

# New Polymer Compositions on the Basis of Appreted Polyethylene and Silicagel

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## Abstract

In work the results of investigations on development of new classes of the composition materials on the basis of appreted HPPE filled with various mineral fillers are presented. It has been shown that the synthesized ternary copolymers used in work as appretes due to polyfunctional composition allow to prepare the composition materials with high strength properties and adhesion. The results of exclusion-chromatographic investigation of molecular characteristics of ternary copolymers synthesized at radical copolymerization of  $\alpha$ -olefins in a series C<sub>6</sub>-C<sub>8</sub> with maleic anhydride and acrylic acid and also some physical-mechanical properties of polymer compositions modified by them are presented

**Keywords-** highly filled polymer composition materials, polyethylene of high pressure, high-effective exclusion chromatography, molecular-weight distribution

## 1 Introduction

The successes of modern material science have been connected with creation of the new highly filled polymer composition materials (PCM) by a complex of valuable exploitation properties. In this plan a modification of polymer matrices, especially thermoplastic polymers in creation of filled polymer compositions is one of the priority directions [1-3].

This new class of polymer composition materials (PCM) has been developed on the basis of appreted polyethylene of high pressure (HPPE) and mineral fillers in a number of which are zeolite, alunite, azerit, silicagel, kaolin, etc. The amount of these fillers in composition of PCM maintained between 20-60%. As the appretes there were used the ternary copolymers (TC) of the radical polymerization reaction of  $\alpha$ -olefins in a series of C<sub>6</sub>-C<sub>8</sub> with maleic anhydride (MA) and acrylic acid (AA). Due to availability of reactive functional COOH, -CHO, -CO, C=C etc groups in the composition of used copolymers it is increased a reactivity of polyethylene matrix, which leads to the creation of PCM with high exploitation properties. The molecular weights (MW) of the most high-molecular TC, being powder substances, reach ~50-60 thousand. This work has been devoted to the investigation of exclusion chromatographic (EC) investigations of molecular weight distribution (MWD) of presented TC, study of some physical-mechanical

properties of filled materials on their basis and possible ways of their application in the fields of technique and industry.

## 2 Results and Discussion

According to the results of exclusion-chromatographic (EC) investigations depending on conditions of synthesis in the composition of high-molecular TC about 20% there have been detected 3 unsaturated polyfunctional oligomer fractions with ( $M_w$ ) and ( $M_n$ ) 800-2000, 5000-7000 and 6500-9000, respectively. As a result of the carried out investigations, depending on experiment conditions (temperature, ratio of the reacting components, quantity of the catalyst and reaction duration) it has been established the optimal regime carried out the reaction to the same or other side, i.e. to the preparation of products up to complete formation or other fraction in the composition of TC with various values of MW and the parameters of MWD. These properties of the studied TC have been determined by a method of EC on the liquid chromatograph of firm Kovo (Czechia) with refractometric detector. Two columns with size of 3.3×150 mm, filled with immobile phase Separon-SGX with size of particles 7  $\mu$ m and porosity 100 Å have been used. Eluent –dimethylformamide, flow rate – 0.3 ml/min., T = 20-25 C°. The calibrating dependence  $\lg M$  on  $V_R$  in the range of  $M = (1.5-100) \times 10^2$  has been prepared with use of polyethylene glycol

standards. The interpretation of MWD-chromatogram was fulfilled on methodology [4].

The results of EC investigations of MWD of low-molecular TC in a series of  $\alpha$ -hexene, heptene and octane are presented below.

**Table 1.** Molecular-weight characteristics of low-molecular TC synthesized during radical cooligomerization reaction of A-olefins (C<sub>6</sub>-C<sub>8</sub>) with maleic anhydride and acrylic acid (1:1:1)

| № | Sample                           | Quantity of fraction, % | MWD*                 |                      |                                    |
|---|----------------------------------|-------------------------|----------------------|----------------------|------------------------------------|
|   |                                  |                         | <i>M<sub>w</sub></i> | <i>M<sub>n</sub></i> | <i>M<sub>w</sub>/M<sub>n</sub></i> |
| 1 | $\left( \text{MA-Hx-AA} \right)$ | ---                     | <b>7988</b>          | <b>3645</b>          | <b>2.13</b>                        |
|   |                                  | 85.5                    | 8908                 | 8206                 | 1.08                               |
|   |                                  | 4.5                     | 5997                 | 5355                 | 1.12                               |
|   |                                  | 10                      | 1021                 | 642                  | 1.59                               |
| 2 | $\left( \text{MA-Hp-AA} \right)$ | ---                     | <b>8034</b>          | <b>3724</b>          | <b>1.48</b>                        |
|   |                                  | 83.0                    | 9148                 | 8550                 | 1,07                               |
|   |                                  | 5.0                     | 6577                 | 5926                 | 1,11                               |
|   |                                  | 12                      | 1150                 | 710                  | 1.62                               |
| 3 | $\left( \text{MA-Oc-AA} \right)$ | ---                     | <b>8905</b>          | <b>4927</b>          | <b>1.81</b>                        |
|   |                                  | 85                      | 9880                 | 9065                 | 1.09                               |
|   |                                  | 7.0                     | 7140                 | 6320                 | 1.13                               |
|   |                                  | 8.0                     | 1206                 | 815                  | 1.48                               |

\* The numbers on columns characterize the total *M<sub>w</sub>* and *M<sub>n</sub>* of the oligomers (bold) and their component fractions, respectively

As follows from data of Table the MW characteristics of oligomers have an identical character. So in all three cases in the composition of the investigated oligomers it is advantageously detected the high-molecular compounds, a quantity of which is changed within the same ranges (83-85%). It is observed only small tendency of growth of total values *M<sub>w</sub>* and *M<sub>n</sub>* of oligomers in this series of olefins from 7988 to 8905 and also their composite fractions in the range of 8908 - 9880, 5997-7140 and 1021-1206, respectively.

The influence of each TC on physical-mechanical properties of filled PCM has been studied individually at appretting of polyethylene matrix. Tendency to decrease of breaking strength ( $\sigma$ ) and increase of specific elongation ( $\epsilon$ ) in change of  $\alpha$ -olefins in composition of TC in a series of hexene-, heptene-, octene-1 has been established. It has been also shown that an introduction of additional polymer binder to the system reinforces an appret influence of TC, i.e. "synergetic" effect is observed. The obtained results are presented in Table 2.

**Table 2.** Strength characteristics of compositions on the basis of HPPE modified by ternary copolymers of A-olefins (C<sub>6</sub>-C<sub>8</sub>) with maleic anhydride and acrylic acid filled with silica gel

| № | Compositions | Indices*       |                |                |                |
|---|--------------|----------------|----------------|----------------|----------------|
|   |              | $\sigma$ , MPa | $\epsilon$ , % | $\sigma$ , MPa | $\epsilon$ , % |
|   |              | 1              | 2              | 3              | 4              |
| 1 | HPPE – 40%   | 18.25          | 20             | 19,72(21.11)   | 19(17)         |
|   | Filler – 60% | 16.66          | 23             | 17.18(18.24)   | 33(31)         |
|   |              | 14.55          | 25             | 16.32(17.95)   | 37(35)         |
| 2 | HPPE – 50%   | 15.33          | 22             | 17,58(19.23)   | 34(29)         |
|   | Filler – 50% | 14.34          | 26             | 15.75(17,56)   | 38(32)         |
|   |              | 13.16          | 28             | 13,82(14.68)   | 42(36)         |
| 3 | HPPE – 60%   | 14.69          | 25             | 17.63(19,32)   | 34(29)         |
|   | Filler – 40% | 12.97          | 34             | 13.91(15.23)   | 40(33)         |
|   |              | 11.24          | 38             | 12.51(14,63)   | 42(37)         |

\*Upper and lower numbers on columns 1 and 2 in a series 1-3 correspond to non-appreted composition filled with silica gel, the numbers on columns 3 and 4 in the same series correspond to the same compositions treated with 3% apprete. The numbers in parentheses in a series 3 and 4 correspond to the appreted composition with epoxide binder ED-20 (5 g).

One of the superior features of used appretes of this TC type is that with changing of ratios of reaction components during their synthesis one can achieve an advantage of those or other functional groups in macromolecule creating a possibility of preparation of PCM by regulated composition and variation of their exploitation properties in wide range. It should be added that the preparation of PCM on the basis of mineral fillers and elaborated HPPE shown in this work is economically advisable, which has been stipulated by their low prices, since they are based on local cheap raw materials.

### 3 References

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