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Mechanochemical Reactions of Hydrogenated Acrylonitrile-Butadiene Rubber

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The summarised results of studies on mastication of hydrogenated acrylonitrile-butadiene rubber (HNBR) are presented. Milling of HNBR on a cold open mill (at 298-300 K, cold mastication) leads to significant decrease both of its Mooney viscosity $V_{\rm M}$ and molecular weight M_n . Prolonged mastication gives the limited $M_{n,lim} = 58,5$ to 66,5 kg/mol of elastomers. The determined degradation rate and degree of elastomer are almost independent on bound acrylonitrile content (34 - 43 wt.-%) and residual double >C=C< bonds content (up to 4 mol. %) in the HNBR used. The decrease of M_n during the cold mastication can be described by the same first order rate constant $k^I = 4,80(\pm0,22).10^{-4}$ s⁻¹. The cold mastication of HNBR is accompanied by narrowing of its molecular weight distribution (MWD) and is not a statistical process. Free macroradicals formed during the cold mastication initiate polymerisation of vinyl monomers that leads to block copolymers. An extent of such reactions and length of polyvinyl compound blocks are small if acrylic, methacrylic, maleic or itaconic acids were used. If acryloamide was used (2 - 5 mmol/g) up to 80 % of amide became attached to HNBR chains forming blocks exhibiting their own glass transition temperature $T_g = 460-467$ K. The formed block-copolymers are not soluble in THF, but reveal an increased swelling in water (up 60 wt.-%).

From M_n and V_M determinations it follows that HNBR is able to degradation during a hot mastication (423–453 K) in internal mixer only to small extend, both in a presence or absence of a peptiser. An extent of the degradation in this case is only slightly influenced by temperature, an amount of the peptiser added and polarity of HNBR investigated. GPC studies showed that the degradation of HNBR chains during hot mastication is not accompanied by narrowing of MWD and is a statistical process.