INVESTIGATION OF SBR/CMC BLENDS BY VULCANIZING AND SWELLING PROPERTIES

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Abstract

Blends of Styrene butadiene rubber (SBR) with varying loading degree from 10 wt% to 100 wt% of carboxymethylcellulose (CMC) have been prepared. The prepared SBR/CMC blends were submitted to measurements of vulcanizing characteristics (M_H, M_L, t_s, $t_{c(90)}$, R_v) as a function of loading degree of CMC. Swelling has been used in the study of elastomeric networks. Swelling equilibrium data, for a new SBR/CMC rubber vulcanizates in xylen, were analyzed by the Flory-Rehner equation simply to obtain a measure of the crosslink density. Results obtained showed that 10 wt% of CMC in blends has comparable properties with standard.

Keywords

Styrene butadiene rubber; carboxymethylcellulose; vulcanization; crosslink density

Introduction

Nowadays, carbon black is the most important filler used in rubber blends, especially in automotive tires. However, due to its polluting nature and its dependence on petroleum feedstock for their synthesis, forces researchers to look out for other "white" environmentally friendly fillers [1]. Fillers are widely used in rubber blends for a variety of reasons, which include improved physical properties and service life, easier processing and reduced production cost [2].

In recent years, interest of scientific at the preparation and characterization of physico-chemical properties of rubber blends filled especially by natural biodegradable polymers such as cellulose, starch and chitosan as well as their derivates has greatly increased. These fillers are used as an eco-friendly replacement for traditional compound reinforcements like silica and carbon black.

Carboxymethylcellulose (CMC) is the most popular and cheapest industrially important cellulose derivative, primarily due to its high viscosity and non-toxicity character.

Styrene butadiene rubber (SBR) is one of the most widely used synthetic rubbers. It consists of the organic compound styrene and the chemical butadiene, with the amount of butadiene usually being about three times more than the amount of styrene. It has good abrasion resistance and good aging stability when protected by additives, and is widely used in all automotive tires, children's toys, shoe soles and even chewing gum.

The using of some polysaccharide fillers is well known. Recently, Mohamend M. [3] prepared and characterized the SBR blends filled by CMC and vulcanized by using γ – radiation. In this case gamma rays as ionizing radiations was suitable means for vulcanization of SBR based blends with CMC as improvement in mechanical as well as physical properties of blends. Mazíková M. [4] prepared hydrophobically carboxymethyl starch oleate (CMSOL) fillers witch used for preparation of SBR/CMS oleate blends with different content (1-100% CMSOL). Content of 10 % of new CMS filler was possible to use without impairing physical and mechanical properties and also examine the use of starch oleate as a plasticizer. In continuation of our research on preparation and investigation of SBR/CMC blends by physical-mechanical and thermal properties [5], this paper is focused on investigation of SBR/CMC blends by vulcanizing and swelling properties as a function of content of CMC.

EXPERIMENTAL

Materials

Commercial synthetic rubber Kralex SBR1500 was used as matrix polymer. Sodium carboxymethylcellulose - CMC (Na^+ salt; DS_{CM} = 0.7; Mw = 90.000 g/mol) used as unconventional filler was supplied by Sigma - Aldrich Chemie GmbH, (Steinhem, Germany). Carbon black Chezacarb A used as the conventional filler was from Unipetrol RPA, s.r.o, (Litvinov, Czech Republic). The formula of this study contained also other additives used as accelerators as well as activators namely: Zinc Oxide (ZnO) from Wiehart G.m.b.H (Wien, Austria) and Stearine 18 RG was from Setuza (Usti nad Labem, Czech Republic).

Preparation of SBR/CMC blends [6]

The rubber model blends and standard were prepared by two-step mixing of the synthetic rubber Kralex SBR1500 with the filler and all vulcanization ingredients (ZnO, Oil fraction from hydrocracking of vacuum distillate of petroleum (NKO oil), Stearine 18 RG) except the sulphur N and N-cyclohexyl-2-benzothiazol sulphenamide (CBS) in mixing chamber of laboratory mixer Plastograf-Brabender at 110°C for 8 min at mixing speed 50 rpm. The second step was made at 110°C for 5 min at the same mixing speed after the sulphur N and CBS had been added. The compositions of the SBR/CMC blends are given in Table 1.

Tab. 1: The composition of the SBR/CMC blends

Ingredient	Content (phr)[a]
Synthetic rubber (Kralex SBR1500)	100
Carboxymethylcellulose	25, 15, 5 or 2.5
Carbon black (Chezacarb A)	10, 20, 22.5 or 25
Zinc oxide	5
Sulphur N	2
CBS[b]	1
Stearine 18 RG	2
NKO oil[c]	5

[a] Parts per hundred parts of rubber.
[b] N-cyclohexyl-2-benzothiazol sulphenamide.
[c] Oil fraction from hydrocracking of vacuum distillate of petroleum.

The vulcanized slabs were obtained by a compression moulding of the prepared model rubber compounds using a laboratory press Buzuluk at the temperature 150°C for periods of time corresponding to optimum vulcanization time determined as ($tc_{(90)}$) using rheometry. For comparison of results, the standard blend was prepared with the filler - carbon black Chezacarb A.

Vulcanization properties

The vulcanizing properties (M_H – maximum torsion moment, M_L – minimum torsion moment, t_s – start of vulcanization, $t_{c(90)}$ – optimal vulcanization time, R_v – rate coefficient of vulcanization) of SBR/CMC blends were measured using a vulcameter Monsanto 100 at the temperature 150°C during 60 min [7].

Determination of crosslink density of blends

From several types of methods, the swelling was used in the study of elastomeric networks. This method is described in detail [8]. The crosslink density was determined by observation of kinetic of swelling of samples vulcanizes with size 5x5x2 mm in xylen (with content of 1% antioxidant Dusantox) at laboratory temperature for 24 h. In the selected time an interval, the samples vulcanizes were removed from xylen and dried of with filter paper and analytical weighed. Increase of weight was monitored.

The equilibrium data, for the vulcanizates in thermodynamics suitable solvents were generally analysed by the Flory-Rehner equation (Equation (1)) simply to obtain a measure of the crosslink density.

$$\upsilon = -\frac{\ln(1-V_r)+V_r+\chi V_r^2}{V_1(V_r^{1/3}-0,5V_r)} \quad (1)$$

where υ is crosslink density ($mol \cdot cm^{-3}$), V_r is volume fraction of the rubber in equilibrium swelled vulcanizate sample, V_1 is molar volume of used solvent (for xylen = 123.45 $cm^3 \cdot mol^{-1}$), χ is Huggins´ parameter (χ = 0.385).

The volume fraction of SBR in the swollen gel V_r, was calculated by Equation (2):

$$V_r = \frac{V_K}{V_K+V_b} \quad (2)$$

where V_b is volume of solution in sample in equilibrium state, V_k is volume of rubber in sample calculated by Equation (3):

$$V_K = m_{vz}\frac{100}{100+a}\frac{1}{\rho_K} \quad (3)$$

where ρ_k is rubber density, *a* is non-rubber additives mass in rubber blends, m_{vz} is the sample mass before swelling.

RESULTS AND DISCUSSION

Vulcanizing characteristics

The vulcanization course and its basic characteristics (M_H, M_L, t_s, $t_{c(90)}$, R_v) were evaluated on the basis of vulcanization curves measured on vulcameter Monsanto 100. The vulcanization curves of the prepared SBR/CMC blends and standard obtained from the registering apparatus of vulcameter Monsanto 100 were scanned and digitalized by Engauge digitizer v.4.1 for graphically presentation in Fig. 1.

As can be seen, the vulcanization curves of SBR/CMC blends are comparable with reference – standard blend, showed plateau, which means that arises network is stable. The values of measured vulcanization characteristics are shown in Table 2. The values of rate coefficients of vulcanization (R_v), which characterize activity of ingredients in rubber compound are increased with content of CMC. The values of the minimum torque (M_L) and the maximum torque (M_H) had decreasing tendency with increase of content of CMC in blends. 60-100wt% of CMC in blends is behaved as partial plasticizer because initial viscosity of rubber blends is markedly lower. The SBR/CMC blend with 10-20wt% CMC filler exhibits the highest value of torque difference (M_H - M_L), which indicates the extent of crosslinking. The start of vulcanization (t_S) of SBR/CMC blend is compared to the standard, except SBR/CMC blend with 100wt% CMC filler. From the comparison of the vulcanizing parameters is clear, that optimal vulcanization time ($t_{c(90)}$) is shorter in comparison with the blend containing only carbon black (standard).

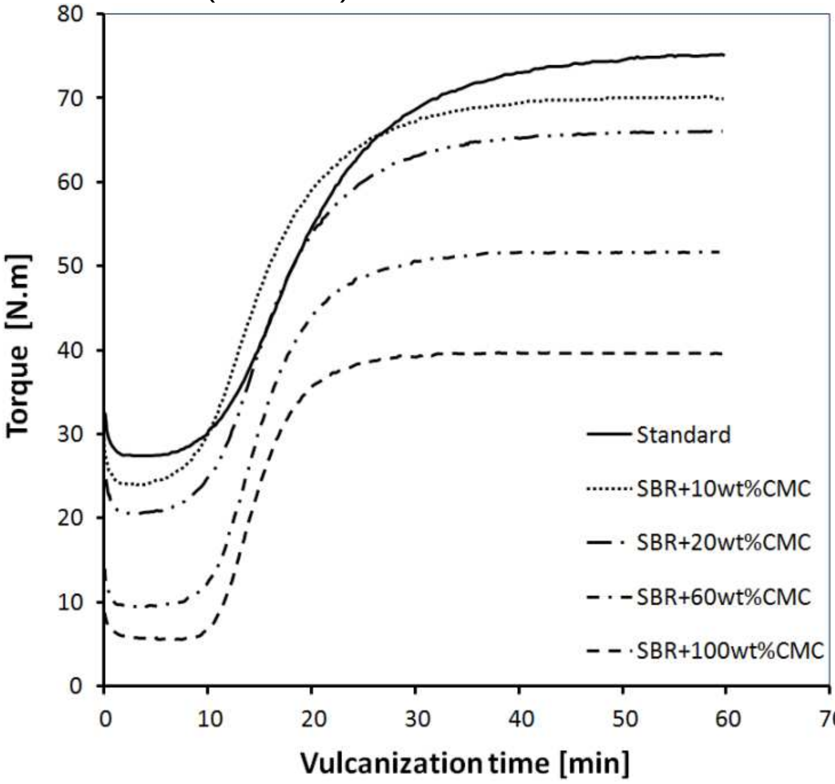

Fig. 1: *Vulcanizing curves of the SBR/CMC blends with different addition of CMC at 150°C*

Tab. 2: Vulcanizing characteristics and crosslink density of the SBR/CMC blends

Blends	M_L (N·m)	M_H (N·m)	$t_{c(90)}$ (min)	t_S (min)	R_v (min^{-1})	υ x e 10^{-4} ($mol \cdot cm^{-3}$)
Standard	27.21	75.07	33	6.0	3.70	1.44
SBR+100wt%CMC	5.42	39.63	21	8.5	8.00	0.58
SBR+60wt%CMC	9.20	52.00	23	5.5	5.71	0.74
SBR+20wt%CMC	20.50	66.06	27	5.0	4.55	1.16
SBR+10wt%CMC	24.00	70.00	26	5.0	4.76	1.29

Crosslink density of blends

The crosslink density expressed as the quantitative size of vulcanization of rubber was determined for all SBR/CMC blends. The curves were described by mathematical function, where constant A represent amount of diffused solvent to vulcanized sample in equilibrium state. The dependence of the amount of solvent diffused to vulcanized samples on time is for studied blends presented in Fig. 2.

The Table 2 summarizes the crosslink density of SBR vulcanizates with varying CMC contents. From Table 2, it can be concluded that the crosslink density of SBR/CMC blends decrease with increasing of content of CMC. The highest value of crosslink density from moderate rubber blends ~$1.29 \cdot 10^{-4}$ $mol \cdot cm^{-3}$ comparable with standard had SBR blend filled with 10wt% of CMC. Even though, used CMC supplied to rubber blend some double bound, in contrast to carbon black, cause of the lower values of crosslink density of SBR/CMC blends can be lower compability of CMC compared with carbon black.

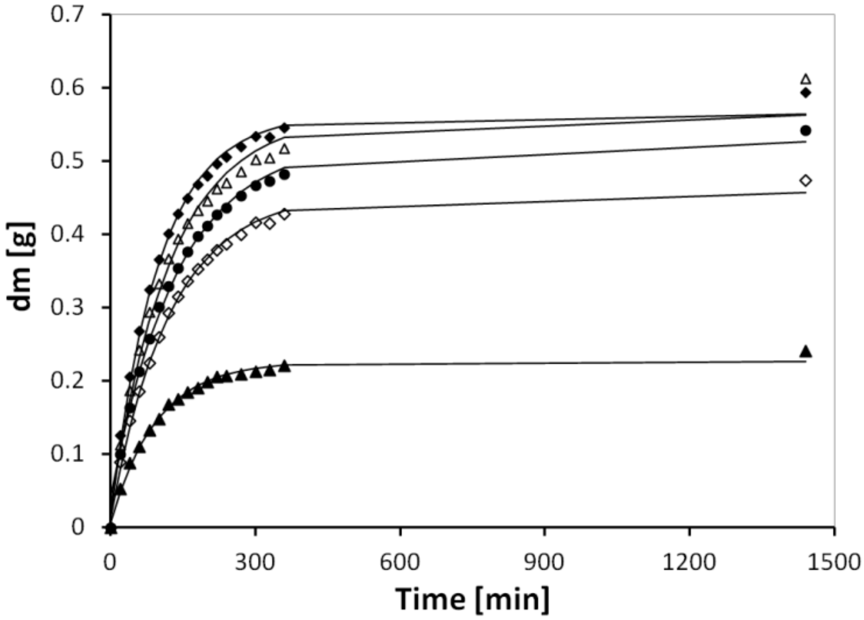

Fig. 2: *The dependence of the amount of solvent diffused to vulcanized samples on time: (♦) SBR+100wt%CMC, (Δ) SBR+60wt%CMC, (●) SBR+20wt%CMC, (▲) SBR+10wt%CMC, (◊) standard*

Conclusions

In the present work we studied the effect of different content of polysaccharide filler - carboxymethylcellulose on the vulcanizing characteristics and crosslink density of SBR/CMC blends. The prepared SBR/CMC blend with 10wt% CMC exhibited the comparable values of studied vulcanizing characteristics with the blend containing only carbon black. This fact can lead to opportunity of the partial replacement of the conventional filler carbon black Chezacarb A by carboxymethylcellulose filler. The crosslink density of SBR/CMC blends decreased with increasing of content of CMC. Prepared SBR/CMC blends can find their use in applications, which don't have high tensile strength requirements. The fact that they are more ecological fillers than commonly used black carbons makes them a prospective material for use in products made of technical rubbers and recyclates.

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