

Effect of linear low-density polyethylene on the properties of elastomeric materials based on synthetic polyisoprene

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ABSTRACT

The work examines the influence of linear low-density polyethylene on the basic technological, physical-mechanical and fatigue properties of elastomeric materials based on synthetic isoprene rubber of the SKI-3 brand. Synthetic polyisoprene rubber of SKI-3 brand manufactured by LLC “Togliattikauchuk” was used as synthetic polyisoprene rubber, and LLDPE 218 BJ manufactured by SABIC was used as linear low-density polyethylene. Rubber blends were made in a Haake PolyLab rubber mixer for 9 minutes with further introduction of sulfur on rollers for 1.5 minutes. It was found that the introduction of linear low-density polyethylene into the rubber mixture leads to a significant increase in green strength (up to the level of natural rubber and even higher). It has also been established that LLDPE increases the Mooney viscosity of the rubber compound, the stress at 100% and 300% elongation and increases the residual elongation after rupture of the vulcanizates, but has virtually no effect on the vulcanization process of the rubber compound and has an insignificant effect on the tensile strength. The fatigue characteristics of vulcanizates containing LLDPE up to 7 wt.% are at the level of the vulcanizate based on natural rubber. It has been shown that the combination of synthetic polyisoprene brand SKI-3 with linear low-density polyethylene LLDPE 218 BJ at a component ratio of 93/7 allows obtaining an elastomeric material approaching the elastomeric material based on natural rubber RRS1 in key indicators (first of all, in terms of green strength). **Polyolefins J (2024) 11: 213-218**

Keywords: Synthetic polyisoprene; natural rubber; green strength; polymer blends, linear low-density polyethylene.

INTRODUCTION

The use of polymer blends is, in most cases, one of the simplest and most effective ways to modify the properties of polymeric materials, in particular vulcanized rubbers, by purposeful selection of blended polymers [1-3]. On the basis of polymer blends (rubbers, thermoplastics, thermoplastic elastomers) it is possible not only to obtain vulcanized rubbers combining the properties of individual polymers, but also to achieve the variety of properties that cannot be achieved with a single rubber. Modification with the listed polymers

allows to improve physical, chemical and technological properties of elastomeric materials [3]. This method of modification significantly expands the range of elastomeric materials, does not require complex special equipment, is economically advantageous and makes it possible to obtain materials with desired properties that cannot be achieved by other methods.

When obtaining vulcanized rubbers based on polymer blends, it is usually assumed that their properties, as well as the properties of rubber blends, are added to the

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ratio of polymers in the blend. Practice shows that this assumption is not always fulfilled, it is often possible to obtain properties better than additive properties, and the change of different properties is not uniform [4]. Therefore, the properties of elastomeric materials based on polymer blends are rather difficult to predict, and real tests of material based on such blends are required.

Natural rubber (NR) is a key elastomer in the rubber industry of many countries. NR is the most important rubber for the production of a large number of rubber products (tires, rubber products, household and medical products) [5-8]. Nowadays, there is a synthetic analogue of NR, which is synthetic isoprene rubber (IR) [9,10]. But it is analogous in polymer structure, but not in properties [11]. The most important parameter for rubbers and rubber compounds is green strength, and IR is significantly inferior to NR. This limits the use of IR in giant off-the-road, all-metal and aircraft tires, as well as in other rubber products, not allowing full replacement of natural rubber in these products [8-10]. At present, full replacement of natural rubber in rubber products is an important and urgent task due to the existing problems in the modern world [8].

One of the most accessible and promising ways to solve the problem of low green strength of synthetic polyisoprene is the use of polymer blends, i.e. physical modification [5, 12-15]. This method can be implemented in the production process of tires and other rubber products without problems. Thus, earlier [16] we considered a method of increasing the green strength of rubber mixtures based on isoprene rubber by combining it with a small amount (up to 10 wt.%) of high-density polyethylene (HDPE), which makes it possible to increase the green strength of the rubber compounds to the level of the rubber compounds based on natural rubber. However, the combination of rubber and high-density polyethylene has a disadvantage. This disadvantage is the need to produce rubber compounds at high mixing temperatures (at 140°C and above), at which the destruction of isoprene rubber occurs.

If we consider polyolefin-rubber blends in a broader sense, the use of IR/NR polymer composites with polyethylene as the polymer base of blended and dynamic thermoplastic elastomers is well known, but the polyethylene content in them is more than 20 wt.% [1, 17-20]. It should be noted that the morphology of blended or dynamic thermoplastic elastomers/thermoplastic vulcanizates (polyethylene is a dispersion medium) differs from the morphology of rubber blends containing a small amount of polyethylene

(polyethylene is a dispersed phase). Moreover, the effect of small amounts of polyolefins (particularly polyethylene) on the properties of rubber compounds and vulcanized rubbers is poorly studied [16].

Recently, the production of such type of polyethylene as linear low-density polyethylene (LLDPE) has been increasing. It is a copolymer of ethylene with higher alpha-olefins including 1-butene, 1-hexene, and 1-octene (monomer content is 2-7 wt.%) [21]. This polymer replaces low-density polyethylene (LDPE) in many applications or is used together with it [22-24]. The properties of LLDPE are intermediate between those of LDPE and HDPE. LLDPE has heat resistance up to 118°C and greater resistance to cracking, impact strength, heat resistance and higher performance properties at both low and high temperatures than low density polyethylene [23]. LLDPE is easily recyclable and has a melting point more than 10°C lower than high density polyethylene. In this regard, it is interesting to consider linear low-density polyethylene as a polymer capable of increasing the green strength of a rubber compound made from synthetic polyisoprene.

EXPERIMENTAL

Materials

The formulations of rubber compounds are presented in Table 1. The following polymers were used as polymer base: synthetic isoprene rubber of the SKI-3 brand (Mooney viscosity 74 (ML 1+4, 100°C)) produced by LLC “Togliattikauchuk” (PJSC “Tatneft”, Russia), natural rubber RSS-1, linear low-density polyethylene LLDPE 218BJ (density 0.918 g/cm³, 2.0 g/10min (2.16 kg, 190°C), and melting point 122°C) produced by Saudi Basic Industries Corporation (Sabic, Saudi Arabia).

Blending

The production of rubber compounds was carried out in two stages. At stage 1, mixing was carried

Table 1. Composition of rubber compounds.

Compounds	Contents, parts per hundred rubber		
	NR	IR	IR/LLDPE
NR (RSS-1)	100.0	-	-
IR (SKI-3)	-	100.0	90.0 93.0 95.0 97.0
LLDPE (218 BJ)	-	-	10.0 7.0 5.0 3.0
Stearic acid	1.0	2.0	2.0
Zinc oxide	5.0	5.0	5.0
Accelerator CBS	1.5	1.5	1.5
Carbon black N330	35.0	35.0	35.0
Sulfur	2.5	2.0	2.0

out in a HAAKE PolyLab mixer (model Rheomix 3000, Germany) for 9 minutes. The initial mixing temperature in the mixer was 130°C. At stage 2, sulfur was added, and mixing was carried out on laboratory rollers LB 320 160/160 (Metallist, Russia) for 1.5 minutes. The mixing procedure is presented in detail in Table 2.

Characterization and measurements

The green strength was determined according to the ASTM D 6747-15. Plates with a thickness of 2 mm were made by forming on a vulcanization press at a temperature of 100°C for 15 minutes. Then, without removing the plates from the mold, they were placed in a cold press for 30 minutes to cool to room temperature. Then standard-sized samples were cut out of the plates. The green strength was measured 24 hours after molding on a Gotech AI-3000-U breaking machine with an active gripper movement speed of 200 mm/min and constant temperature (25°C).

The strength characteristics of vulcanizates were determined on a Gotech AI-3000-U tensile testing machine according to ASTM D 412. The test was done at a speed of 500 mm/min and constant temperature (25°C).

Vulcanization characteristics were determined on a MonTech MDR 3000 Professional rheometer according to ASTM D 5289 (temperature 150°C, time 60 minutes). Mooney viscosity was determined on a MonTech MV 3000 Basic viscometer according to ASTM D 1646 (temperature 100°C, and measurement time 4 minutes).

Fatigue endurance of rubbers under repeated elongation ($\epsilon = 125\%$ at 3 Hz) and repeated puncture bending (3 Hz) was determined on a MonTech FT 3000 CH according to ISO 6943 and ASTM D 813, respectively. Hardness was determined on a MonTech HT 3000 instrument according to ASTM D 2240. Rebound resilience was determined on a Gotech

Table 2. Procedure for mixing rubber compounds.

Compounds	Duration, min	General time, min
1st stage		
Rubber (IR or NR)	1 or 3	1
LLDPE (218 BJ)	2	3
Stearic acid	1	4
Zinc oxide	1	4
Accelerator CBS	1	4
Carbon black N330	5	9
2nd stage		
Sulfur	1.5	10.5

7042-RDA in accordance with ISO 4662.

RESULTS AND DISCUSSION

The results of determination of green strength of rubber compounds are presented in Figure 1. As follows from the obtained data, combining IR with LLDPE leads to a significant increase in the green strength of the rubber compound. The introduction of polyethylene allows approaching the green strength of NR-based rubber compound and even exceeding it to some extent. Thus, at IR/LLDPE ratio equal to 93/7 green strength of rubber compound is close to NR, and at IR/LLDPE ratio equal to 90/10 green strength of rubber compound is 140% higher than that of NR. Polyethylene also affects other technological properties of rubber compounds (Table 3). As the polyethylene content increases up to 10 wt.% (IR/LLDPE equal to 90/10) in the rubber compound, the Mooney viscosity increases by 12% and the elongation-at-break of the rubber compound decreases by 81% compared to the rubber compound based on IR alone. The increase in Mooney viscosity is due to the fact that polyethylene at viscosity measurement temperatures is almost in a solid state, and its effect on Mooney viscosity is similar to that of fillers. It should be noted that the decrease in the elongation-at-break of a rubber compound containing more than 7 wt.% LLDPE may limit its use in prefabrication and assembly operations in tire production, where an elongation-at-break of at least 300% is required [14].

The analysis of vulcanization curves, which are shown in Figure 2, showed that the combination of synthetic isoprene rubber with linear low-density polyethylene practically does not affect the vulcanization process. A

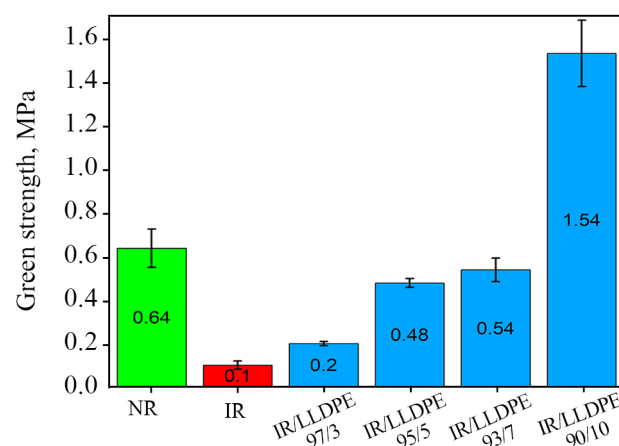


Figure 1. Green strength of rubber compounds.

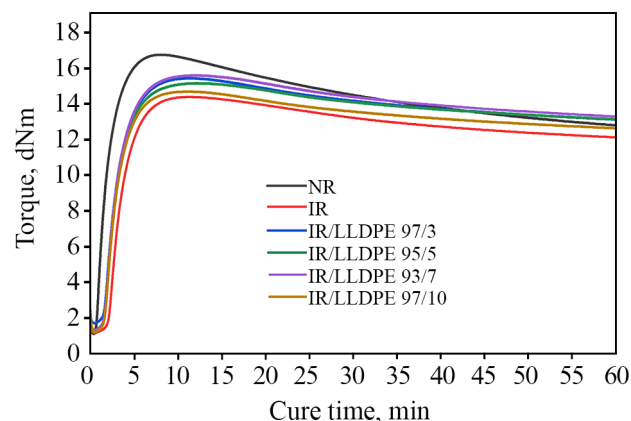
Table 3. Technological properties of rubber compounds.

Polymer base	Mooney Viscosity, MU	Elongation-at break of rubber compound, %
NR	39	612
IR	39	1137
IR/LLDPE (97/3)	43	1431
IR/LLDPE (95/5)	44	534
IR/LLDPE (93/7)	47	458
IR/LLDPE (90/10)	48	212

slight decrease in the induction period and an increase in the torque increment (ΔM) in the vulcanization process are observed. This is due to the fact that the amount of curing system per unit of rubber increases, since polyethylene under these conditions is practically not crosslinked.

The results of the physical and mechanical tests of the vulcanizates are presented in Table 4. As shown in these data, as the LLDPE content increases up to 10 wt.%, there is a significant increase in the stress at elongation of 100 and 300% (increases by 76 and 28%, respectively) and the residual elongation after rupture (increases by 105%). However, the tensile strength, tear resistance and elongation-at-break change insignificantly (not more than 10%). It should be noted that vulcanized rubber based on the mixture of IR with LLDPE with the ratio of 93/7 and vulcanized rubber based on NR have the same stress at 100% elongation and close values of stress at elongation of 300%, tensile strength and elongation-at-break.

The data in Table 4 show that the hardness of vulcanizates increases with increasing LLDPE content, while the rebound elasticity decreases. The changes in these properties occur as well as when IR is combined with HDPE [16]. The increase in hardness is due to the fact that polyethylene is in the solid state under normal conditions. And the decrease in rebound resilience is probably caused by the insignificant amount of physical or chemical bond of the rubber matrix with polyethylene and the existence of the

**Figure 2.** Vulcanization curves for rubber compounds.

interface, preventing the distribution of vibrations over the volume of the material. It should be noted that at LLDPE content up to 7 wt.% the changes in these parameters are not more than 11%, which to some extent can be considered insignificant.

Fatigue characteristics of vulcanizates are presented in Figure 3. These features partly determine the durability of rubber products. As can be seen in Figure 3, with an increase in the LLDPE content, there is a slight decrease in the fatigue endurance at repeated elongation in the mode of specified deformations ($\epsilon = 125\%$) and fatigue endurance under repeated bending with puncture (the number of cycles before crack growth is 12 mm). This is probably due to the fact that vulcanizates containing polyethylene have a higher modulus (high stress values at a given elongation) than a vulcanizate based on a single IR. Also, this may be due to the fact that IR and LLDPE are thermodynamically incompatible and have a rubber/polyethylene interface, leading to increased hysteresis losses. It should be noted that the vulcanized rubber based on the IR/LLDPE blend with a ratio of 93/7 and the vulcanized rubber based on NR have the same stress at elongation of 100% and almost the same values of fatigue characteristics.

Table 4. Physical and mechanical properties of vulcanizates.

Properties	Polymer base					
	NR	IR	IR/LLDPE (97/3)	IR/LLDPE (95/5)	IR/LLDPE (93/7)	IR/LLDPE (90/10)
Stress-at-elongation of 100 %, MPa	2.7±0.1	1.7±0.1	2±0.1	2.2±0.1	2.7±0.1	3±0.1
Stress-at-elongation of 300 %, MPa	14.3±0.3	10.2±0.4	11.5±0.4	11.6±0.6	12.8±0.4	13.1±0.7
Tensile strength, MPa	27.7±1.4	27.4±1.0	29.9±1.6	28.7±1.6	28.5±1.1	26.8±1.6
Elongation-at-break, %	473±23	520±17	502±18	506±22	494±20	470±15
Residual elongation, %	23±2	20±1	28±3	31±3	35±2	41±3
Tear resistance, kN/m	108.9±17.9	95.8±17.0	90.5±17.6	90.1±16.0	93.7±11.6	99.6±16.3
Hardness (Shore A), units	58±1	55±1	57±1	59±1	61±1	64±1
Rebound resilience, %	61±1	56±1	53±1	51±1	50±1	49±1

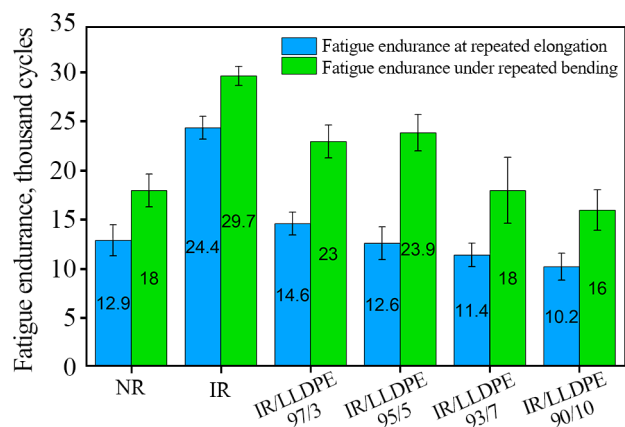


Figure 3. Fatigue characteristics.

The fatigue endurance of vulcanizates is significantly affected by their modulus and dynamic loading mode [25]. Since the deformation value does not depend on the elastic properties of the vulcanized rubber in the given deformation mode, then in a more rigid material (with a higher modulus) greater stresses develop, i.e. this vulcanized rubber is in less favourable conditions and is characterized by lower fatigue endurance. For this reason, vulcanized rubber based on IR alone has greater fatigue endurance values than vulcanized rubber based on NR and based on a mixture of IR with LLDPE

CONCLUSION

Thus, in this work the possibility of increasing the cohesive strength of rubber mixtures based on synthetic polyisoprene by combining it with linear low-density polyethylene was considered for the first time, and the influence of this polyethylene on the basic properties of IR-based vulcanizates was investigated.

The combination of IR with LLDPE leads to a significant increase in the cohesive strength of rubber compounds. Also, the addition of LLDPE up to 10 wt.% leads to an increase in the Mooney viscosity and a decrease in the elongation-at-break of the rubber compounds. This polyethylene contributes to a significant increase in 100 and 300% elongation stress and residual elongation after rupture of vulcanizates, but has a low effect on tensile strength, tear resistance, elongation-at-break, hardness and rebound elasticity (at LLDPE contents up to 7 wt.%). With increasing LLDPE content the modulus increases and fatigue properties of vulcanizates decrease.

The test results showed that the optimal ratio of

IR with LLDPE in the rubber compound is 93/7. At this ratio of polymers, the cohesive strength of the rubber compound approaches the green strength of the rubber compound based on natural rubber RSS-1, and the physical-mechanical and fatigue characteristics of vulcanizates are practically the same as those of natural rubber.

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CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest.

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