganic particles the bentonite and zeolite were used, respectively. In table 1 are listed the main parameters of used inorganic particles.

Table 1. The selected physical-chemical properties and main characteristics of used inorganic particles for modification of pure or recycled PE-LD

Used inorganic particles	Locality	Particle size [mm]	Cation exchange capacity [meq.g^{-1}]	Specific surface area [m^2.g^{-1}]
zeolite KNI	Nižný Hrabovec	0-0.5	2.16	25.2
zeolite NaY*	-	0-0.5	3.55	421
bentonite (0 - 0.5 mm)	Lutila I, Slovakia	0-0.5	0.82	480
bentonite (0 - 0.063 mm)	Lutila I, Slovakia	0-0.063	0.94	502

**mixture of Na form synthetic Y zeolite and halloysite nanoclay ($Al_2Si_2O_5(OH)_4$) (30% wt.)*

2.2. Methods

2.2.1. Preparation of LDPE samples with inorganic particles

The polymer (based on low density polyethylene) was prepared with the addition of fillers such as natural zeolite-clinoptilolite, synthetic zeolite NaY and bentonite. All potential fillers are from domestic sources and their selection was made according to available literature data. The identification of the appropriate concentration of the filler as well as the fraction of the powder filler for LDPE was carried out. The starting additives were ground in a vibratory disc mill to a grit size of (0-0.5) mm and (0-0.063) mm, respectively, and dried at 80°C for about 14 h before use. Subsequently, 5 kg of each sample were prepared on a lab size twin-screw extruder. The addition of additives caused a sensory (colour) change in the polymer.

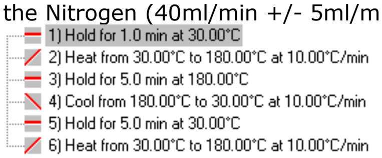
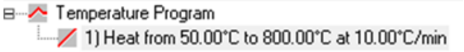
The aim was to prepare polymers to identify the appropriate concentration of the filler as well as the fraction of powder filler for LDPE. Initially, the changes on virgin LDPE and then on waste regranulated LDPE after modification with filler (zeolite, bentonite) were analysed and rheological and thermal parameters were evaluated. The list of prepared samples is described in Table 2. The range of analyses that were carried out for all samples is shown in Table 3.

Table 2. Identification of tested polymer samples - marking and composition of all used polymer samples in this research study

Sample marking	Composition
Sample No 1	LDPE + 5 % natural zeolite clinoptilolite
Sample No 2	LDPE +5 % bentonite semi-activated, grain size: (0-0.5) mm
Sample No. 3	LDPE +5 % bentonite semi-activated, grain size: (0-0.063) mm
Sample No 4	LDPE + 5 % synthetic zeolite NaY (13Y)
Sample No 5	LDPE + 5 % $CaCO_3$
Sample No 6	LDPE waste regranulated which could represent the ideal 100% one-component recycled polymer
Sample No 7	LDPE virgin polymer

Preparation of modified bitumen with LDPE (pure, waste regranulated LDPE and pure LDPE with the addition of fillers - based on zeolites and bentonites)

Table 3. Range of analyses that were carried out on polymer samples

Property	Testing method	Unit	Short description of analysis and used device
Melt mass flow rate,190°C/2.16kg	STN EN ISO 1133-1	g/10min	Device: melt indexer Dynisco LMI 5500 Principle: amount of material in grams flowing out of specific nozzle under specified conditions of temperature and load. (190°C/2.16kg)
Crystallization temperature	STN EN ISO 11357-3	°C	Device: DSC 8000 Perkin Elmer Principle: determination of temperature and enthalpy of melting and crystallization of partially crystalline plastics by differencial scanning calorimetry with pro grammed heating and coling cycle under the Nitrogen (40ml/min +/- 5ml/min)  1) Hold for 1.0 min at 30.00°C 2) Heat from 30.00°C to 180.00°C at 10.00°C/min 3) Hold for 5.0 min at 180.00°C 4) Cool from 180.00°C to 30.00°C at 10.00°C/min 5) Hold for 5.0 min at 30.00°C 6) Heat from 30.00°C to 180.00°C at 10.00°C/min
Melting temperature	STN EN ISO 11357-3	°C	
5% weight loss	PP SIV 0216*	°C	
10% weight loss			
Decomposition temperature			Device: TGA 4000 Perkin Elmer Principle: determination of decomposition of polymers - weight loss in dynamic mode (mass change versus temperature or time under programmed temperature conditions) by thermogravimetry under the nitrogen (20mL/min +/- 5mL/min)  Temperature Program 1) Heat from 50.00°C to 800.00°C at 10.00°C/min
Ash content	PP SIV 0202*	% (m/m)	Device: Microwave oven Phoenix airwave Principle: weighing the residue after combustion of prescribed amount of polymer
Rheological curves			Device: Rheometer 5000 Ceast Principle: At constant temperature (190°C) melted polymer is loaded with a piston with a step-varying rate, while the pressure arising an individual load is recorded. As a result is rheological curve - shear stress and viscosity as a function of shear rate.

* *Internal method VÚRUP, a.s.*

To prepare the modified bitumen the base bitumen was heated to 165°C and blended with the inorganic particles, e.g. bentonite and zeolite using shear mixer at a rate of 1500 – 2000 rpm for 90 minutes. The inorganic particles were blended with the base bitumen at the concentration 6 wt. %. After homogenization process, the modified bitumen samples were filtered through a sieve to remove any undissolved modifier residues. The marking of all used samples with composition is listed in Table 4.

Table 4. The marking and composition of all used samples in this research study

Binder description	Composition
A1	AC 50/70
A2	PMB 45/80-75
A3	A1 + virgin PE-LD
A4	A1 + PE-LD – zeolite KNI
A5	A1 + PE-LD – zeolite NaY
A6	A1 + PE-LD – bentonite (0 – 0.5 mm)
A7	A1 + PE-LD – bentonite (0 – 0.063 mm)
A8	A1 + PE-LD – $CaCO_3$
A9	A1 + regranulated PE-LD

2.2.2. Methods of analysis

The standard test methods of net bitumen AC50/70, PMB 45/80-70 and modified bitumen were carried out. The penetration according to the EN 1426 and softening point according to the EN 1427 was determined, respectively.

The rotational viscosimeter (DV-III, Brookfield, Harlow, UK) was used to investigate the kinematic viscosity. Even though the rotational viscosimeter test can be conducted at various temperature, according to the literature data, recommendation and according to the EN 12595 measuring binder viscosity and modified bitumen viscosity at 135°C was performed.
Microscopic methods using a scanning electron microscope (SEM), Tabletop Scanning Electron Microscope TM4000Plus (Hitachi High-Tech Corp., Japan) and an energy dispersive X-ray spectrometer (EDX) attached to SEM, AZtecOne (Hitachi High-Tech Corp., Japan) were used to assess the homogeneity of the prepared modified asphalts.

3. Results and discussion

3.1. Preparation and characterization of commercially available LDPE and LDPE modified with inorganic particles and waste regranulated LDPE samples

All LDPE based samples were prepared from pure/virgin commercially available pellets by adding 5% of specific filler (which was dried at 80°C for 14hours in the oven) and mixing altogether in plastic bags by shaking it several minutes. Then pellets with evenly distributed filler on the surface of pellets were processed by lab size twin screw extruder to prepare final samples listed in Table 2. Regranulated LDPE (Sample no 6, Table 2) was prepared by extrusion the waste LDPE without adding any filler. After the preparation of the modified polymers, analyses were carried out for further characterization of mainly rheological properties. Selected rheological parameters such as melt mass flow rate and rheological curves were determined, thermal properties were investigated by DSC and TGA methods. The results of analyses that were carried out for all samples are shown in Table 5 and Figure 1 and 2.

Table 5. The selected physical-chemical parameters of commercially available LDPE and LDPE modified with inorganic particles and regranulated waste LDPE polymer samples used in this study

Property	Test method	units	sample						
			no 1	no 2	no 3	no 4	no 5	no 6	no 7
Melt mass flow rate (MFR)190°C/2,16 kg	STN EN ISO 1133-1	g/10 min	1.68	1.65	1.59	1.53	1.67	1.86	1.89
Crystallisation temperature	STN EN ISO 11357-3	°C	96.9	97.0	96.5	96.9	97.2	96.7	95.7
Melting point	STN EN ISO 11357-3	°C	111.1	111.2	110.7	111.4	110.3	111.5	110.4
5 % weight loss	PP SIV 0216	°C	408.2	410.6	412.8	402.7	420.5	427.4	425.1
10 % weight loss	PP SIV 0216	°C	428.3	429.0	431.1	421.0	435.2	442.7	439.8
Decomposition temperature	PP SIV 0216	°C	448.2	446.3	447.1	438.8	448.0	454.6	452.9
Ash content	PP SIV 0202	% (w/w)	4.58	5.12	4.40	5.51	3.15	0.00	0.00

The addition of inorganic fillers to the primary polymer causes a decrease in the melt flow mass rate comparing to the pure/ virgin LDPE as well as differences in decomposition temperatures as assessed by TGA analysis. These differences may be due to the specific properties of the fillers and their particle size distribution over the polymer matrix or content of other contaminants. The melting and crystallization temperatures are at the comparable level – not even big differences between pure/virgin LDPE and waste regranulated LDPE which refers to great thermal stability and very good predisposition for repeated usage with maintaining great properties of origin pure/virgin LDPE material. Taking into account the discrepancies caused by not perfect dosing of fillers into the pellets of LDPE samples and their consequent extrusion the homogeneity of the prepared granulates (the ash content as inorganic fraction of unburnt residue after calcination) at the selected LDPE dosage of 5 % (w/w) is at an acceptable level.

Graphical plots of the rheological properties of the individual polymer matrices are shown in Figure 1 and in Figure 2 some selected rheological curves with the biggest differences in rheological properties.

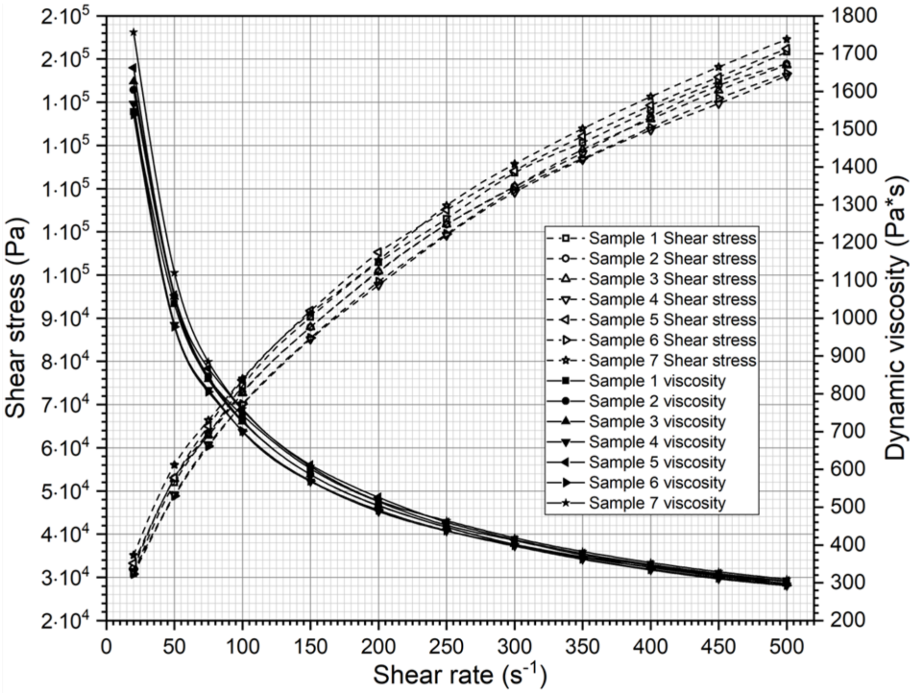


Fig. 1. The rheological curves of commercially available LDPE and LDPE modified with inorganic particles and regranulated waste LDPE samples used in this study

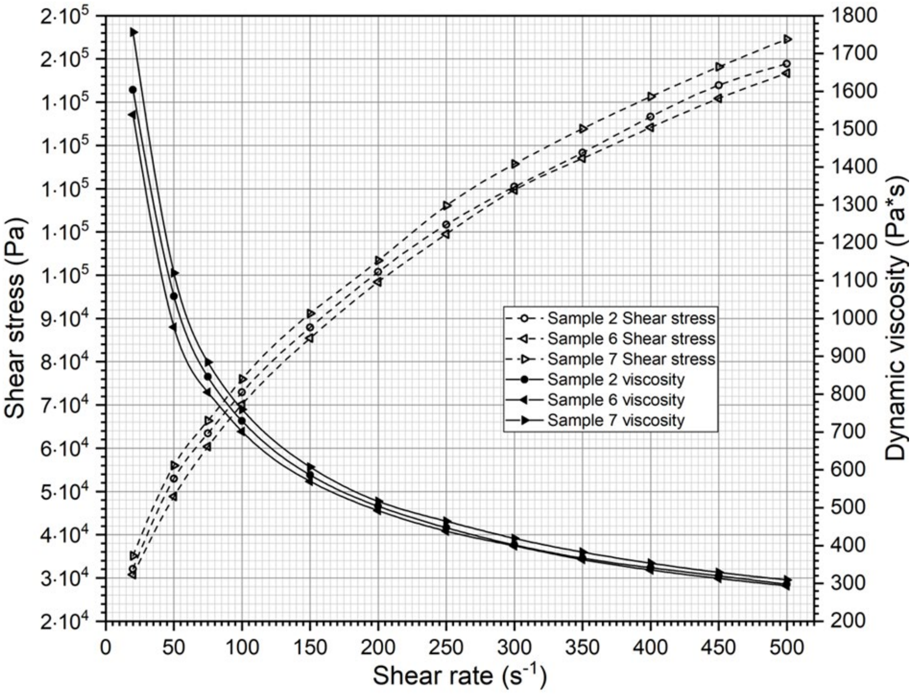


Fig. 2. The rheological curves of selected polymer samples

The rheological properties indicate a slight increase in shear stress of the filled polymers compared to the primary natural polymer or its regranulate with increasing shear rate. At higher shear rates the filled samples show comparable viscosity values no matter of what filler was used.

3.2. Softening point of studied bitumen samples

As it was described above bitumen is a viscoelastic material without sharply defined melting points; gradually becomes softer and less viscous as the temperature rises. The softening point helps in the determination of the temperature beyond which the bitumen is softened - a pre-specified softness. In the Table 6 are listed the softening points of the studied systems. For comparison, the values of the neat bitumen and commercially available polymer-modified bitumen (samples A1 and A2) are also given. The measured results show the change in softening point values compared to the blank bitumen. For all samples, there was a change in the temperature of the softening point but not as significant as the commonly used polymer-modified asphalt (sample A2). It should be noted that this bitumen is modified by styrene-butadiene-styrene copolymer and not LDPE modified. The softening point values do not differ significantly between the different samples, from which it can be concluded that the inorganic fillers (in our case zeolite and bentonite) do not have a significant effect on the values determined. Chemically, both materials are aluminosilicates but are different in chemical and/or crystallographic structure. While zeolites have a three-dimensional crystalline structure, inside which there are channels, bentonites have a layered structure, between the layers there are hydrated cations, which can adsorb water and various polar and non-polar substances, thus increasing their volume many times [19]. However, according to our results, in this case the crystalline structure of the additive does not have a significant effect on the final properties of the modified bitumens. Very interestingly the bitumen modified with regranulated LDPE sample (A9) has shown higher value of softening point. For our opinion this result indicates that the regranulated LDPE sample should be a very good modificator for bitumen. This result is of high value from the technological point of view and it also will have a good economically impact.

Table 6. The penetration values, softening points and viscosity of studied systems

Binder description	Penetration value [mm]	Softening point [°C]	Viscosity at 135°C [Pa.s-1]
A1	54.5	50.8	539.1
A2	73.8	76.4	1745.5
A3	42.5	58.6	1944.7
A4	36.9	57.6	1830.3
A5	40.8	58.7	1585.1
A6	15.6	60.7	1604.2
A7	43.1	57.2	1799.1
A8	40.1	52.3	2548.3
A9	43.8	58.7	2249.3

3.3. Penetration of studied bitumen samples

In general, penetration is a measure of consistency or hardness of a bitumen and is the most common control test for penetration grade bitumen. The Table 6 shows the effect of the prepared inorganic particles-modified polymer samples and regranulated polymer on the penetration value of the binder. It is notable that the adding of the polymer or modified polymer leads to the significant reducing in penetration value in all cases. In our study we used the polymer content of 6 weight % according to the literature data, but in our experiments, we also studied the addition of 2, 4 % of polymer content to pure bitumen. Our results (not shown in this article) clearly showed a decrease in penetration values, respectively. On the other hand, the adding of less polymer as 6 weight % leads to a smaller reduction in viscosity. Our goal is to add as much polymer or modified polymer as possible until the system reaches saturation degree. Although the differences are not significant, in this case the LDPE modified binders with the addition of zeolites show lower values than the LDPE binders with the addition of bentonites.

In accordance with the measured value of softening points we can conclude that the regranulated polymer sample has a very good effect to the penetration values. We can conclude that these results clearly confirm that regranulated waste polymer can improved the physical-chemical properties of bitumen.

3.4. Kinematic viscosity of studied bitumen samples

Viscosity is a very important parameter for assessing the suitability of an addition to asphalt binders. Based on the measured values, it is possible to obtain the quantities necessary for the evaluation of the rheological properties of used bitumen. The viscosity can be defined as the ratio of shear stress applied to the rate of shear strain. It is measured in Pascal seconds. Data on the measured viscosity values are given in Table 6.

Moreover, this parameter is also important from the point of view of both the use and storage of bitumen, since viscosity is a property that characterizes the dynamics of the internal movement of the substance and, in the case of asphalts, mainly influences their storability and workability. The resistance to movement is due to the internal friction of the fluid, which is dependent on the boundary conditions (temperature, mode of stress). The measured values clearly show that the asphalt binder has been modified. While the viscosity value for road asphalt is only at 539.1 Pa.s^{-1}, the values have increased significantly in the case of modification. On the basis of these data, we can conclude that the pure LDPE polymer as well as LDPE modified with zeolite and bentonite-based additives significantly affected the rheological properties of the road asphalt. Thus, we have shown that the systems of asphalts modified in this way are very similar to those of standard polymer-modified asphalt (sample A2). Based on the measured values, all our prepared samples behave as asphalt binder modifiers and the resulting systems exhibit all the characteristic features of viscoelastic systems.

3.5. Microstructural characterization of studied bitumen samples

As previously mentioned, the chemical and/or physical-chemical modification of bitumen with polymers, especially with the waste or recycled polymers is still under investigation and not completely understood, therefore for the better investigation and for the overall view for the problems the microstructural changes the pure, commercially available PMB and modified bitumens were analyzed by SEM and EDX analysis. The SEM photographs of some selected systems are shown in the Figure 3. All samples allocate a homogenous surface with a smooth zone. There were not identified any impurities or other zones where ideal mixing of components would not occur or in other words heterogeneous phases would occur.

The SEM image for pure bitumen shows a very homogenous structure of the surface. The inserted image is the image of the same sample but recorded at different magnification. We can really observe the inner structure of the organic chain molecules of bitumen. On the other hand, the commercially available PMB bitumen (denoted as A2) shows a small irregular particles pattern. We can observe the small irregularities or so-called islands on the left side the SEM image. In contrast, images bitumen of zeolite and bentonite modified bitumen with LDPE (A4 and A7) displays a regular circle around the sample particles. The EDX measurements (results not shown here) have identified a small amount (around 3 – 5 %) of silicon and aluminium atoms. There should be from the inorganic particles. Very interesting features were observed on the SEM images of the bitumen modified with LDPE with $CaCO_3$ (sample A8) and the bitumen modified with the regranulated polymer sample (A9). A regular homogenous inner structure is observed in both cases, respectively. We can conclude that the blending process was successful, and the polymer chains are very homogenously dispersed in the bitumen structure.

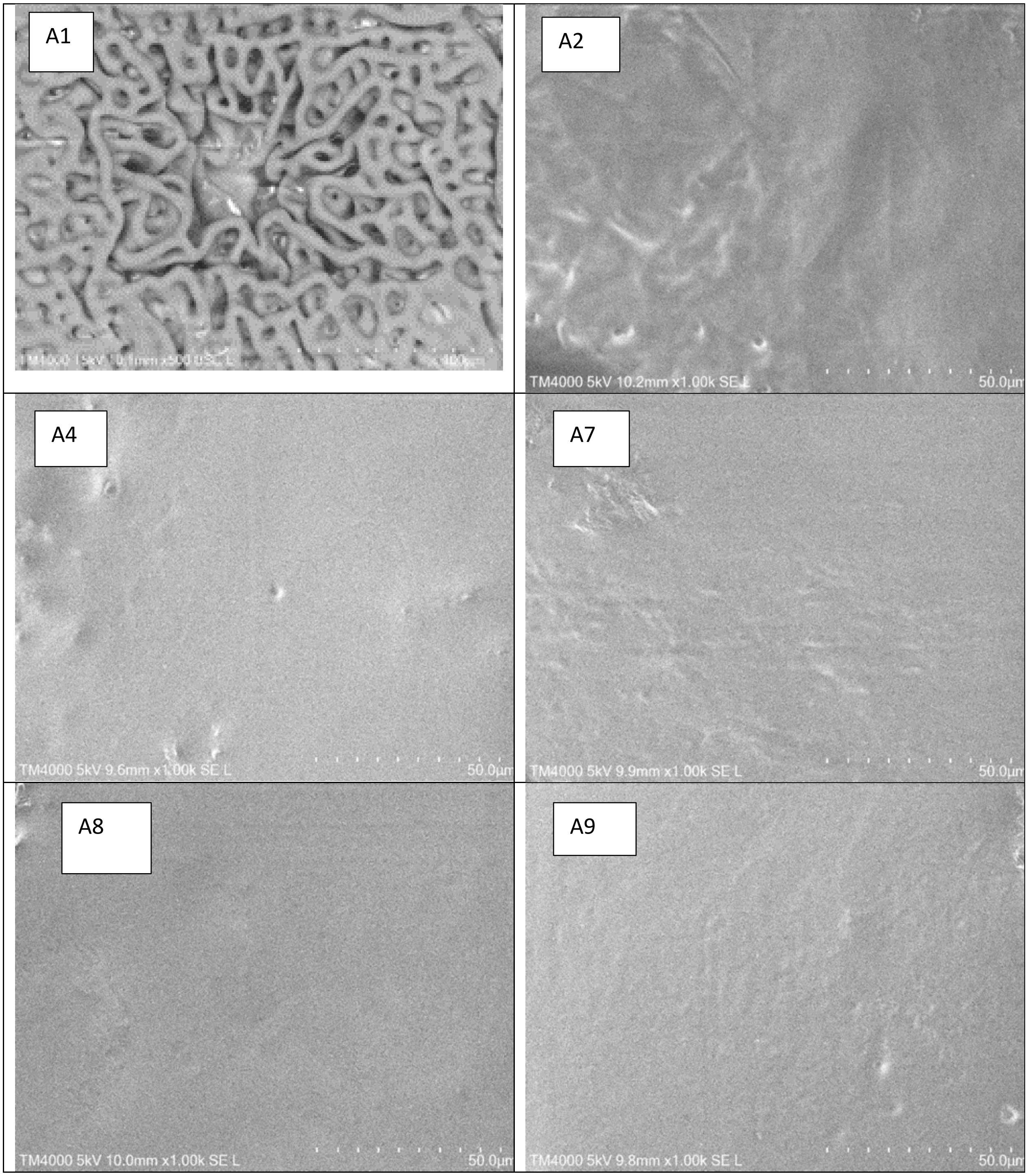


Fig. 3. The SEM micrographs of selected samples

4. Discussion

In this research study the LDPE was chosen as a polymer modifier to bitumen. In general, it has a highly saturated aliphatic nature, tends to be insoluble in asphalt even at high temperatures and will form two separate phases. It should be pointed out that it has the lowest solubility out of the whole polyolefin group.

Polymer-modified bitumen is a binder obtained by the incorporation of various types of polymers in bitumen using simple mechanical mixing or by chemical reactions. This process is not a simple process, this is not just the preparation of solution of bitumen and polymeric chain. The main idea of this process is the principle of compatibility. In our study we rely in a colloidal model of bitumen. Basically it means that bitumen must contain a sufficient amount of oily fractions to swell the polymer. It must also contain a high content of condensed components (aromatic hydrocarbons are often condensed and very well miscible, especially with polar aromatic polymers), in order to guarantee the resistance of the mixtures. Taking into account the types of the used polymer, they must have an ability to form a physical network, which in turn originates from the presence of both rigid (below glass transition temperature or crystalline) and flexible chains. The ideal situation is obtained if the polymer chain remains (internal structure) intact after mixing with bitumen the molecules of which determine only a macroscopic swelling. If the network is swelled by the asphalt molecules during the mixing phase without losing its main structure, it will become a determining factor for the binder properties. Moreover, the interaction between polymer chain and bitumen is obviously dependent on the chemical affinity of the interacting compounds.

Therefore, in our study we used the very common, commercially available bitumen with grade 50/70 which is one of the most used and characterized bitumen in Slovakia. As it was mentioned there are several factors affecting the properties of polymer-modified bituminous composite materials, such as; chemical composition of bitumen, type of polymer and filler, compatibility of bitumen and polymer, amount of bitumen, polymer and filler, particle size of filler and process conditions.

Moreover, our main idea in the future is to study the incorporation of recycled polymer material to bitumen and to find the optimal reaction conditions for mixing of bitumen with waste plastics. Fuentes-Audén *et al.* [20] have reported the challenges associated with using recycled polymers as binder modifiers, as the recycling process will inevitably lead to a loss in mechanical properties of the polymer. They investigated the rheology of binders incorporating large amounts (up to 40%) of recycled plastic and found these blends to be thermodynamically incompatible. Ho *et al.* [21] investigated the use of recycled low-density polyethylene with polyethylene/wax and found that polymers with lower molecular weights tended to disperse more evenly within the asphalt binder but again focused on rheological behavior of the modified binder. In general at low polymer content, the small polymer spheres swollen by bitumen compatible fractions are spread homogeneously in a continuous bitumen phase. By increasing polymer content, a continuous polymer phase may be obtained. The minimum percentage of polymer to ensure the formation of its continuous phase depends on a great extent of the base bitumen, the polymer itself and its ability to swell with maltene molecules [22]. Polymer stabilization can be achieved by mechanical dispersion of the modifier, swollen by compatible components in the maltene fraction. It is well known that the polymer may dissolve and/or disperse into maltene medium enhancing the mechanical properties of mixtures [23].

Our result was based on the study of incorporation of commercially available LDPE and by inorganic particles modified LDPE into bitumen on the one side and the study of regranulated waste LDPE into bitumen on the other side. The results from the first part are very useful and were chosen as a blank sample. But the main idea is to find a reaction conditions and parameters for incorporation of recycled polymer based on LDPE.

The addition of some types of fillers/ nanoparticles were chosen as a way to improve the affinity of LDPE to bitumen. By simply mixing the two components of polymer and bitumen, we will be not able to prepare the mixture needed for ideal mixing into the final mixture. In our project we consider the use of clay minerals, e.g. bentonites and zeolites. They consist of plates with a thickness of approximately 1 nm and exhibit unique physical-chemical properties; such as swelling properties, high specific surface area and adsorption of various substances. In this case, we do not consider the use of nanoparticles as a filler, but based on our experience, we consider binding this nanoparticle to the polymer before mixing. Such an interaction would improve the properties of the polymer, especially the polymer would gain a greater degree of freedom, which would in turn affect its swelling in bitumen, therefore gaining greater adhesion to the aggregate. In addition, we assume that these nanoparticles, in addition to improving the properties, should allow control of the rheological properties of bitumen.

In all studied parameters there were identified the improving the physical-mechanical-chemical properties. Our results show improving of the studied parameters although there was identified only a small change. On the other hand, the inorganic particles have a high impact on the viscosity of the studied systems. This should be a good research study in a future how to control the viscosity of the bitumen.

Very interesting feature were found out for incorporation of regranulated LDPE. In all studied parameters improvement was observed. When using of recycled plastics, the physical-chemical properties may differ from those of synthetic/commercially available polymers. These differences in quality add even more variables to the overall process mechanism and can have a major impact on the use of recycled plastic, the technological process, and the quality of the resulting bitumen/recycled polymer materials. Our results clearly show the homogenously incorporated regranulated waste LDPE which could represent the ideal 100% one-component recycled polymer to the inner structure of bitumen. The mechanical properties allocate also an improving tendency. We can conclude that using this simple methodology we are able to incorporate a recycled polymer to the bitumen and thus decrease an amount of the recycled waste polymer. Our future work is related to the preparation of asphalt mixture with the modified bitumen studied in this system.

5. Conclusions

Modification of bitumen can enhance the proportion of conventional, commercially available and used bitumen. This process can serve several purposes, which are of economical, technological and environmental importance. First of all, it can increase the overall performance of a bitumen by widening the range between the bitumen´s high and low-temperature grades or it can be useful for improvement in a bitumen´s performance in response to a service condition.

On our study we used several bitumen samples which were modified by polymer (LDPE) and inorganic particles. Moreover, we applied our procedure also for a modification of bitumen with a regranulated LDPE sample which could represents the ideal 100% one-component recycled polymer. For a polymer to be effective in the practical applications it should properly blend with bitumen to produce a homogenous mixture to improve the physical-chemical and technological parameters. Our result clearly showed the possibility to use all studied systems. We can conclude that any material which changes the chemical structure of bitumen consequently changes the properties of bitumen, and as a result, it can be a modifier. Ideally, modified bitumen has more adhesion than pure bitumen and lower thermal sensitivity in the range of service temperatures which is a very important finding from the technological point of view.

The main goal of our research study was to find a suitable recycled polymer sample which should be also useful for modification of bitumen. Our measured parameters of all modified samples with pure bitumen – especially with the regranulated LDPE – have shown a very similar or improved features as pure bitumen respectively commercially used PMB. Our results clearly show the modification of bitumen with regranulated LDPE sample, which opens the way to use of recycled materials in asphalt materials as a modifier. Usage such type of modifier will not be only cost-effective, but moreover will have a positive environmental effect.

Acknowledgements

This work was supported by the Slovak Research and Development Agency under the contract No. APVV-19-0520.

Conflict of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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