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Multifunctional Action of *in situ* Formed Zn-Salt of Monoallylmaleamic Acid

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Summary: Monoallylmaleamic acid (CH_2=CH-CH_2-NH-CO-CH=CH-CO-OH; MAMA) when used in combination with zinc basic carbonate (ZBC) shows multifunctional action during processing and peroxide curing of hydrogenated nitrile rubber (HNBR). It follows from the lower viscosity, higher crosslinking degree and higher tensile strength of samples prepared from HNBR, MAMA, ZBC and peroxide, compared with the HNBR cured with the peroxide only. This kind of activity of the such system is connected with the *in situ* formation of very small particles of Zn-MAMA salt dispersed in the rubber matrix and in part chemically bound to the rubber.

Introduction

The degree of crosslinking and mechanical properties of nitrile or hydrogenated nitrile rubber (HNBR) can be improved if their peroxide curing occurs in the presence of such coagents as triallyl cyanurate, isocyanurate or trimellitate, acrylates or methacrylates of di- and polyfunctional alcohols, N,N'-m-phenylenedimaleimide [1-3] and Zn- or Mg-salts of acrylic and methacrylic acids.[4] The salts mentioned act especially effective as coagents and active fillers if they are formed *in situ* from acid and metal oxide added to the rubber before its crosslinking.[4-7] The *in situ* formation of such salts is however connected with some troubles due to the volatility and unpleasant smell of the acids used. These problems can be overcome by the use of selected maleamic acids, e.g. the products of reaction of maleic anhydride with unsaturated amines of general formula R_1-NH-CO-CH=CH-CO-OH (R_1 = alkenyl), instead of acrylic or methacrylic acid, and Zn inorganic salt instead of ZnO.[8] The maleamic acid used reacts during processing and heating with Zn salt dispersed in the rubber matrix and forms *in situ* fine particles of dimension of 10^{-6} m and lower. Due to the presence of double bond both in unsaturated alkenyl chain and in maleic rest of maleamic acid the salt formed in this way showed interesting behaviour during processing and curing of HNBR. The paper presents selected data of the systems composed of HNBR, dicumyl peroxide (DCP), monoallylmaleamic acid (MAMA; R_1 = CH_2=CH-CH_2-) and zinc basic carbonate (ZBC; HO-Zn-O-CO-O-Zn-OH), especially the multifunctional action of MAMA/ZBC

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combination and/or the Zn-MAMA salt formed during processing and crosslinking of the rubber.

Experimental

Hydrogenated nitrile rubber Therban 3907 (HNBR, 39 wt. % of bound acrylonitrile) from Bayer AG, dicumyl peroxide (DCP) from Schuhardt, zinc basic carbonate (ZBC) from Merck, maleic anhydride and allyl amine from Reachim (Russia) were used for the experiments. The monoallylmaleamic acid (MAMA) were synthesized from maleic anhydride and allyl amine and purified according to standard procedure (N content: calc.: 9,03 wt. %; determ.: 9,09 wt. %). The compounding ingredients (MAMA, ZBC, DCP and others) were mixed with HNBR using the 150x300 mm two-roll mill at 300-310 K. The behaviour of the rubber compounds during heating was determined from standard vulcametric data using the WG-02 vulcameter. The compounds were press-moulded and cured at 433 K for 45 min. For DMTA analysis the Rheometrics Inc. DMTA Analyser Mk III was used. The IR spectra of thin samples (< 30 μm) prepared by compression moulding were obtained with the BIO-RAD 175 C spectrometer. SEM studies were carried out with Joels 35C microscope using the samples fractured in the glass state. Others measurements were performed in accordance to standard procedures (ISO).

Results and Discussion

The HNBR compounds containing MAMA alone or MAMA/ZBC show better flow properties and higher degree of crosslinking than the rubber cured only with peroxide. It is manifested by lower minimum torque V_{min} and higher increase of vulcametric torque ΔV_{max} comparing with the values determined for the peroxide cured rubber, Table 1. It means that MAMA, even in low concentration acts as a lubricant in HNBR and improves in this way the processing properties of the rubber compounds. This kind of MAMA behaviour seems to be similar to the action of known lubricants in PVC or to the action of fatty acids amides in rubber-carbon mixes [9]. The observed decrease of the minimum torque V_{min} and increase of the vulcametric torque ΔV_{max} depend on the amount of MAMA used and the molar proportion of MAMA/ZBC in the compound.

The presence of MAMA and ZBC during curing of HNBR with DCP results in significantly higher tensile strength and curing degree of the products. The higher degree of crosslinking is manifested by higher tensile stress, lower swelling ratio Q_v in suitable solvent and lower compression set than in the case of HNBR cured with peroxide only. These effects are strongly influenced by the amount of MAMA used and by the proportion of MAMA/ZBC in the system and were established in the unfilled rubber and in HNBR reinforced with HAF carbon black as well, Table 1. It means that MAMA used alone or combined with ZBC increases the efficiency of crosslinking of HNBR by peroxide and acts as a crosslinking coagent. This action is connected with the presence of >C=C< double bond in allyl chain of MAMA.

From extraction experiments it follows that the MAMA used alone or combined with ZBC cannot be extracted with suitable hot solvents (hexane, acetone or water) from the cured rubber. It means that during heating MAMA or its *in situ* formed Zn-salt were chemically bound to HNBR. The data show that more than 60-70 % of added MAMA

Table 1. Effect of the rubber compounds composition (phr) on peroxide curing and selected properties of crosslinked HNBR.

	I	II	III	IV	V	VI
Therban 3907	100	100	100	100	100	100
DCP	3,6	3,6	3,6	3,6	1,8	1,8
MAMA	-	6	6	6	-	2
ZBC	-	-	11,4	17	-	6
Carbon black N336	-	-	-	-	40	40
Vulcametric data at 433 K						
Scorch time t_{02}, s	118	121	92	87	130	150
Minimum torque V_{min}, dNm	21,2	17,3	18,8	18,9	24,7	16,4
Torque increase ΔV_{max}, dNm	75,1	79,3	86,1	85,2	52,4	64,8
Properties of samples cured at 433 K for 45 min						
Volume swelling*, ml/ml	4,18	3,03	2,97	3,03	9,20	5,52
Stress at 200 % elongation, MPa	1,15	2,01	2,10	2,74	3,57	5,81
Tensile stress, MPa	10,8	8,2	11,2	14,0	20,8	24,2
Elongation at break, %	590	415	390	560	550	550
Relative compression set**	1,00	0,843	0,647	0,630	1,00	0,725
T_g: from E''_{max}, K from $\tan\delta_{max}$, K	246,5 257,4	250,1 259,9	252,5 259,2			
E''_{max} (at $T = T_g$), MPa $\tan\delta_{max}$ (at $T = T_g$)	112 1,775	126,5 1,748	118,3 1,654			

**rubber phase in methyl ethyl ketone;* ***after 120 hrs at 423 K; E", δ - loss modulus and angle* became insoluble during crosslinking.

New absorption bands at 1540-1720 and ~3320 cm^{-1} are present in the IR spectra of HNBR cured with DCP in the presence of MAMA or MAMA/ZBC systems and than purified by the hot extraction with suitable solvents, Figure 1. These bands are connected with the presence of carboxyl, hydroxyl and amine groups in -CO-OH, $-CO-O^{-}$ ^{+}Zn and –NH-CO- groups in the rubber crosslinked with DCP in the presence of MAMA or MAMA/ZBC. It confirms the intermolecular reaction of MAMA with ZBC and MAMA or its Zn salt with HNBR during heating.

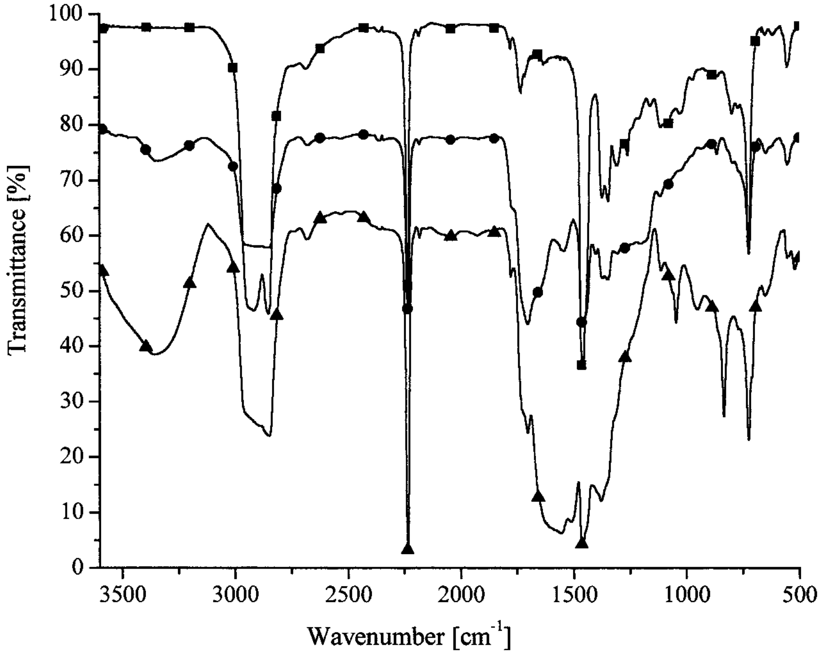

Figure 1. IR spectra of HNBR cured with: DCP (3,6 phr) (■), DCP+MAMA (4,5 phr) (●) and DCP+MAMA+ZBC (6+11,4 phr) (▲); samples purified by hot extraction

From SEM studies it follows that the heat treatment during processing of the HNBR/MAMA and HNBR/MAMA/ZBC compositions and their curing with the peroxide changes both the crystalline form and dimensions of MAMA and ZBC particles, Figure 2. In uncured state MAMA is dispersed in the HNBR matrix in the form of needle crystals exceeding of~ 20 μm in dimension and shows rather moderate adhesion to the rubber matrix. It is manifested by the visible voids at the interface between the MAMA crystals and the rubber matrix, Figure 2a. During heating and crosslinking the needles disappear and globular species not exceeding of 1-2 μm in dimension are formed. These species have different form (no edges) and show good adhesion to the rubber matrix, Figure 2b. In the case of the uncured system HNBR/MAMA/ZBC the particles of MAMA and ZBC are dispersed in the rubber matrix in the globular form of ~ 10-20 μm in dimension, Figure 2c.

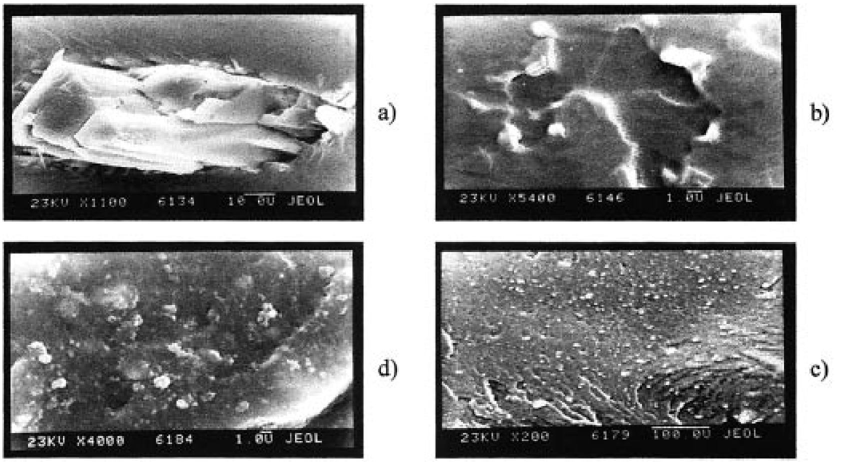

Figure 2. SEM fractographs of HNBR containing 3 phr MAMA before (a) and after curing with DCP 433 K for 45 min (b); MAMA + ZBC (6 + 34 phr) before (c) and after curing with DCP at 433 K for 45 min (d)

Due to the heating and crosslinking the average dimension of these species decreases at least one order of magnitude, Figure 2d. It means that the heat treatment of HNBR/MAMA/ZBC compositions during their processing and curing brings the formation of finely dispersed particles of Zn-MAMA salt, which react with the rubber and act as crosslinking coagent and reinforcing filler as well. This reinforcing effect of the MAMA/ZBC system or the Zn-MAMA salt follows from the data in Table 1. It should be underlined that the reinforcing effect of ZBC in peroxide cured HNBR is much lower than produced by ZBC used alone. The heat treatment of the HNBR-DCP-ZBC system brings no changes to the form and dimension of ZBC particles dispersed in the HNBR matrix. These observations indicate that from unsaturated maleamic acid and Zn inorganic salt of basic nature (ZBC) the fine particles of the Zn-MAMA salt are formed *in situ* in the HNBR matrix during processing and heating of the rubber compound. The formed salt particles have probably partially the structure of ionic clusters dispersed in the rubber and there are in part bound to the rubber. The clusters can be destroyed by action of strong polar solvents (e. g. pyridine) during swelling of the crosslinked samples in the mixture of toluene and pyridine.

Conclusion

The results show that the monoallylmaleamic acid used in combination with the zinc basic carbonate decreases the viscosity of the rubber during processing and increases the tensile strength and the degree of crosslinking of hydrogenated nitrile rubber cured with peroxide. Thus the *in situ* formed Zn-MAMA acts as a multifunctional agent in HNBR, e.g. as processing aid, crosslinking coagent and reinforcing filler as well.

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