Properties of natural rubber/carboxilated styrene-butadiene latices blends

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The study reports features of natural rubber and styrene-butadiene latices blends, and the influence of dithiocarbamate accelerated sulphur cure system on the properties of the cured rubber blends. Blend NR/SBR = 80/20 (C) shows some synergistic effect in mechanical properties. Most of the mechanical properties decrease with increased SBR in blends. The crosslink density is calculated using swelling measurement and correlated with vulcanized properties. The homogeneity of NR/SBR latices blends was determined by differential scanning calorimetry.

Key words: natural rubber latex, styrene-butadiene latex, blends, mechanical properties, crosslink density, differential scanning calorimetry.

Introduction

VARIOUS types and grades of latex on the market are summarized in the following outline: natural latex (Hevea), styrene-butadiene latices, polychloroprene latices, butadiene-acrylonitrile latices and polyurethane latices. Natural rubber and SBR are the "all-purposes" types, which are completely compatible [1].

As the name implies, Hevea latex (natural) is derived from the Hevea Brasiliensis tree.

The production of latex is distinguished from crude rubber in a much more careful technical control required and considerable capital investment that is required for receiving storage tanks, creaming tanks centrifuges, transfer pumps, air compressors, and other auxiliary equipment. The latex, as collected from the tree, is a milk-like liquid containing about 38 to 40 percent solids with a density 0.980 or thereabouts. This is the so-called "normal" latex of commerce. Normal latex preserved with ammonia is passed through a centrifuge and separated into two approximately equal volumes of fluid; the inner layer containing about 62 percent solids, the outer about 11 percent.

The processes with natural latex were developed in the 1920s and 1930s. Since World War II, most of the widely used types of synthetic rubber have become available in latex form [2].

Synthetic latices are aqueous colloidal dispersions of synthetic rubbers consisting of one or more monomers and usually produced by emulsion polymerization [3].

In contrast to natural latex, which from the aspect of colloidal chemistry represents a heterodisperse system, synthetic latices are, practically speaking, homediperse systems. In other words, the particles of synthetic rubber, which is dispersed in latex, are of substantially the same size. Usually the particles that are present in synthetic latices have a much smaller diameter than the particles type of natural rubber latices. It is between 5 and 150 milimicrons, depending on the type of latex and can be adjusted while the polymer is being synthesized. The particles of natural rubber latex have a diameter of 50 to 400 milimicrons and also vary in size.

Vulcanizates made from synthetic latices have largely the same characteristics as those made from the corresponding solid rubbers.

It must however be pointed out that, with regard to mechanical properties, i.e. tensile strength, modulus, tear resistance etc., synthetic latex vulcanizates are considerably inferior to the corresponding natural latex vulcanizates. As with solid rubbers, the properties of latex mixes and vulcanizates are naturally influenced by the formulation of the mix [1].

Although the characteristic technological properties of synthetic latex goods are not equal in all respects to those of natural latex goods, they suffice to explain why synthetic latices are becoming more and more important. Synthetic latices, apart from finding new applications, have indeed substantially replaced the natural product in many applications.

The rheological behaviour of blends of natural rubber (NR) and styrene-butadiene rubber (SBR) latices have been

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studied with reference to the effects of the blend ratio, shear rate, surface agents and temperature [5, 6].

This article presents features of two rubber blends and the influence of the dithiocarbamate accelerated cure system on the properties of NR and SBR latices cured rubber blends. In this work the mechanical properties and crosslink density are investigated. DSC determines the homogeneity of NR/SBR blends.

Experiment

The polymer used were high ammonia (HA) preserved 60% centrifuged NR latex (Revertex-Malasian) and carboxilated styrene-butadiene latex (Revinex 91Y50-Serbia) (Table 1).

Table 1 Specifications for Revinex 91 Y 50*

Specifications	
Average Size diameter, nm	210
Total Dry Solids, %	50
Density, 25°C, g/cm³	1.01
Boiling point, °C	100
pH	7.5 - 8.0
Viscosity, mPas	250 - 300
Colour of latex	Milk white
Water Soluble	soluble

Sulfur, zinc oxide and zinc diethyldithiocarbamate were of commercial grade and were used as 50% dispersions in water, prepared by ball milling [7]. Other chemicals were of laboratory grade and were used as solutions in water. Latex samples were compounded according to recipes of Table 2. Compounds B-E represented NR/SBR blends in following ratios: NR/SBR=90/10 (B); NR/SBR=80/20 (C); NR/SBR=70/30 (D); NR/SBR=50/50 (E); while A represented component NR latex and F component SBR latex.

Table 2 Formulation of the mixes

Mix	A	B	C	D	E	F
Centrifuged NR (60%) latex	167	150	133	117	83	-
SBR (50%) latex	-	20	40	60	100	200
Potassium hydroxide (10%) solution	2.5	2.5	2.5	2.5	2.5	2.5
Potassium laurate (20%) solution	1.3	1.3	1.3	1.3	1.3	1.3
Zinc oxide (50%) dispersion	0.4	0.4	0.4	0.4	0.4	0.4
ZDEC[1] (50%) dispersion	1.0	1.0	1.0	1.0	1.0	1.0
Sulphur (50%) dispersion	2.0	2.0	2.0	2.0	2.0	2.0

[1] Zinc diethyldithiocarbamate

The latex compounds were cast in shallow glass dishes to a film thickness of ~2 mm. After that, the prepared samples in glass dishes were put into the air oven and vulcanization took place at 110°C for 40 min. The films were removed from the glass dishes after 24 h and the mechanical properties of blend elastomers examined [8]. The tensile properties of the vulcanizates were determined according to ASTM D 418, using dumb-bell specimens at 25°C at crosshead speed of 500 mm/min, with Monsanto Tensometer 10, a universal testing device [9]. Hardness was determined according to ASTM 2240.

Crosslink density

Vulcanizate samples were accurately weighed (w) and immersed in about 25 ml of toluene in closed sample

bottles. The samples were taken out after 7 d. The surfaces were dried with filter paper and the samples were quickly weighed by using an electronic balance (w'). Mass of the specimen after drying for 6 d at the laboratory temperature was w'' [10].

Volume swelling ratio (r_υ) or the weight swelling ratio (r_ω) was calculated using sample weights before and after swelling, w and w', and the densities of solvent and polymer ρ_1 and ρ_p [11-14].

$$r_\upsilon = 1 + \left(\rho_p/\rho_1\right)\left(w'/w - 1\right) \tag{1}$$

$$r_\omega = w'/w \tag{2}$$

$$\upsilon_{2_g} = 1/r_\upsilon \tag{3}$$

where υ_{2_g} is the volume fraction of polymer in the swollen gel. Based on the swelling measurements, sol fraction (soluble in toluene) - W_s, gel fraction (insoluble in toluene) - W_g, and degree of swelling - D. S. can be calculated using relations:

$$W_s = 100\left(w - w''\right)/w \tag{4}$$

$$W_g = 100 - W_s = w''/w \tag{5}$$

$$\text{D.S.} = 100\left(w' - w''\right)/w'' \tag{6}$$

From the value of υ_{2_g}, thus obtained, $\overline{M}_c$, was then calculated using relation (7):

$$-\left[\ln\left(1 - \upsilon_{2_g}\right) + \upsilon_{2_g} + \chi\upsilon_{2_g}^2\right] = \\ = \left(V_s\, \rho_p/\overline{M}_c\right)\left(\upsilon_{2_g}^{1/3} - \upsilon_{2_g}/2\right) \tag{7}$$

Crosslink density ν was calculated using relation (8):

$$\nu = 1/2\overline{M}_c \tag{8}$$

where χ is a parameter characteristic of interaction between the rubber network and the swelling agent. For NR toluene system the value of χ could be taken as 0.393 whereas for SBR - toluene it could be taken as 0.482 [15]. For the blend average additive value could be taken. V_s - is the molar volume of toluene (106.4 cm³/mol), R is the gas constant and T is the absolute temperature.

Differential scanning calorimetry

For determining T_g, Perkin-Elmer Differential Scanning Calorimeter, model PEPC-DSC 7 is used.

Results

Mechanical properties

On the bases of values from Table 3, it can be calculated that tensile strength, tensile modulus, tear strength and stress-strain hysteresis decreases with the increased SBR in blends, with the exception of the blend NR/SBR = 80/20 (C). Here tensile strength and some mechanical properties (elongation at break, hardness, tear strength) are better in blend C compared with NR and SBR. NR/SBR=80/20

blend show some synergistic effect. The mechanical properties of NR/SBR blends are inferior with increased SBR concentration, due to the fact that synthetic SBR latex vulcanizates are inferior compared to natural latex vulcanizate. Also, the mechanical properties of NR/SBR rubber blends are inferior with increased SBR concentration because of the cure-rate incompatibility between the two rubbers, the NR removing curatives from the system long before the time required for complete vulcanization of the SBR rubber.

Table 3 Mechanical properties of blends

Mix	A	B	C	D	E	F
Tensile strength, MPa	11.5	9.5	12.8	9.8	8.3	5.0
100% Modulus, MPa	1.1	0.9	1.0	1.3	1.5	1.0
200% Modulus, MPa	1.7	1.3	1.4	1.8	2.3	1.4
300% Modulus, MPa	2.3	1.8	1.8	2.5	3.5	2.1
400% Modulus, MPa	3.5	2.8	2.6	3.9	5.8	3.2
500% Modulus, MPa	8.0	5.7	4.4	7.5	-	4.6
Elongation at break, %	551	554	785	553	645	510
Hardness, H Sh A	41	44	43	44	50	-
Tear strength, KN/m	37.2	36.3	38.6	34.3	26.3	-
Stress-strain hysteresis, %	22.0	34.3	37.2	45.0	68.3	-
Density, g/cm³	0.920	0.868	0.863	0.939	0.952	1.002

Crosslink density

Values of sol fraction (w_s), gel fraction (w_g) and degree of swelling (D.S.) are given in Table 4.

Table 4 Sol and gel fraction of vulcanizates

Mix	W_s, %	W_g, %	Degree of swelling (D.S.)
A	3.35	96.65	309
B	3.29	96.71	370
C	4.32	95.68	435
D	4.00	96.00	411
E	4.56	95.44	399
F	9.50	90.50	682

Values of sol fraction and gel fraction are similar in blends and corresponding NR vulcanizate. With increased SBR concentration in NR/SBR blends, degree of swelling is greater in blends compared to NR. This is the consequence of the strong swelling of SBR in toluene.

Values of υ_{2_g} for component rubbers and blends are given in Table 5.

Table 5 Values of volume fraction of polymer in the swollen state (υ_{2_g})

Mix	w	w'	w'''	ρ_p	ρ_l	υ_{2_g}
A	0.3161	1.25	0.3055	0.920	0.866	0.240
B	0.4342	1.98	0.4199	0.868	0.866	0.219
C	0.4672	2.39	0.4470	0.863	0.866	0.196
D	0.5580	2.74	0.5357	0.939	0.866	0.191
E	0.6417	3.06	0.6124	0.952	0.866	0.195
F	0.5240	3.71	0.4740	1.002	0.866	0.124

From Table 5 it is evident that values of volume fraction of polymer in swollen gel υ_{2_g} are decreases in blends compared to NR.

Values of $\overline{M}_c$ and crosslink density ν of vulcanizates NR, SBR and NR/SBR blends are given in Table 6.

Table 6 Values of $\overline{M}_c$ and crosslink density ν

Mix	A	B	C	D	E	F
Weight swelling ratio, R_w	3.95	4.55	5.12	4.91	4.76	7.82
Volume swelling ratio, R_v	4.13	4.55	5.10	5.24	5.13	8.02
υ_{2_g}	0.240	0.219	0.196	0.191	0.195	0.124
Crosslink density, $\nu \times 10^5$	11.99	9.78	7.19	5.87	2.24	1.06
$\overline{M}_c$ (swelling in toluene)	4168	5112	6952	8513	22239	47028

In blends with increased SBR concentration it can be noticed that values crosslink density ν is decreased compared to NR vulcanizate. The lowest crosslink density is shown for example F (carboxilated SBR latex), which is cured without adding sulphur and accelerators. The reason why the $\overline{M}_c$ increases in blends compared to NR can be explained by the fact that the same quantity of curatives share bigger volume of elastomers in the blend.

Differential scanning calorimetry

Glass transition temperatures of A (NR), F (SBR) and T_gs of blend E (NR/SBR=50/50) are studied by DSC at -80°C to 30°C. T_g for NR is about -70°C (Fig.1) [16-18], while T_g for SBR is about -59°C (Fig.2). Blend E shows single glass transition temperature of about -62°C, which indicates that NR and SBR are compatible (Fig.3).
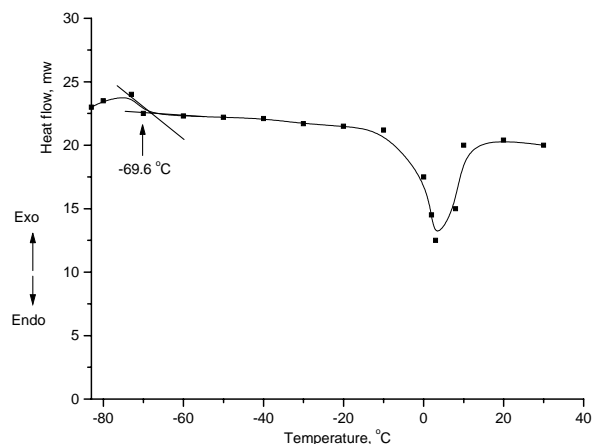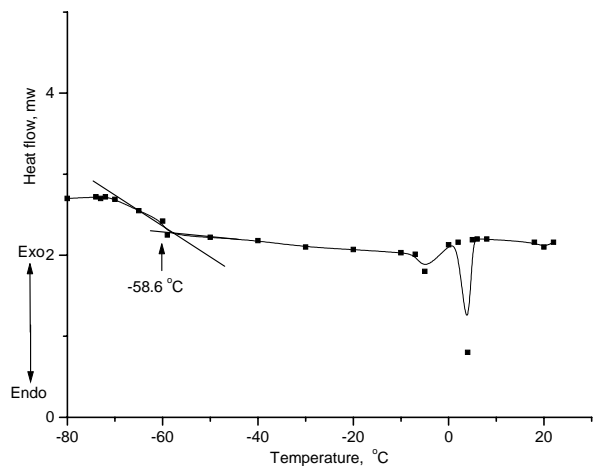

Figure 1. DSC curve of NR
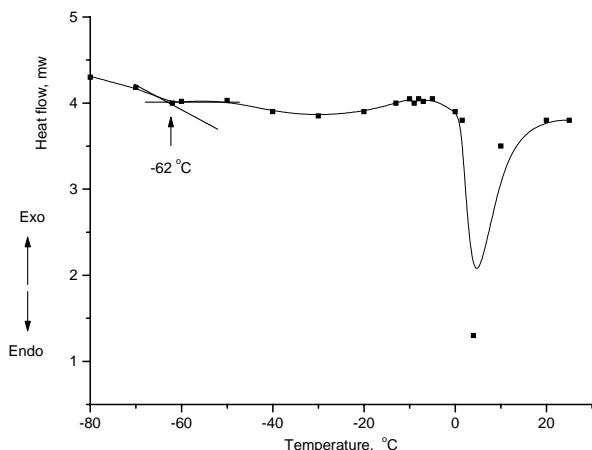

Figure 2. DSC curve of SBR

Figure 3. DSC curve of NR/SBR blend E

Conclusions

– The latices of natural (NR) and carboxilated styrene-butadiene (SBR) rubbers are easily mixed, they are compatible and vulcanizates of their blends have shown satisfactory technical and technological characteristics, which makes these materials extremely suitable to use in production of rubber-technical goods and latex foam production.

– Some of the mechanical blends properties: hardness, elongation at break and hysteresis are increases with the rising concentration of SBR in blends. On the other hand, tensile modulus, tensile strength and tear strength are decreased with increasing the portions of SBR in such blends.

– Blend C (20 phr SBR) showed synergistic effect in tensile and tear strength and elongation at break.

– The swelling measurements shows that with increasing SBR concentration in blends, crosslink density is decreased, while molecular mass between effective crosslinking $\overline{M}_c$ and degree of swelling are increased compared to NR rubber vulcanizate A.

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Karakteristike blendi na bazi NR/karboksilovani SBR lateks

U ovom radu prikazane su karakteristike blendi na bazi lateksa dva kaučuka (NR i SBR), kao i uticaj sumpornog umreživačkog sistema ubrzanog ditiokarbamatom na svojstva umrežnih elastomernih blendi. Kod blende NR/SBR = 80/20 javlja se sinergistički efekat. Mehanička svojstva se, uglavnom, pogoršavaju sa povećanjem sadržaja SBR-a u blendi. Gustina umreženja određuje se iz ogleda bubrenja i dovodi u korelaciju sa svojstvima vulkanizata.

Ključne reči: lateks prirodnog kaučuka, lateks stirenbutadienskog kaučuka, blende, mehanička svojstva, gustina umreženja, diferencijalna skanirajuća kalorimetrija.

Характеристики бленд на основе латекса двух каучуков - натурального и бутадиен-стирольного

Здесь приведены характеристики бленд на основе латекса двух каучуков - натурального (НР) и бутадиен-стирольного (СБР)), как и влияние сернистой объединённой в сеть системы ускоренной дитиокарбаматом на свойства объединённых в сеть эластомерных бленд. У бленды НР/СБР = 80/20 является синергический эффект. Механические характеристики в основном ухудшаются с увеличением содержания бутадиен-стирольного каучука (СБР) в бленде. Плотность каучука определяется из эксперимента набухания и приводится в корреляцию с характеристиками вулканизатов.

Ключевые слова: каучук, натуральный каучук, бутадиен-стирольный каучук, бленда, механические характеристики, плотность каучука, дифференциальная сканирующая калориметрия

Les propriétés du caoutchouc naturel et des mélanges latex styrène-butadiene

Ce papier présente les propriétés des mélanges à la base du latex de deux caoutchoucs (NR SBR) ainsi que l'influence du système de liage sulfurique accéléré à l'aide de ditiocarbomate sur les propriétés des mélanges élastomères. Chez le mélange NR SBR-80 se manifeste l'effet synérgétique. En général, les propriétés mécaniques décroissent avec l'accroissement du contenu de SBR dans le mélange. La densité du liage est déterminé par l'essai d'enflure et met en corrélation avec les propriétés du vulcanisant.

Mots clés: latex, caoutchouc naturel, caoutchouc styrène-butadiene, mélange, propriétés mécaniques, densité de liage, calorimétrie différentielle scannante.