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## Investigation of structure and thermophysical characteristics of chlorinated ethylene-propylene-diene rubber (EPDM)

Macromolecular structure of chlorinated ethylene-propylene-diene rubbers (CEPDM) and their probable changes, which happen in process of rubber vulcanization were studied by method of infrared spectroscopy. Rubbers CEPDM-2, CEPDM-4 and CEPDM-16, consequently containing 2, 4 and 16% (mole) chlorine were taken for the investigation. As sample for comparison was used initial ethylene-propylene-diene rubber EPDM, not containing halogen. To determine thermostability of macromolecular structures of investigated polymers under vulcanization temperature, the specimens of rubber subjected to heating vulcanizing press under temperature 151°C during 5, 10, 20, 30, 40, 50 and 60 minutes. To study thermophysical characteristics of chlorine-containing EPDM were used methods of differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA). In result of spectral investigation of specimens were established that in process of obtaining CEPDM-2, chlorine combine with fragment of ethylidenenorbornene (ENB), but the structure of the main chain wasn't touched. As a result of elimination of hydrochloride new double linkage is forming and halogen in  $\alpha$ -position to this linkage, that increases vulcanization rate of CEPDM-2 based rubber. When obtaining CEPDM-4 and CEPDM-16 chlorine associated as to ENB fragment as well as to the main chain of polymer, in the result of elimination of hydrochloride another double linkages can occur. This process permanently will result in decrease of ozone resistance of vulcanized rubbers CEPDM-4 and CEPDM-16.

**Key words:** chlorination, rubber, mechanical chemistry, chlorinated ethylene-propylene-diene rubber (CEPDM), elimination of hydrochloride, elastomer.

## Badania struktury i właściwości termofizycznych chlorowanego kauczuku etylenowo-propylenowo-dienowego (EPDM)

Wielkocząsteczkową strukturę chlorowanych kauczuków etylenowo-propylenowo-dienowych (CEPDM), a także prawdopodobne zmiany zachodzące w procesie ich wulkanizacji, badano metodą spektroskopii w podczerwieni. Badaniom poddano kauczuki CEPDM-2, CEPDM-4 i CEPDM-16 zawierające odpowiednio 2, 4 i 16% mol. chloru. Jako próbki do porównania użyto wyjściowego kauczuku etylenowo-propylenowo-dienowego EPDM, niezawierającego chloru. Aby określić stabilność termiczną struktury makrocząsteczkowej badanych polimerów pod wpływem temperatury wulkanizacji, próbki kauczuku ogrzewano w prasie wulkanizacyjnej, w temperaturze 151°C w czasie 5, 10, 20, 30, 40, 50 i 60 min.

W celu zbadania właściwości termofizycznych EPDM zawierającego chlor użyto metod różnicowej analizy termicznej (DTA) i analizy termogravimetrycznej (TGA). W wyniku badania spektralnego próbek ustalono, że w procesie otrzymywania CEPDM-2 atomy chloru przyłączają się do wiązania podwójnego we fragmencie etylidenonorbornenu (ENB), lecz struktura łańcucha głównego pozostaje niezmienną.

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W wyniku eliminacji chlorowodoru powstaje nowe wiązanie podwójne, a chlor pozostaje w pozycji alfa do tego wiązania, co powoduje zwiększeniem szybkości wulkanizacji kauczuku CEPDM-2. W przypadku CEPDM-4 i CEPDM-16 atomy chloru mogą być przyłączone zarówno do fragmentu ENB, jak i do łańcucha głównego polimeru, gdzie w wyniku reakcji odszczepienia chlorowodoru mogą powstawać inne wiązanie nienasycone. Proces ten może spowodować trwały spadek odporności na ozon zwulkanizowanych kauczuków CEPDM-4 i CEPDM-16.

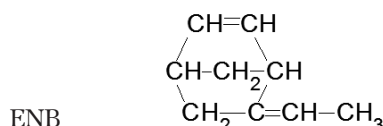
**Słowa kluczowe:** chlorowanie, kauczuk, mechanochemia, chlorowany kauczuk etylenowo-propyleno-dienowy (CEPDM), elastomer

## 1. Introduction

It is known [1–7] ethylene-propylene-diene rubbers (EPDM) and vulcanized rubbers, which based on them possess very valuable properties, as thermo-, weather-, ozone stability, chemical stability to range of aggressive environments, high dielectric indexes, high tensile strength and elasticity; rubbers have high filler loading capacity and are well mixed with ingredients.

Combination of EPDM with all purpose rubbers permits to obtain composition with wider complex valuable properties [1–5]. But widespread using of these compositions are limited due to degraded rate of vulcanization of EPDM and as a rule, it's bad co-vulcanization with high unsaturated all purpose rubbers [8].

All named above complex of EPDM properties are explained by special tips of structural framework of it's macromolecules. Haloid modification of EPDM with the aim of saving of these properties carried out, trying to remove defects, appropriate of EPDM. Among other factors, chlorination of ethylene-propylene-diene rubber with diene co-monomer of ethyлідenenorbornene (ENB) – SKEPTE-40 – was carried out.



It was interesting to carry out haloid modification of this rubber, to study structure of modified rubber, and also probable structural changes, occurring in process of its heating under vulcanization temperature. As specimens of investigation were taken EPDM with ethyлідenenorbornene (SKEPTE-40) and its chlorinated derivatives (CEPDM) with content of chlorine 2, 4 and 16% mole, marked in this work as CEPDM-2, CEPDM-4 and CEPDM-16 respectively. Also it's well-known from literature that the addition of big amount of halogens in macromolecule of polyolefin rubber may result in destruction of macromolecular chain and decrease of polymer thermo-stability. So, for example, destruction of polymer under chlorination more than 2% is observed [2]. So it was interesting to study thermo-stability of chlorinated ethylene-propylene-diene rubbers, which have different content of halogen.

## 2. Experimental

In the work were accepted the forthcoming time intervals of heating 5, 10, 20, 30, 40, 50 and 60 minutes, considering that optimum of vulcanization of chlorinated EPDM (under 151°C) in the different systems of accelerators can range in wide time diapason.

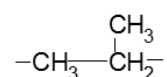
Investigated EPDM and CEPDM preliminary extracted by hot acetone during 24 hours, then exposed to drying before permanent weight with the purpose of removal volatile impurity. From rubbers, purifying from impurities by hot pressing method obtained polymer chain.

Structural investigations were carried out by infrared of spectroscopy method. The temperature of specimens 151°C, that correspond the temperature of rubber vulcanization based on EPDM with different duration of heating time under 151°C: EPDM (heat 5–60 min); CEPDM-2 (heat 5–60 min); CEPDM-4 (heat 5 min); CEPDM-4 (heat 10–40 min); CEPDM-4 (heat 50–60 min); CEPDM-16 (heat 5 min); CEPDM-16 (heat 10–40 min); CEPDM-16 (heat 50–60 min).

Differential thermal (DTA) and thermo-gravimetric analysis (TGA) of investigated polymers for studying of influence of chlorination extent on thermo-stability of macromolecular of CEPDM were carried out [3]. Tenderness of DTA and TGA was changed depending on size of heat effect and amount of emitting of volatile products.

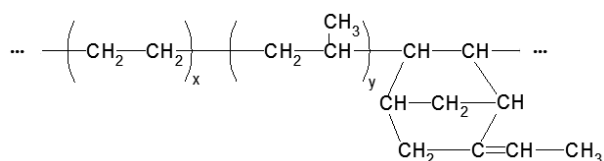
## 3. Results and discussion

Data obtained by Infrared spectroscopy show that structure of macromolecules of EPDM depends on heating time doesn't change. In all the interval of heating time the spectrum of EPDM has distinctive bands of absorption in the field 720, 800, 1150 and 1680 cm<sup>-1</sup>. The absorption band in the field 720 cm<sup>-1</sup> characterizes pendulum oscillation sequentially combined three or five methylene groups. The absorption band in the field 800 cm<sup>-1</sup> characterizes not plane deformation oscillation of CH group in the presence of double linkage in the compound CRR'=CHR". The absorption band in the field of 1150 cm<sup>-1</sup> is determined the oscillation of propylene unit



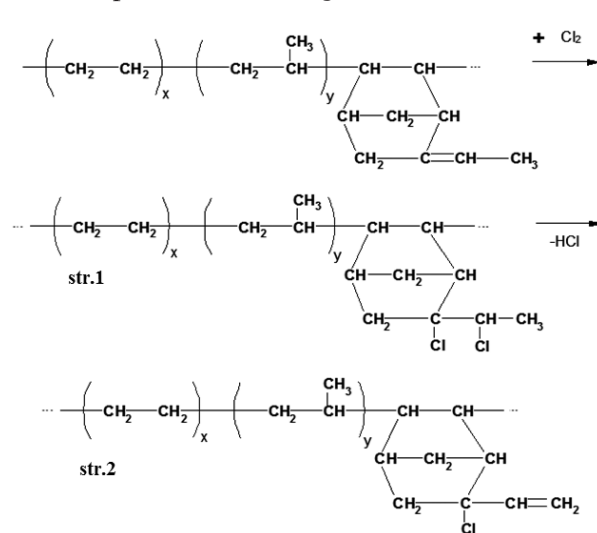
in case of non-conjugated double linkage.

The bands of absorption characterize EPDM, which has the structure.



When considering of spectrum CEPDM-2 we can see, that absorption band disappears in the field 800, 1680  $\text{cm}^{-1}$  and appear two new absorption band in the field 1510 and 1570  $\text{cm}^{-1}$ , characterizing oscillation of cyclical compound. Then under heating in all time interval in infrared-spectrum of CEPDM-2, the changes didn't observe, that shows us the stability of its structure.

Based on obtained data we can suggest the next scheme of changes of macromolecular structure of EPDM in process of obtaining CEPDM-2.



In process of obtaining of CEPDM-2, the attaching of chlorine proceeds after double linkage of ethylenenorbornene fragment, that explains disappearing absorption band 800  $\text{cm}^{-1}$  and 1650  $\text{cm}^{-1}$ .

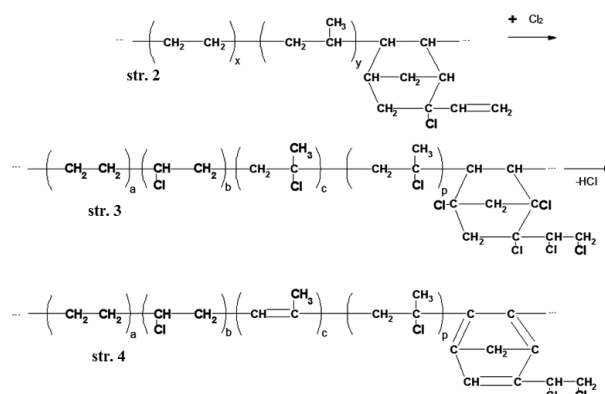
The next elimination of hydrochloride of formed structures results in forming of double linkage. The chlorine atom in this structure is situated in  $\alpha$ -position to double linkage.

When considering of spectrum CEPDM-4 in its spectrum we can observe new absorption band: band in the field 687  $\text{cm}^{-1}$ , characterizing of oscillation of CCl group; 820  $\text{cm}^{-1}$ , characterizing of oscillation of CH group in aromatic cycle; 1265  $\text{cm}^{-1}$ , characterizing of oscillation of double linkage. After heating polymer during 10 minutes the absorption band 1150  $\text{cm}^{-1}$  disappears, all others absorption bands remain without changes.

When heating during 20, 30 and 40 minutes in spectrum CEPDM-4 we don't observe changes, but when heating during 50 minutes is observed wide absorption band in the field 1040  $\text{cm}^{-1}$ , characterizing the presence of ester group. When heating during 60 minutes, the spectrum of CEPDM-4 doesn't change.

When considering of spectrum CEPDM-16 and its changes depending on heating time, we found, that their similarity of spectrums of CEPDM-4, with difference, in absorption band 1040  $\text{cm}^{-1}$ , which was observed after 20 minutes of polymer heating.

Based on obtained experimental data we can suppose the next structural changes in macromolecule of EPDM in process of obtaining of CEPDM-4 and CEPDM-16:

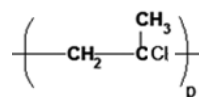


where  $x = a + b$ ,  $y = c + p$ ;  $a, c = 8 \div 12$ ;  $b, p = 2 \div 3$

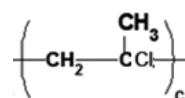
On the first stage the structural changes the similar to observed, when obtaining CEPDM-2 (str. 2). On the second stage we can see adjoin chlorine to cyclical fragment CEPDM-2, and to the main chain of polymer. In process of chlorination of the structure 2 is formed the intermediate structure 3, which in consequence of elimination of hydrochloride modify to structure 4. Structure 3 characterizes building of macromolecule of CEPDM-4 and CEPDM-16 with difference that in macromolecule of CEPDM-16 more the content of units  $-(\text{CHCl}-\text{CH}_2)-_b-$  and are units  $-\text{CH}=\text{CH}-$ , obtained in process of elimination of hydrochloride of part of units  $-\text{CHCl}-\text{CH}_2-$ .

Content of chlorine in the final product, which determines by its amount, adjoined to ethylene macromolecule fragments, and also partially its content of fragments.

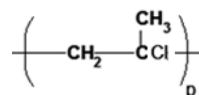
From shown structural formulas we can see, that fragment



in structure 3 has more stability in process of elimination of hydrochloride, that



In process of heating of CEPDM-4 and CEPDM-16, which have structural formula 4, and on the 10<sup>th</sup> minute the elimination of hydrochloride of fragment



is begun, it's explained, that absorption band  $1150\text{ cm}^{-1}$  disappears. Thereof, that percent of unsaturation in CEPDM-4 is less, than for CEPDM-16. Oxidation of the CEPDM-4 is begun after 50 minute of heating, and CEPDM-16 – after 20, as is evidenced by appearance of band  $1040\text{ cm}^{-1}$  in spectrums of these rubbers.

Then investigation associated with influence of extent of chlorination on thermo-stability of macromolecule of CEPDM was carried out. Data of investigation of EPDM and CEPDM are collected on Figure 1.

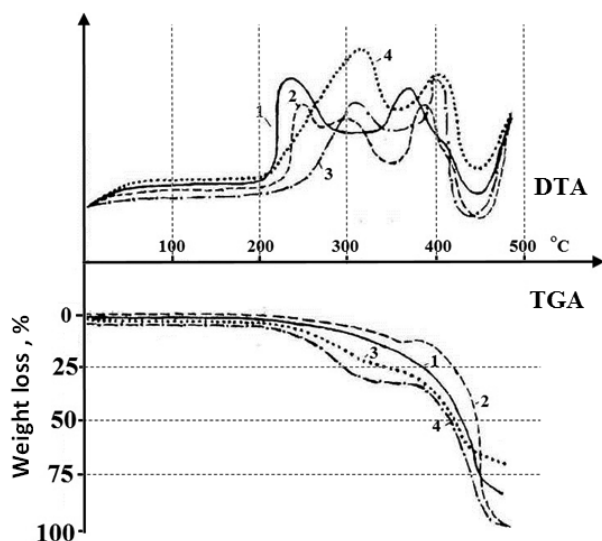


Fig. 1. Curve of differential thermal and thermo-gravimetric analysis of investigated rubbers: 1 – EPDM; 2 – CEPDM-2; 3 – CEPDM-4; 4 – CEPDM-16

Rys. 1. Krzywe z analiz termicznych różnicowej i termo-grawimetrycznej badanych kauczuków: 1 – EPDM; 2 – CEPDM-2; 3 – CEPDM-4; 4 – CEPDM-16

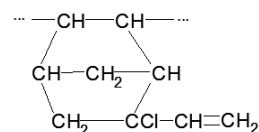
We can see from represented data of DTA, that oxidation of investigated polymers depending on extent of their chlorination is begun in interval of temperatures from  $210^{\circ}\text{C}$  to  $240^{\circ}\text{C}$ , i.e. polymers possess high thermo-stability. So, for example, the beginning of oxidation is observed in EPDM and CEPDM-16 (curve 1 and 4) under  $210^{\circ}\text{C}$ , in CEPDM-2 under  $230^{\circ}\text{C}$  (curve 2), in CEPDM-4 under  $240^{\circ}\text{C}$  (curve 3).

Effective destruction of polymer chains of all types of investigated polymers is begun in the field of temperatures  $410\text{--}420^{\circ}\text{C}$ .

Pyrolysis of polymers is observed under  $480^{\circ}\text{C}$ , when the future increasing of temperature takes place, polymers are carbonized.

Curves of DTA for EPDM and CEPDM have the same character. Each curve has two maximums, which depending on type of polymers are stated in direct temperature fields. So, for EPDM (curve 1) the first maximum is observed under temperature  $230^{\circ}\text{C}$ , the second – under  $380^{\circ}\text{C}$ . It shows, that macromolecule of EPDM has two distinguished by it's capability to oxidation of

structure; apparently it is structural blocks of polyethylene and propylene. Gradual removal of maximum in the field of high temperatures occurs with increase of content of chlorine in polymer. So, it's observed little removal in CEPDM-2 (c. 2), i.e. the first maximum is under  $250^{\circ}\text{C}$ , the second – under  $390^{\circ}\text{C}$ . Maximums under similar temperatures in CEPDM-4, and CEPDM-16 (curve 3 and 4): the first under  $315^{\circ}\text{C}$ , the second under  $405^{\circ}\text{C}$  were observed. It's necessary to note, that curve of DTA depending on type of polymers have differed angle of inclination, characterizing pyrolysis rate. So, curve 1 and 2, characterizing the behavior of EPDM and CEPDM-2, which have similar inclination angle, which can consider approximate to  $90^{\circ}\text{C}$ , and CEPDM-4 and CEPDM-16 have inclination angle, which similar and equal approximately  $45^{\circ}\text{C}$ . The proximity of temperatures, under which we can observe maximum on curve of DTA, and also the proximity of inclination angles of these curves show us the proximity of structural parameters of polymers macromolecules. Here, it's necessary to pay attention to proximity of maximums and inclination angles of EPDM and CEPDM-2 (curve 1 and 2), on the curve 2, characterizing thermal changes CEPDM-2, appears the third maximum in the temperature interval  $300\text{--}310^{\circ}\text{C}$ , that shows us formation of new structure in consequence of chlorine modification. We can suggest, that this changed fragment of ethylenenorbornene:



That assumption confirms data about investigation of structures of these polymers by infrared spectroscopy method. When analyzing the data, obtained in the process of conducting of thermo-gravimetric analysis (TGA), we can see that the method is less sensitive to structural changes of investigated polymers, however on thermo-stability of polymer. So, weight loss of investigated polymers on 10% occurs in EPDM under  $315^{\circ}\text{C}$ , in CEPDM-2 under  $350^{\circ}\text{C}$ , in CEPDM-4 under  $277^{\circ}\text{C}$ , and CEPDM-16 under  $250^{\circ}\text{C}$ . This shows us that thermo-stability of CEPDM-2 is higher than thermo-stability of all other types of investigated ethylene-propylene rubbers. Lower stability of CEPDM-4 and CEPDM-16 is explained by processing in them under heating of elimination of hydrochloride and oxidation reaction.

## 4. Conclusion

Carried out investigation of structure of chlorinated ethylene-propylene-diene rubbers (CEPDM) showed, that in process of obtaining of chlorinated EPDM with the content of chlorine 2% (mole) occurs adjoin halogen on fragment of ENB, in consequence of which is formed new double linkage, in relation to which chlorine is in  $\alpha$ -position. The main chain of macromolecule doesn't change in process of chlorination.



When obtaining CEPDM-4 and CEPDM-16 chlorine adjoins to fragment of ENB and to the main chain of polymer, where in consequence of elimination of hydrochloride is formed additional unsaturation as double linkage.

Data obtained, when investigating of polymers took place by DTA and TGA method, confirm hypothesis about, that when we added in ethylene-propylene-diene rubber of 2% (mole) chlorine, the halogen adjoins to fragment of ENB, not touched the main chain when adding chlorine in amount of 4 and 16 mole, the last one adjoins to fragment of ENB and to the main chain of polymer, where in consequence of elimination of hydrochloride is formed additional unsaturated.

Destructions of macromolecular chains of EPDM in the result of chlorination and elimination of hydrochloride reaction, which lay in base of haloid modification, apparently, weren't observed, because chlorine-containing of ethylene-propylene-diene rubbers have high thermo-stability.

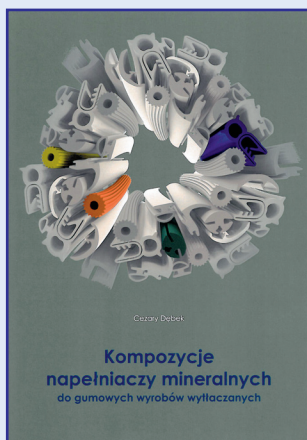
Thus, carried out structural and thermo-physical investigation of chlorinated ethylene-propylene-diene rubbers (CEPDM) allows to estimate macromolecular structures of ethylene-propylene-diene rubbers, which is formed in process of haloid modification and possible changes of these structures under thermal condition.

## References

1. Sadhan K. De, Jim R. White. *Rubber Technologist's Handbook – Rapra Technology Limited, 2001, 61–64.*
2. Brennan P.Y. *First Look at Terpolymer Rubber Synthesis. Chemical Engineering 1965, 72, 14, 94–96.*
3. Sutton M.S. *Blends of Royane with Other Polymers. Rubber World 1964, 149, 5, 62–68.*
4. Livanova N.M., Popov A.A., Karpova S.G., Shershnev V.A., Ivashkin V.B. *Vysokomolek. Soed. 2002, 44, 1, 71–77.*
5. Richard Karpeles and Anthony V. Grossi, "EPDM Rubber Technology", *Handbook of Elastomers, 2nd Ed., Anil K. Bhoomick and Howard L. Stephens, pp. 845–876, Marcel Decker, Inc., New York (2001).*
6. John A. Riedel and Robert Vander Laan, "Ethylene Propylene Rubbers", *The Vanderbilt Rubber Handbook, 13<sup>th</sup> Ed., pp. 123–148, R.T. Vanderbilt Co., Inc., Norwalk 1990.*
7. Gary Ver Strate, "Ethylene Propylene Elastomers", *Encyclopedia of Polymer Science & Engineering, 6, 1986, 522–564.*
8. Ronkin G.M., Andriasyan Yu.O. *Investigation of ethylene-propylene-diene co-polymers chlorination process and properties of obtained materials. Promyshlennost SK 1981, 6, 8–11.*

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