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PHYSICAL CHARACTERISTICS OF POLYMER MICROSPHERES, FILLED WITH MAGNETITE NANOPARTICLES

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INTRODUCTION: Polymer magnetic microspheres (PMMS) have been synthesized from collagen and polystyrene [1,2]. Four types of magnetite nanoparticles with average particle sizes of 9.48±0.15 (I), 7.7±0.15 (II), 7.3±0.07 (III) and 5.48±0.11 (IV) nm respectively have been used as magnetic filler. PMMS was synthesized in three sizes of 255.49±1.55, 179.09±1.49, 46.92±7.33 µm with narrow size distributions. Figure 1 shows PMMS filled with sample IV magnetite nanoparticles (PMMS-IV).

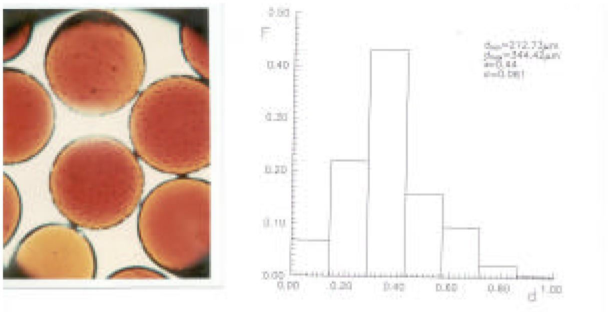

Fig. 1: Microphotography of PMMS-IV (left) and size distribution of PMMS-IV (right).

The object of the present work is to investigate the physical characteristics, structure and mechanism of magnetization of PMMS.

METHODS: *Determination of concentration of magnetite nanoparticles.* Density of polymer microspheres without magnetite nanoparticles (PMS) and with magnetite nanoparticles (PMMS) is determined by following formulas:

$$r_{PMS}=r_1V_1/V_{PMS}+r_2V_2/V_{PMS} \quad (1)$$

$$r_{PMMS}=r_1V_1/V_{PMMS}+r_2V_2/V_{PMMS}+r_3V_3/V_{PMMS} \quad (2)$$

where r_{PMS}, r_{PMMS}, r_1, r_2, r_3 are the density of PMS, PMMS, polymer matrix (collagen, polystyrene), carrier medium and magnetite, respectively. V_{PMS}, V_{PMMS}, V_1, V_2, V_3 are the volume of PMS, PMMS, polymer matrix (collagen, polystyrene), carrier medium and magnetite, respectively. r_{PMS} =1.0597 g/cm^3, r_1=1.1608 g/cm^3, r_2=0.9982 g/cm^3, r_3=5.24 g/cm^3.

The concentration of carrier medium in PMMS is determined as $j_2=V_2/V$ and consequently we obtained $j_2=(r_{PMS}-r_1)/(r_2-r_1)$. We substituted the value of φ_2 to (2) and receive $j_3=(r_{PMS}-r_{PMMS})/(r_3-r_2)$ for the concentration of magnetite nanoparticles in PMMS.

The density of PMS and PMMS is determined on the basis of measurement of mass of fixed number of PMS and PMMS in a Mettler HE20 sedimentometer. The density is determined as $r=M/V$, where M, V are total mass and volume of microspheres.

Preparation of section of PMMS for electron microscopy investigation. PMMS was deprived of water by consequently transferring to 50, 60, 70, 80 and 96% ethanol for 20 min each, followed by 1 h in acetone. Then PMMS was transferred to solution of mixture I-acetone = 1:3; 1:1; 3:1. Mixture I consists of DMP=57:0.67, where mixture is 54(812 EPON):36(DDSA):24(MNA). PMMS were sectioned to about 50 nm in a LKB UM IV Ultrotome.

Measurement of magnetic susceptibility of individual PMMS. Magnetic susceptibility of individual PMMS was determined on the base analysis of velocity of movement of microspheres under gradient magnetic field, created with ferromagnetic cylinder, placed in uniform magnetic field. Apparatus for determination of magnetic susceptibility of PMMS and mathematical formula for its calculation has been described in [3].

RESULTS: Structure of PMMS and size of magnetite nanoparticles in PMMS was carried out by electron microscopy (Figure 2).

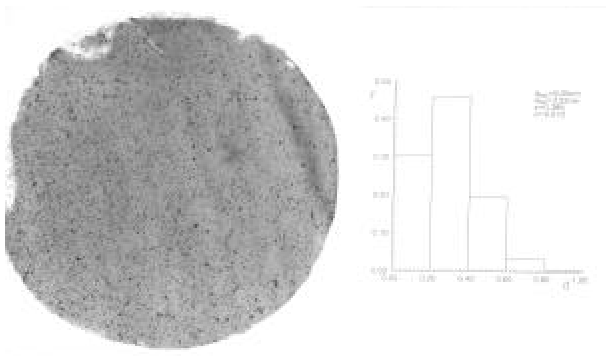

Fig. 2: Microphotography of sectioned PMMS-IV (left) and size distribution of enclosed magnetite nanoparticles-IV (right).

The magnetite nanoparticles are homogeneously distributed throughout the polymer matrix. The average distance between magnetite nanoparticles, as determined by EM sections of PMMS-IV is 17.4 nm. Determination of average diameter of magnetite nanoparticles before and after filling into PMMS-IV is shown. No change in size of the magnetite nanoparticles takes place, and there are no aggregates formed during microsphere synthesis. Figure 2 also shows the size distribution of magnetite nanoparticles.

Magnetic susceptibility of 120 individual PMMS with concentration of magnetite nanoparticles equal to j_t=0.013 at H=206.4 kA/m was determined. The average value of magnetic susceptibility of PMMS equaled to $4.79 \cdot 10^{-3}$.

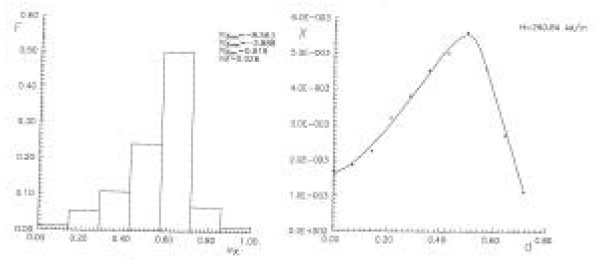

Fig. 3: Distribution of PMMS-IV versus logarithmic value of magnetic susceptibility (left), and dependence of magnetic susceptibility on the diameter of PMMS-IV (right).

Figure 3 (left) shows the histogram of distribution versus the logarithmic value of magnetic susceptibility of PMMS. Agreement of histogram of distribution on diameter and logarithmic value of magnetic susceptibility of PMMS has been investigated by χ^2 criterion method. It is shown that 95% agreement is presented and correspondingly the dependence between diameter and magnetic susceptibility of individual PMMS exists. In preliminary calculations, a coincidental value of magnetic susceptibility of PMMS with certain diameter has been discarded by 4th-D and Q methods. The dependence of magnetic susceptibility of PMMS-IV on diameter has been determined and is presented in Figure 3 (right).

We suggest that the magnetization of PMMS occurs by magnetization of the sum of sections magnetic moment of PMMS, which consists of magnetic moment of chains formatted along an external magnetic field. Value of magnetic moment of chain depends on the magnetic moment and the number of magnetite nanoparticles. At a small diameter of PMMS-IV, magnetization occurs by magnetization of all chains. At larger diameters of PMMS, the number of magnetite nanoparticles in chains is increased and chains are destroyed.

We investigated the magnetic susceptibility of PMMS at different concentration of magnetite nanoparticles j_m=0.0007, 0.001, 0.003, 0.008, 0.01 to exam our hypothesis about magnetization of PMMS at small diameter. Our results show that at small concentrations of magnetite nanoparticles, the magnetic susceptibility of PMMS-IV is a leaner function of concentration ($\chi = 0.69 \cdot \varphi_m - 0.52 \cdot 10^{-3}$). The value of magnetic susceptibility is increased with increasing concentration of magnetite nanoparticles.

At increasing diameters of PMMS-IV, chains of magnetite nanoparticles are destroyed. The length of chains depends on the magnetic field and the energy interaction between magnetite nanoparticles. The number of magnetite nanoparticles with average diameter d=5.48 nm, localized in diameter of PMMS-I d=304.36, 314.51, 324.13 μm at concentration of nanoparticles j_t =0.0258 is equal to 17913, 18510, 19076 respectively. The number of magnetite nanoparticles in chaines determined by formula in [4] is equal to 16130, 13096, 14310 respectively. As shown, the real value of magnetite nanoparticles is larger than the value determined by formula in [4]. Thus, at big diameters of PMMS occurs a transformation of chains to clusters with decreased magnetic susceptibility.

DISCUSSION & CONCLUSIONS: The analysis of our experimental results shows that magnetite nanoparticles are homogenously localized in PMMS. Magnetization of PMMS at small diameters occurs by magnetization of chains of magnetite nanoparticles, located along the diameter of microspheres. At larger diameters of PMMS, the chains are converted to clusters, with consequently decreased values of magnetic susceptibility.

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