



CHEMICAL MODIFICATION OF OXIDIZED POLYMERS

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ABSTRACT

In the process of research, a device to determining the rheological, dilatometric, relaxation and deformation characteristics of individual polymers and polymer compositions under the conditions corresponding to operating conditions has been developed. A mechanical-chemical modification of a mixture of ethylene-propylene copolymers (SREP-5, ... = 1.7-1.8 x 10⁵ ρ = 870 kg / m³, EPDM - 60, propylene content - 40%, antioxidant - 0.3% (m.), Mooney viscosity - 60, unsaturability - 1.7% (m.) and polyvinyl chloride (PVC)). Mechanochemical mixtures of polymers were preliminarily processed on rollers at 60 ° C within 5-7 minutes. The basic considered concerning destruction of ethylene-propylene and isobutylene-isoprene copolymers affected by high-frequency deformation due to common impact of temperature, pressure, ultrasonic oscillation (US) and other factors have been considered. Graft copolymerization mechanisms have been studied for a number of industrial polymers as well as the primary kinetic regularities for polymer modification by graft copolymerization.

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INTRODUCTION

Oxidizing of copolymers by atmospheric oxygen in solutions has been carried out to study the macro-hydroperoxide impact in low-temperature modification reaction of ethylene-

propylene copolymers atmospheric oxygen in $\begin{matrix} \text{OOH} \\ | \\ -\text{C}- \\ | \\ \text{CH}_3 \end{matrix}$ are the primary products of the polymer thermal oxidation, the

destruction of which resulted in formation of free $\begin{matrix} \text{O} \\ | \\ -\text{C}- \\ | \\ \text{CH}_3 \end{matrix}$ radicals and OH. In this regard, accumulation of hydroperoxide groups during polymer oxidation is used to carry out modification:

Formation of hydroperoxide groups in a macromolecule was shown by controlled oxidation of partially isopropylated polystyrene.

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It was succeeded to produce "pure" grafted copolymers during the hydroperoxide group decomposition in the oxidizing agent presence: Macro peroxide groups were used to initiate polymerization of styrene, acrylonitrile, vinyl acetate and vinylidene chloride. Free-radical initiators accelerate polymer oxidation in the solution and admit to accumulate a sufficient amount of hydroperoxide groups at relatively low temperature (70 °C to 90 °C) to carry out grafted polymerization. Modification is carried out in the presence of different metal ions, to slow down homopolymer synthesis reactions activated by OH-radicals. The impact of the initiator amount, temperature, time, air feed rate and polymer concentration in the solution on the oxidation degree has been studied. At constant EPDM solution concentration in toluene 3% and air feed rate- 200 ml/min, active oxygen content in the polymer increases to a certain value with the increase of the initiator amount and the feed rate (Fig.1.). EPDM-50 oxidation temperature is 85°C. The highest active oxygen content in the polymer is achieved within 300 minutes. However, the study of EPDM-50 destruction process has shown that it was also accelerated with the reaction time increase.

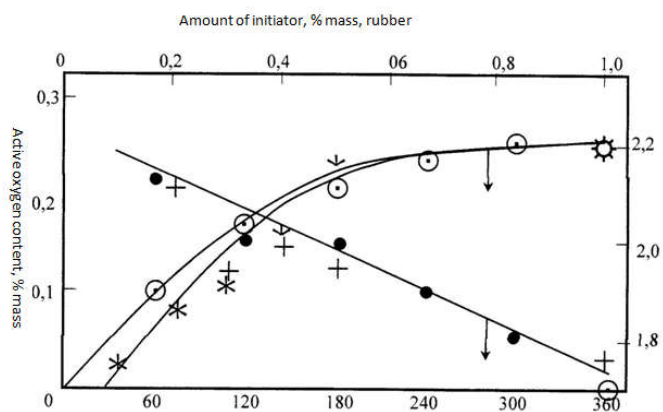
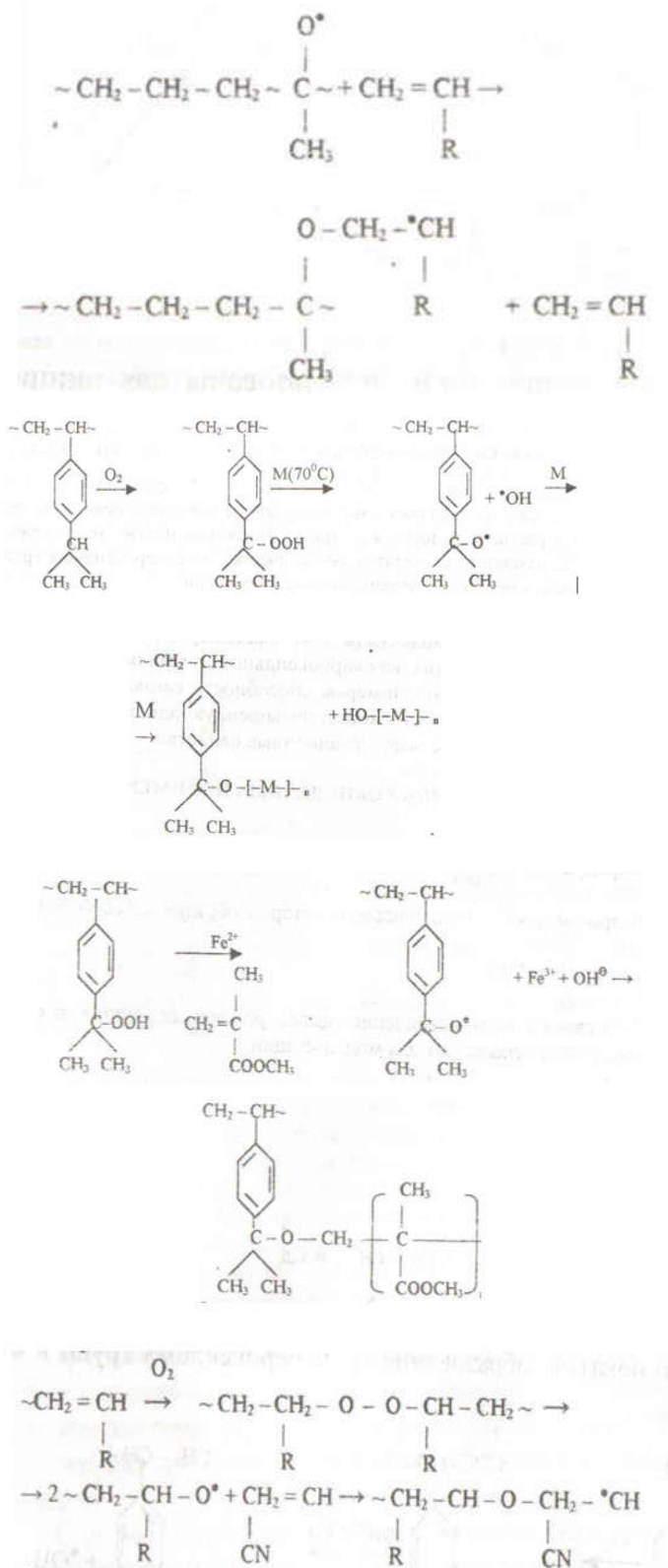


Fig.1. Dependence of the active oxygen content and EPDM intrinsic viscosity on oxidation time (○ and •, correspondingly) and the initiator amount at 240 min. reaction time 240 min. (* and +, correspondingly)

Decrease of the active oxygen content at higher solution concentrations is explained by the difficulty of oxygen diffusion into the polymer phase. Based on the analysis of the obtained analysis, the conditions for EPDM oxidation: have been defined $T, ^\circ\text{C} - 85$, $\tau_{\text{reac}} = 180$ min., $C_{\text{initiat}} = 0.5\%$ (mass.) of the EPDM amount. Researches showed that in order to obtain the samples containing up to 0.5% (mass.) of active oxygen, it is necessary to use EPDM with higher viscosity (Montecatini Edison). ($\bar{M}_\eta - 2.0 - 2.2 \cdot 10^5$ Mooney viscosity 90 at 125°C ; $[\eta] = 2.82$ at 135°C ; propylene content $\sim 55\%$ (mol.)) and tert-butyl hydro peroxide as an initiator.

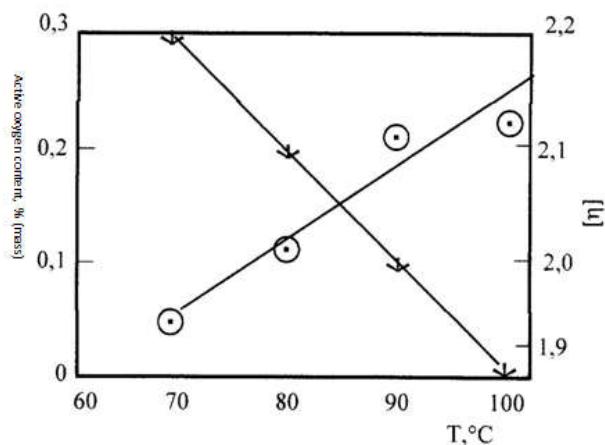
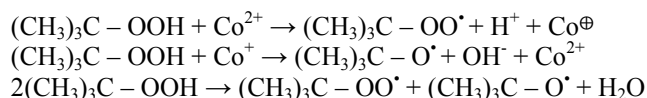


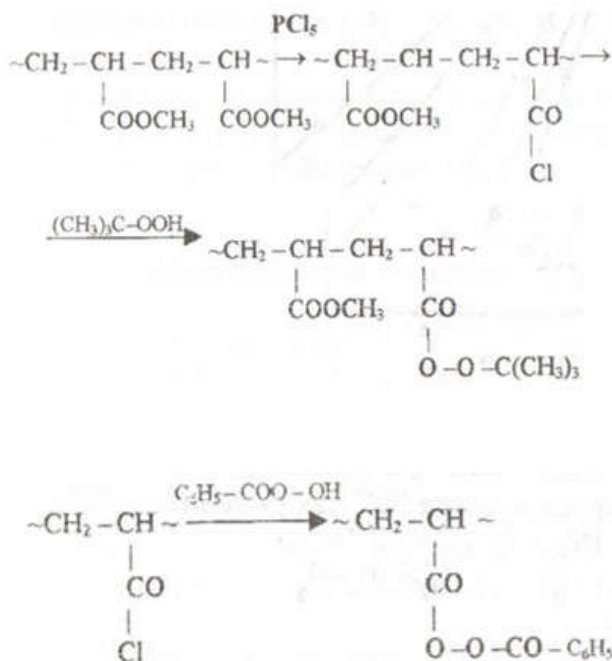
Fig.2 The plot of the active oxygen content (○) and intrinsic viscosity (*) vs the EPDM-50 oxidation temperature. Reaction time was 180 minutes, initiator concentration is 0.5% (mass), air feed rate is 100 ml/min

That is why 180 minutes were taken as optimum reaction time. By changing the air feed rate from 50 ml/min to 100 ml/min, active oxygen content increased from 0.16% to 0.22% (mass). and remains the same at the further air feed increase [6,15]. Increase of the active oxygen content in final product due to temperature increase may be explained by the fact that higher temperatures EPDM macromolecule mobility and air diffusion into the polymer phase increase. Taking into account this circumstance and polymer destruction, oxidation temperature was chosen to be 85° (Fig. 2). When concentration of EPDM-50 solution changed from 3.5% to 7%, the active oxygen content varied accordingly: 0.22%, 0.20%, and 0.18% (mass.).

The small amount of organic peroxides and oxidizing agents promoted formation of active peroxide radicals [107, 108]:



Upon availability of reactive groups in the polymer chain, hydroperoxides might react with them forming new copolymers. Polymethyl methacrylate is modified by tert-butyl hydroperoxide: or by perbenzoic acid:



At 90 °C decomposition of ~ROOH group in EPDM samples with higher viscosity finished within 3.5 hours and at 30 °C within more than 15 hours. The active oxygen feed rate was measured by iodometric titration by the difference between the initial amount of active oxygen and the residual one at the measurement time point (Fig. 1.3).

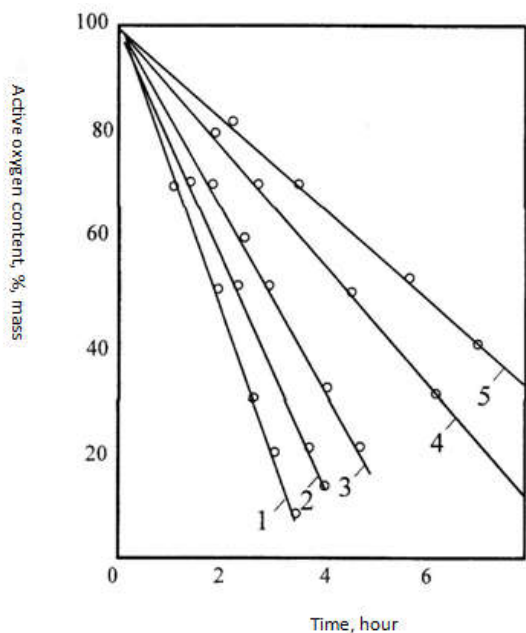
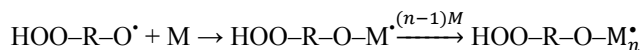
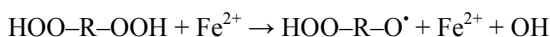
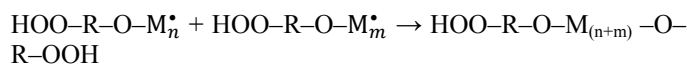


Fig. 3. Dependence of the active oxygen content vs. the reaction time at different temperatures, T, °C: 1 - 90; 2 - 70, 3 - 60, 4 - 40, 5 - 30

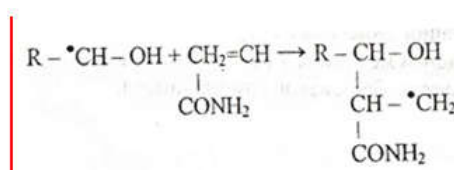
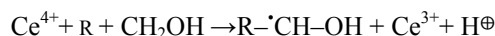
It was shown that the higher output of modified elastomer was achieved in the system oxidized by EPDM – polyvinylidene chloride at lower temperatures; is not observed when using peroxide initiators. During copolymerization of oxidized EPDM with vinylidene chloride in the presence of a small amount of metal ions, homopolymer formation decreases due to their interaction with OH-radicals. These reactions were used during monomer polymerization in emulsion at the presence of Fe²⁺ dihydroperoxide as an oxidizing agent [59]:



Then, the reaction was carried out in oil for the fast formation of polymer chain



It was shown the possibility to activate alcohols and to initiate grafted copolymerization with their vinyl monomers has been shown:



Copolymerization at low temperatures showed that monomer conversion drastically increased in the presence of Ce³⁺ ions and completely finished within 24 hours. Monomer conversion was very high in the presence of Fe²⁺, Co²⁺, VO²⁺ metal ions; but it does not depend much on the ion type (Table 1). The effect of the [M] / [EPDM] ratio on the output of the elastomer modified in emulsion differed from the impact of this ratio during mass modification, which was explained by the difference between the copolymerization mechanism for the EPDM – vinylidene chloride system in mass and in emulsion. During modification in emulsion, monomer diffusion was essential. Modification of oxidized EPDM with vinylidene chloride and MA in emulsion at 65 °C for 24 hours showed that the high conversion degree was observed only at low [M] / [EPDM] ratios. During modification with monomer mixtures, the high conversion degree and high output of modified elastomer was observed when using benzoyl peroxide as an initiator. The study of the oxidized EPDM modification with methacrylic acid (MAA) showed that the highest conversion degree was achieved at a temperature of 95 °C; however, the content of MAC homopolymer in the prepared product was (3-5)% (mass.). Taking into account the sufficiently high conversion degree and formation of homopolymer small amount (1.1-2.3% (mass.)), reaction was carried out at 90 °C. Activation energy of the process was -71.0 kJ/mole when using its graphical calculation and -67.0 kJ/mole using analytical procedure. \overline{M}_n of monomer units grafted to the polymer macromolecule, i.e., monomer polymerization was one of the basic characteristics impacted physical-mechanical and chemical properties of modified polymers. PMAA homopolymer was selected to measure the MAA polymerization degree during modification of oxidized EPDM at different temperatures and its molecular weight was calculated (Fig. 4.). Δ was the dependence of the MAA polymerization degree on the grafted copolymerization temperature. [-O₂-] content was 0,2% mass. Kinetic study and analysis of the obtained copolymers allowed to define optimum conditions for the MAA interaction with oxidized EPDM: T, °C = 90; C_{O₂} = (0.20-to 0.02) % (mass.), τ = 2.7 hours. The mechanism was proposed to describe formation of SREP-MAA grafted copolymers.

Table 1. Modification of oxidized EPDM with vinylidene chloride in emulsion in the presence of metal ions

T, °C	Time, hours	Active [-O ₂ -] content, % (wt.)	Ions	[M] [EPDM]	Monomer conversion degree, %	Modified EPDM, % (mass.) of initial EPDM
50	24	0.4±0.06	Ce ⁺³	0.666	91.0	56.3
-	-	-	Fe ⁺²	0.666	85.0	54.0
65	-	0.23±0.02	Ce ⁺³	0.675	100	50.5
-	-	-	Co ⁺³	0.675	100	57.0
-	-	-	Vo ⁺³	0.675	88.0	62.0
-	-	0.40±0.06	Ce ⁺³	0.666	100	55.4

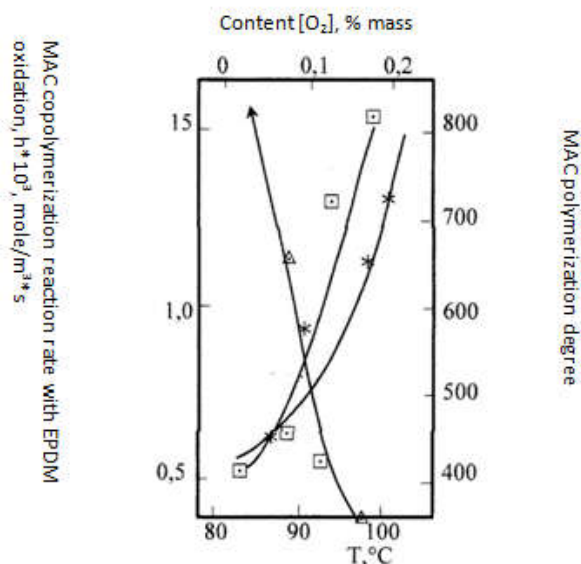
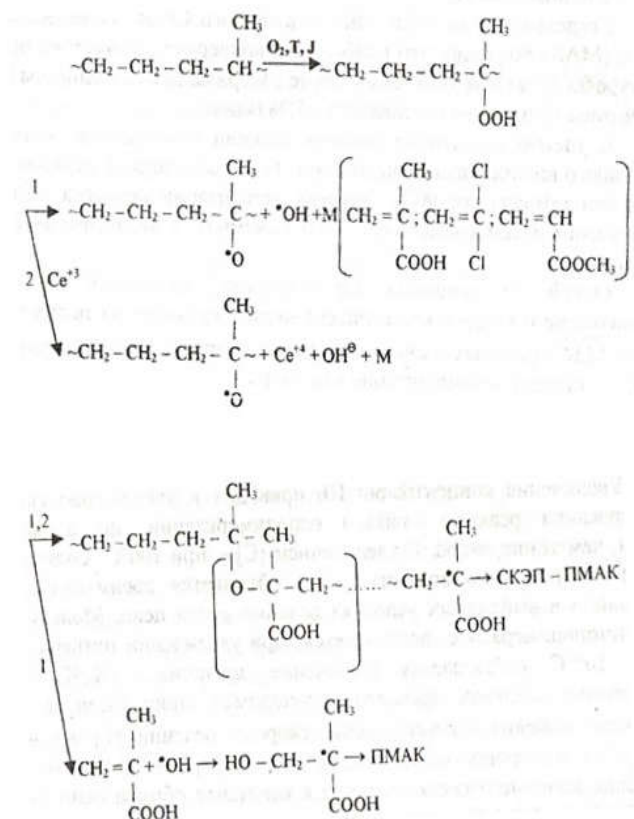
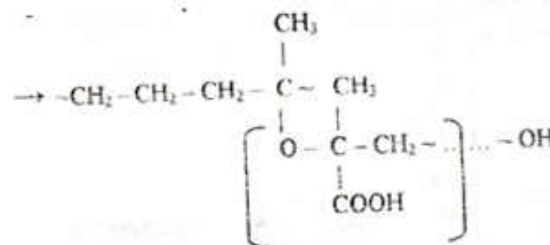


Fig.4. Dependence of the MAA copolymerization rate with oxidized EPDM on the temperature (□) and the active oxygen content (*). Δ was the dependence of the MAA polymerization degree on the grafted copolymerization temperature. [-O₂-] content was 0.2% mass



Chain breakage – recombination of RO_{EPDM}^\bullet and $R_M^\bullet \rightarrow$



There was no modification of oxidized EPDM with acrylamide (AA) under the EPDM-MAA synthesis conditions. It was not also possible to carry out this reaction at higher temperature (95 °C and 100 °C) within 12 hours. N₂ was found in grafted copolymer during EPDM modification with acrylamide in the presence of benzoyl peroxide. Absorption bands (3,100-3,600)cm⁻¹ and (1,600-1,700) cm⁻¹ appeared in IR spectra typical for stretching vibrations of -CONH₂ groups. Based on these data, the conclusion was made that EPDM modification with AA should be carried out in the presence of the initiating system. Thus, the problem was solved concerning production of polymers having necessary properties for their application in extreme conditions has been solved.

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