

Effect of Different Types of Plasticizers on the Properties of Elastomeric Blends Filled with Biopolymer

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Abstract

The oil derivatives plasticizers are commonly used to achieve better processing and the desired properties of elastomeric blends. Plasticisers based on oil derivatives have a negative impact on the environment due to their production and application. For the above reasons, research has been focused on finding the alternatives of conventional plasticisers, namely from renewable sources. The aim of the study was to determine the impact of sustainable plasticizers on the properties of elastomeric blends based on natural rubber (NR) filled with cellulose (CEL). The effect of low-content polycyclic aromatic hydrocarbon plasticizers – RAE (residual aromatic extracts) and MES (slightly extracted solvate) compared with natural oil plasticizers – linseed oil (LO), rapeseed oil (RO) was investigated. Vulcanisation characteristics, rheological, and physical–mechanical properties were studied for prepared NR/CEL blends with different types of plasticisers. Based on the obtained results, NR/CEL blends with LO showed comparable values to the conventional plasticisers. In the case of blends filled with bio-fillers, it is possible to eliminate an ingredient based on petroleum products in order to preserve the possibility of biodegradation.

Keywords

Natural rubber, Bio-fillers, Cellulose, Plasticiser

Introduction

Depending on the diversification properties of polymer materials, their demand on the market is constantly increasing. The monomer as well as architectural organization of macromolecules decide the dominating properties of the polymers. The high prices of petroleum-based polymers, the scarcity of the raw materials, their nonbiodegradable nature, the significant amount of greenhouse gas emission as well as their cancerous harmful components it represents big environmental problems. From the given reasons, more and more scientists are interested in the use of biopolymers or by preparing biodegradable polymers with the required properties, that can be degrade biologically [1].

Natural oils are obtained from plants, i.e., vegetables, fruits, seeds and nuts, animal fats, but also from other organic materials (except oil, minerals and hydrocarbon-based substances). Natural oils can be produced in various ways and methods used in the field of vegetable oil processing. From a chemical point, vegetable oils are ester compounds and consist of glycerol molecules linked to three saturated and/or unsaturated fatty acids (triglycerides) [2]. Obtaining and using materials from biological products, such as vegetable oils, animal fats and extracts from plant products in the production of polymeric materials, represent an alternative option to reduce the high demand for fossil raw materials in the production of polymeric materials and prevent the pollution that would result

from their disposal at the end their lifespan [3, 4]. Consequently, many attempts have been made to use various vegetable oils including their derivatives such as coconut oil [5], castor oil [6] sunflower oil [7], palm oil [8, 9], and soybean oil [10]. Most research dealing with the utilization of natural processing oils has been carried out in carbon black filled rubbers. Little attention is given to cellulose-filled NR blend and bio-fillers.

This research aims to study vulcanisation characteristics, rheological and physical-mechanical properties of elastomeric blends consists of natural rubber (SMR 10) and cellulose blends (bio-filler) mixed with two vegetable oils (linseed oil, rapeseed oil) compared to petroleum-based oils (residual aromatic extracts, slightly extracted solvate) with the same content in blend.

Materials and Methods

Materials

Natural rubber type SMR 10 (Kuala Lumpur, Malaysia) was used as matrix for all prepared blends. Cellulose (Bukóza Invest, Hencovce, Slovak Republic) was used as filler in blends. Zinc oxide (Bayer, Kuala Lumpur, Malaysia) and Stearic acid (Setuza a.s., Ústí nad Labem, Czech Republic) were used as activator of vulcanization process. Flavex 595 B – RAE (Shell, Chennai, India), Paramil MES-15 (Paramo, Pardubice, Czech Republic), Linseed oil (Novochema, Levice, Slovak Republic) and Rapeseed oil (Cargill, Wayzata, United States) were used as plasticizers. As crosslinking agent was used sulfur (Bayer, Kuala Lumpur, Malaysia) and sulfur curing accelerator was used N-tert-butyl-2-benzothiazole sulfonamide - TBBS (Duslo a.s., Šaľa, Slovakia).

Preparation of elastomeric blends with different types of plasticizers

For preparation of blends were used laboratory mixer Plastograph Brabender type with chamber volume 80 cm³ and 50 revolutions per minute (Brabender, Duisburg, Germany). All elastomeric blends were prepared at 55 °C in one stepsat. For easier manipulation of the filler and its dosage, the filler was modified using a pressing process at 110 °C with pressure 200 kN at 4 minutes. To ensure the possibility of mutual comparison of plasticizers was prepared elastomeric blends with same content of plasticizers. Elastomeric blends were homogenized by using laboratory twin roll VOGT LaboWalz W 80 T I in order to obtain better homogeneity (VOGT, Berlin, Germany). Before another processing procedure, the blends

were left for 24 hours at laboratory temperature of 25 ± 2 °C. The specification of all prepared blends is given in table 1.

Rheological properties and vulcanization characteristics

The rheological properties and vulcanization characteristics were determined by using RPA 200 (Alfa Technologies, Akron, OH, USA). From prepared slabs, the samples were cut to the needed shape for rheological measurement by using Cutter 2000 (Instron Ltd., HighWycombe, UK). For protection of testing chamber and rotor was used a cellophane film. All tests were performed for uncured elastomeric blend at 150 °C with frequency of 1.66 Hz at 20 minutes and 5% oscillation.

Hardness shore A

The hardness of the elastomeric blends was determined by using hand hardness tester with Shore A scale (Wallace LTD, Croydon, UK). Measurement of each sample was performed 5 times, and the results were statistically evaluated. All samples were measured according to ASTM [11].

Mechanical properties

Mechanical properties of the prepared blends with a cellulose were measured on a tensile tester machine Shimadzu AG-X Plus (Shimadzu, Tokyo, Japan) with the two pneumatic clamping jaws. The samples were prepared for tensile test by using Instron cutter machine (Instron, Norwood, MA, USA) in shape of dumb-bell type II (ISO 37, ASTM D 412). Speed of tensile tests was determined at 100 mm min⁻¹.

Results and Discussion

Rheological properties and vulcanization characteristics

Measured values of rheological properties of prepared blends with different type of plasticizer are in table 2. The first described properties are minimum and maximum torques. The lowest torque in the vulcanization curve and it is equal to viscosity of the blend heated to vulcanization temperature – this torque value characterizes the blend stiffness. Highest torque in the vulcanization curve is a maximum torque and it is equal to the value of the shear modulus of the vulcanized blend at the given temperature. Maximum torque value characterizes the stiffness at the end of vulcanization [12].

In table 2, it can be seen values of minimum (M_{min}) and maximum torque (M_{max}) for elastomeric blends with different type of plasticizers in blend as well as the standard blend

Table 1: Specification of prepared blends.

Component Blend type	Rubber (phr)	Cellulose (phr)	Crosslinking agent – sulphur (phr)	Plasticizer (phr)			
				RAE	MES	LO	RO
NR/W	100	45	2.7	-	-	-	-
NR/RAE	100	45	2.7	4.3	-	-	-
NR/MES	100	45	2.7	-	4.3	-	-
NR/LO	100	45	2.7	-	-	4.3	-
NR/RO	100	45	2.7	-	-	-	4.3

without plasticizer (NR/W) for mutual comparison of results. The highest value of the minimum torque was detected for NR/W blend, the reason being that the given blend did not contain a plasticizer that would reduce the resistance to flow (viscosity) and thus blend reached the highest stiffness value at the beginning of the vulcanization process. By adding plasticizers to the blend, a reduction of the viscosity of the matrix was achieved, which improves the flow of the matrix around the filler fibres under stress. The minimum torque thus corresponds to the stiffness of the blend at the beginning of the vulcanization process, and according to its value compared to the NR/W blend, it is therefore possible to determine the plasticizing effect of the used plasticizers. The plasticizer with the best plasticizing effect reached the lowest minimum torque value, in this case the RAE plasticizer. RAE plasticizer contains residual aromatic substances that are characterized by interference with free radicals. In case of mixing elastomeric blend, the rubber chain breaks, and it leads to formation of radicals with aromatic components in the RAW plasticizer readily react [13]. Other types of plasticizers (LO, RO, MES) were reached an almost identical M_{\min} value, and thus their plasticizing effect in the case of the same composition of the blend is identical.

Another monitored parameter was the maximum torque (M_{\max}). The highest M_{\max} value and thus the highest stiffness at the end of the vulcanization process (stiffness of the vulcanizate) was achieved for the blend without plasticizer. By absence of a plasticizer was increased viscosity of the blend as well as reduced gaps between matrix chains, which increases the resistance to creep under stress and manifests itself in a higher M_{\max} value. Blends with linseed oil and RAE plasticizer were reached a comparable M_{\max} value. The NR/RAE blend was achieved the lowest M_{\max} value, due to the already mentioned best plasticizing effect of the plasticizer (M_{\min} value). The blend with LO content was reached a value of 0.43 dNm higher comparison with NR/RAE blend. Thus, the NR/LO blend has a slightly higher stiffness compared with NR/RAE. The NR/LO blend was showed a higher M_{\min} value and therefore a higher stiffness value of the blend at the beginning of the vulcanization process, which indicates a lower plasticizing effect compared to the RAE plasticizer. A lower plasticizing effect of the plasticizer will cause a higher stiffness value in the case of a cross-linked blend. Interestingly, the blend containing linseed oil plasticizer was achieved the lowest difference between M_{\max} and M_{\min} . In the case of NR/MES and NR/RO blends, the plasticizing effect of the plasticizers used is demonstrated on the M_{\max} values. The NR/MES blend was achieved the highest M_{\max} value among the blends containing plasticizers, by this value can indicate a poor interaction of the plasticizer with the matrix and can lead to extrusion of the plasticizer from the matrix of the unvulcanised blend and thus additionally increase the M_{\max} value.

Table 2: Rheological properties and vulcanization properties of prepared blends.

Blend type	M_{\min} (dNm)	M_{\max} (dNm)	t_{90} (min)	t_{02} (min)
NR/W	3.00	29.87	6.15	12.17
NR/RAE	1.54	26.45	5.67	11.23
NR/MES	2.17	28.20	7.88	13.87
NR/LO	2.01	26.83	5.85	11.15
NR/RO	2.19	27.13	7.18	12.83

In table 2, it is possible to see values of optimum cure time (t_{90}) and scorch time (t_{02}) for elastomeric blends with different type of plasticizers in blend as well as the standard blend without plasticizer (NR/W). In the case of view of scorch time, it is interesting that the blend without the plasticizer did not reach the highest nor the lowest value. Adding RAE type plasticizer to the blend, resulted in a decrease of scorch time and this blend reached the lowest value of scorch time among the blends containing plasticizers. The lowest value and thus the fastest onset of vulcanization can be attributed to the fact that RAE plasticizer contains aromatic hydrocarbons that can interact with free radicals during the vulcanization reaction, while aromatic groups are not found in vegetable oils [13]. Among the blends containing a plasticizer, the blend containing a plasticizer of the MES type has the highest value. An increase in vulcanization characteristics in the case of blends containing plasticizers usually indicates the incompatibility of the selected plasticizer with respect to the matrix of the blends [14]. The blend containing natural linseed oil achieved a slightly higher scorch time value than the NR/RAE blend (difference 0.18 min). This value can be attributed to the content of stearic acid in the linseed oil plasticizer, which together with ZnO during the vulcanization process forms an activator of sulfur vulcanization [15]. In the case of a blends containing rapeseed oil and MES plasticizer were recorded an increase of scorch time and this increasing of values indicates the incompatibility of the plasticizers with the matrix of blend. Rapeseed oil contains more acid compared to linseed oil (the acid content prolongs the vulcanization reaction). The values of the optimal vulcanization time have the same trend as in the case of scorch time, with the difference of the lowest value. The lowest value was achieved for the NR/LO blend. The lower value of t_{90} in the case of using linseed oil can be attributed to the content of stearic acid in the plasticizer. By increasing the stearic acid content (added raw material as well as content in linseed oil) can be accelerate the reaction with ZnO and the formation of zinc stearate – an activator of sulfur vulcanization [15].

Hardness shore A

Measured values of prepared blends hardness are in table 3. From table 3, it can be seen the effect of plasticizers on the hardness of all elastomeric blends. All prepared blends were

Table 3: Hardness of prepared blends.

Blend type	NR/W	NR/RAE	NR/MES	NR/LO	NR/RO
Hardness (Shore A)	77.42 ± 0.583	73.60 ± 0.34	74.23 ± 1.11	75.16 ± 0.33	74.21 ± 0.53

prepared with the same filler content, the decrease in hardness value can be attributed directly to the influence of the used plasticizer.

The blend without plasticizer was achieved the highest hardness value (77.42 Shore A). A plasticizer has a function in elastomer blends of increasing the gaps between the rubber chains and it is connected with decreasing of viscosity value of the matrix and greater flexibility [16]. By reduction of viscosity, it is possible to achieve better dispersion and distribution of filler particles at the process of mixing and preparation of elastomeric blend. After the vulcanization process, the plasticizer itself remains between the individual rubber chains (bound by a chemical bond), which means that the vulcanizate itself also achieves a lower hardness value. By adding the content of plasticizer to the blends, it is possible to see a decrease of the hardness values of the blends. The lowest hardness value was achieved by the NR/RAE blend containing a commonly used plasticizer (RAE). The lowest hardness value in the case of RAE plasticizer is caused by the already mentioned content of aromatic hydrocarbons and their reaction during vulcanization with the matrix [13, 17]. The elastomeric blend containing the industrially commonly used plasticizer of the MES type was achieved a higher hardness value compared to the NR/RAE blend. The higher hardness value of the NR/MES blend can be attributed to lower plasticization of the blend, which was also reflected in the values of the minimum torque corresponding to the stiffness of the blend at the beginning of the vulcanization process. The highest hardness value among the blend's containing plasticizer was measured for the blend containing linseed oil. Linseed oil is known mainly for its property of oxidation in air and especially at higher temperatures. Therefore, even its effect in the case of elastomeric blend can be limited by these properties, especially due to the influence of temperature during the mixing and vulcanization process. In the case of the second type of natural plasticizer – rapeseed oil, the phenomenon of oxidation and solidification, compared to linseed oil, is mainly suppressed by the lower content of linolenic and linoleic acids [18, 19].

Mechanical properties

Measured values of tensile strength and elongation at break of prepared blends with different type of plasticizer are in table 4.

In the case of tensile properties, the plasticizer plays an important role, as it increases the gap between the rubber chains, thereby indirectly supporting the length of the transverse bonds formed during vulcanization, as well as the possibility of their movement under tensile stress. The lowest tensile strength value was achieved by the NR/W blend without the content of plasticizer. Without the content of a plasticizer, the rubber chains in the blend are arranged without increasing the gaps, and this effect of the plasticizer is taken over by the filler itself. In this case, the filler – cellulose is not bound on the matrix by means of chemical reactions and therefore acts as a stress concentrator during tensile stress. The tensile strength of the NR/W blend is thus limited by the filler, which limits the movement of the transverse bonds (sulfur bridges) under tensile stress [20]. By adding the content of plasticizer to the

Table 4: Tensile strength and elongation at break of prepared blends.

Blend type	Tensile Strength (MPa)	Elongation at break (%)
NR/W	6.54 ± 0.43	347.58 ± 11.89
NR/RAE	7.70 ± 0.35	411.59 ± 13.96
NR/MES	6.80 ± 0.44	364.37 ± 16.36
NR/LO	7.71 ± 0.48	408.36 ± 28.42
NR/RO	7.52 ± 0.16	389.10 ± 8.33

blends, in the case of synthetic commonly used plasticizers, an increase in the tensile strength value can be seen in the case of the RAE plasticizer, as well as the preservation of the tensile strength value without change in the case of the MES plasticizer. By comparing synthetic commonly used plasticizers, RAE has a positive effect on tensile strength value, this can be justified by its effect on the stiffness of the blend and its higher plasticizing effect on the matrix. By using natural plasticizers, the tensile strength values increased also. For this blends were obtained comparable tensile strength values with synthetic plasticizer RAE and higher values comparison with MES plasticizer. The RAE plasticizer also has a positive effect on the elongation at break values due to the more complex (branched) chain as well as its higher viscosity compared to other plasticizers. The branching of the RAE plasticizer chain fulfils the primary function of a plasticizer – it increases the gaps between the rubber chains, and during tensile stress, the filler particles in the rubber chains are less restricted in their movement compared to other plasticizers [13]. A positive effect of natural plasticizer (LO) on elongation at break value can be also seen. The blend with natural plasticizer – linseed oil was obtained comparable elongation at break values with the NR/RAE blend, the possible reason being that linseed oil contains high concentrations of linoleic and linolenic acid, which are the main polymerizing agents [19].

Conclusion

In present work, the impact of sustainable plasticizers on the properties of elastomeric blends based on natural rubber and bio-filler was studied. The replacement of petroleum plasticizers in the production of polymer materials represents an alternative option to reduce the demand for fossil raw materials and reduce the negative impact on the environment. The results show that the best plasticizing effect was achieved by the plasticizer based on petroleum (RAE), which was confirmed by the values of the minimum and maximum torque. For blends with natural plasticizers (LO, RO) were achieved comparable values of minimum and maximum torque with second petroleum plasticizer (MES). Lower values of scorch time and optimal vulcanization time were recorded for the blend containing natural plasticizer (LO) compared to the petroleum plasticizer RAE. The reason for achieving lower values can be attributed to the presence of stearic acid in the natural plasticizer (LO), which with zinc oxide during the vulcanization process forms an activator of sulfur vulcanization. The lowest hardness value of elastomeric blends with plasticizer was achieved by the blend with petroleum plasticizer (RAE), the reason being the presence of aromatic hydrocarbons and

their reaction during vulcanization with matrix. The highest hardness value was measured for the blend with natural plasticizer (LO) and can be attributed to oxidation in air and especially at higher temperature during the mixing and vulcanization process. The results of the mechanical properties show that the petroleum plasticizer (RAE) has a positive effect on the values of tensile strength as well as elongation at break. In the case of natural plasticizer (LO), comparable values of mechanical properties with petroleum plasticizer (RAE) and higher values comparison with the second petroleum plasticizer (MES) were recorded.

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