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Crosslinking of new elastomers functionalized with carboxyl groups

RAPID COMMUNICATION

Summary — The new carboxylated acrylonitrile-butadiene (XNBR) and styrene-butadiene (XSBR) rubbers produced were crosslinked with zinc oxide. The cure products are characterized by acceptable stress-strain properties. The increase in ZnO amount used, after exceeding of stoichiometric quantity with respect to -COOH groups content, does not improve the stress-strain properties. The curing of new XNBR and XSBR with ZnO leads to the formation of ionic crosslinks. An increase in swelling degree in toluene after action of NH_3 vapors, capable to destroy the ionic bonds, confirms this conclusion. The best stress-strain properties of cured products were achieved when carboxylated rubbers were hybrid cured, *e.g.* using simultaneously zinc oxide and sulfur, in the presence of *N*-cyclohexyl-2-benzothiazolesulfenamide as vulcanization accelerator. The products of such crosslinking contain both ionic and sulfide bonds and are characterized by the tensile strength of 8 MPa in cured state.

Key words: elastomers, carboxylated rubbers, crosslinking, metal oxides, hybrid crosslinking, hybrid network.

SIECIOWANIE NOWYCH ELASTOMERÓW FUNKCJONALIZOWANYCH GRUPAMI KARBOKSYLOWYMI

Streszczenie — Nowe karboksylowane kauczuki butadienowo-akrylonitrylowe (XNBR) i butadienowo-styrenowe (XSBR) (tabela 1) sieciowano za pomocą tlenku cynku użytego w ilości stechiometrycznej względem grup karboksylowych. Usieciowane elastomery charakteryzują się lepszą wytrzymałością na rozciąganie niż ich nieusieciowane analogi (rys. 1). Zwiększenie dodatku ZnO powyżej stechiometrycznej względem ilości grup -COOH nie wpływa na poprawę właściwości mechanicznych usieciowanych produktów. W wyniku sieciowania XNBR lub XSBR za pomocą ZnO powstają jonowe węzły sieci, rozkładające się pod wpływem par amoniaku (rys. 2). Najlepsze właściwości osiągane są jednak podczas sieciowania hybrydowego, tj. jednocześnie tlenkiem cynku i siarką, w obecności przyspieszacza wulkanizacji. Wytworzone w ten sposób produkty charakteryzują się najlepszą wytrzymałością na rozciąganie (ok. 8 MPa) wynikającą z obecności zarówno jonowych, jak i siarczkowych wiązań poprzecznych.

Słowa kluczowe: elastomery, kauczuki karboksylowe, sieciowanie, tlenki metali, sieć hybrydowa.

Polymers functionalized with ionogenic groups containing both covalent and ionic bonds are termed ionic polymers [1]. Carboxylated styrene-butadiene (XSBR) and acrylonitrile-butadiene (XNBR) rubbers are main precursors of ionic elastomers or elastoionomers [2, 3] known up to date.

XNBR and XSBR are produced during the emulsion terpolymerization of butadiene and acrylonitrile or styrene in an alkaline medium, in the presence of unsaturated monocarboxylic (acrylic or methacrylic) acid or dicarboxylic acid (maleic or fumaric one) as termonomers [4, 5]. However, the incorporation of carboxyl groups into rubber chains in this way is connected with some difficulties. The low solubility of the salt formed under these conditions in the hydrocarbon phase causes that only the insignificant amount of carboxyl groups is attached into rubber chain. Thus the terpolymerization in acidic medium, in the presence of cationic emulsifiers, is an applied and widely used method. However such manufacturing method needs to use acid resistant apparatus and leads to problems connected with the pollution of waste water [5].

We have elaborated a new method of producing of carboxylated elastomers [6, 7] based on the emulsion terpolymerization, in an alkaline medium, of the butadiene and acrylonitrile or styrene with selected monoalkylmaleamides as termonomers, which are characterized by

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higher solubility in organic phase. This method seems to be an alternative to above mentioned one.

The purpose of our work was to study the crosslinking of new elastomers functionalized with carboxyl groups and the investigation of properties of products obtained.

EXPERIMENTAL

Materials

Carboxylated acrylonitrile-butadiene rubbers (XNBR) and styrene-butadiene rubbers (XSBR) were produced according to the patent declarations [6, 7], in the Research and Development Centre of Rubbers and Vinyl Plastics in Oświęcim during the emulsion terpolymerization in alkaline medium with monooctylmaleamide as termonomer, in the presence of potassium persulfate activated by triethanolamine as a radical initiator. The characterization of elastomer studied is presented in Table 1. The rubber mixtures were prepared using cold two roll mill, according to standard procedure, and pressure cured in the press during heating of plates placed in closed steel form.

Methods

The carboxyl groups content in functionalized elastomers was determined by FT-IR spectroscopy using BIO-RAD 175C Spectrometer and calculated from an acid number of rubber determined by alkalimetry. The rubber was purified by extraction with suitable solvent (hexane or methanol), dried in vacuum, solved in tetrahydrofurane-toluene (or xylene) mixtures and then titrated with KOH solution in ethanol [8].

Nitrogen content in purified rubber was determined by Schöniger method.

The crosslinking degree and structure of functionalized rubber were characterized by IR method and by the swelling degree in selected solvents, determined with standard procedures used in our earlier studies [8, 9].

The tensile strength (TS_b) was determined using Zwick tensile tester Model 1435, according to PN-ISO 37:1998.

RESULTS AND DISCUSSION

The analysis of new carboxylated elastomers produced according to the new method used shows that the application of selected monoalkylmaleamides as new modyfing agents and suitable reaction conditions leads to macromolecular compounds of controlled contents of pendant carboxyl groups. It follows from FR-IR analysis and determination of acid number (Table 1).

The characteristic feature of carboxylated rubbers is their possibility to crosslinking with metal oxides [10, 11]. We have found that new carboxylated acrylonitrile-butadiene and styrene-butadiene rubbers obtained are capable to undergo the curing with metal oxides. XNBR and XSBR cured with ZnO are characterized by higher TS_b than uncured ones, what is shown in Fig. 1. As an example TS_b of uncured XNBR equals 0.88 MPa whereas TS_b of the rubber cured with 105 mmol ZnO/100 g equals 3.60 MPa. The further increase in ZnO amount used, after an exceeding of stoichiometric quantity with respect to -COOH groups content, does not improve the stress-strain properties of cured rubber. The crosslinking

Table 1. Characterization of the elastomers studied; denotations: AN — acrylonitrile, Bu — butadiene, St — styrene, OMA — monooctylmaleamide

Elastomer	Content of monomers in polymerization mixture			Acid number mg KOH/g	Content of -COOH groups mmol/100 g	Bound nitrogen content wt
XNBR	AN 300 g	Bu 650 g	OMA 110 g	39.0	69.5	7.03
XSBR	St 500 g	Bu 400 g	OMA 125 g	40.0	71.2	0.65

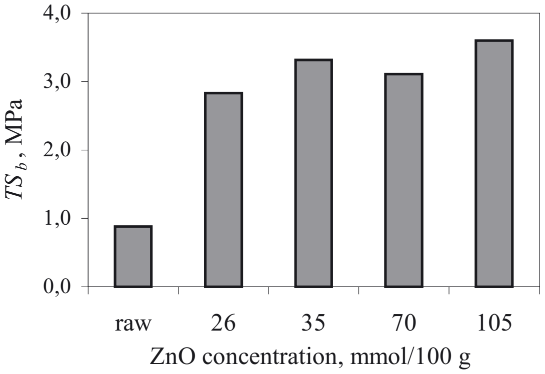

Fig. 1. Tensile strength (TS_b) of raw XNBR and XSBR after curing with different amounts of ZnO

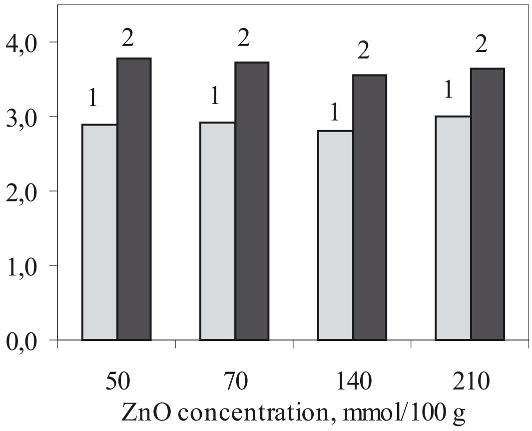

Fig. 2. Effect of ammonia vapor on the swelling degree of XNBR cured with different amount of ZnO: 1 — in toluene, 2 — in toluene after action of ammonia vapor

with metal oxide leads to the formation of ionic crosslinking. Such structure was confirmed by FT-IR spectra of carboxylated rubbers cured with ZnO. Wide band at 1550—1670 cm^{-1} ascribed to the asymmetric carboxylate ($-R-COO^{(-)}$) stretching and the band at 1415 cm^{-1} asigned to the symmetric carboxylate stretching are present in FT-IR spectra (not shown here). An increase in swelling degree in toluene after action of NH_3 vapors, capable to destroy the ionic bonds, also confirms the formation of the ionic crosslinks during the heating (Fig. 2).

The most characteristic feature of unsaturated carboxylated elastomers is their ability to hybrid crosslinking, *e.g.* using sulfur-accelerator-metal oxide system [4, 12—14]. Our studies confirm these conclusions. We have found that new carboxylated rubbers obtained can be cured with zinc oxide and sulfur, in the presence of suitable accelerators. Tensile strength of XSBR cured with ZnO only (5 phr) does not exceed 1.50 MPa, whereas tensile strength of this rubber cured with ZnO (5 phr) and sulfur (2.5 phr) used together, in the presence of *N*-cyclohexyl-2-benzothiazolesulfenamide (1 phr) as an accelerator, equals 8.85 MPa. All new carboxylated elastomers cured with hybrid system are characterized by much better stress-strain properties due to the presence of both ionic $(-COO^{(-)})_2Zn^{2+}$ and sulfide $>C-S_x-C<$ (where $x \geq 1$) crosslinks in their network formed simultaneously during heating of rubber with ZnO and sulfur, in the presence of accelerator.

CONCLUSIONS

On the basis of our studies we can confirm that new elastomers functionalized with carboxyl groups during the emulsion terpolymerization in an alkaline medium with monooctylmaleamide as termonomer, in the presence of potassium persulfate activated by triethanolamine used as a radical initiator, can be cured with zinc oxide, which leads to the formation of ionic crosslinks. The best properties of cured products were achieved when new carboxylated rubbers were hybrid crosslinked using zinc oxide and sulfur, in the presence of selected accelerator. The products of such crosslinking contain both ionic and sulfide cross-bonds and are characterized by best stress-strain properties in cured state.

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