

# Recovery of PET Wastes to Obtain Anticaking Additives for Nanoparticles Synthesis

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## Abstract

*Use of material in the form of nanoparticles have advantages due to their size, leading to a series of notable physical properties. The present study aims at obtaining dispersions of nanoparticles by precipitation method in the presence of additives obtained by using the polyethylene terephthalate (PET) waste. Six additives were synthesized by treating PET waste with DEG and DEA in alkaline homogeneous catalysis. The performance of anticaking additives were evaluated by use in the preparation of magnetite nanoparticles by precipitation method. The presence of additives obtained by using the waste PET favors reducing the average size of particles.*

**Key words:** polyethylene terephthalate waste, nanoparticles, recovery, transesterification.

## Introduction

Use of material in the form of nanoparticles has advantages due to their size, leading to a series of notable physical properties. These properties are related to their size, material properties differ significantly from the original. Multitude of methods for the synthesis of nanoparticles expresses interest and importance of this area. Synthesis of nanoparticles in the presence of additives has an important influence on the average size and particle size distribution. In the literature are highlighted various types of preparation of nanoparticles in the presence of suitable additives.

Hydrophilic magnetite nanoparticles with sizes ranging from 10 to 30 nm can be prepared by ultrasonic irradiation of  $\text{Fe}(\text{OH})_2$  in solutions water/diethylene glycol and water/tri ethylene glycol (volumetric ratio 3:7 .... 7:3) [1]. Size of magnetite nanoparticles synthesized by chemical co-precipitation method was controlled by varying the reaction temperature and surface modification. As coating agents were used hexanoic acid and oleic acid during the initial phase of magnetite crystallization [2].

Magnetite nanoparticles were synthesized in liquid polyols and high temperature. Polyol solvent determines particle morphology and colloidal stability results. Monodisperse nanoparticles were obtained, highly crystalline and easily dispersible in aqueous medium [3].

Monodisperse magnetite nanoparticles with average diameter of 4-5nm are obtained by introducing  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and sodium oleate in ethanol/water solvent mixture and

refluxed at 74°C [4]. By thermal decomposition of iron (III) acetylacetonate in the presence of oleic acid as a surfactant result monodisperse magnetite nanoparticles of 7 and 19 nm [5].

Magnetite nanoparticles with controlled size, with a diameter between 6-20 nm were obtained by thermal decomposition of an organic iron precursor in organic medium in the presence of oleic acid. Oleic acid molecules covalently binds nanoparticle surface resulting in stabilization of nanoparticles [6].

Magnetite nanoparticles with sizes between 20-30 nm were obtained by electrochemical oxidation of iron in the presence of amine surfactant, which acts as agent to the surface, causing the particle size and aggregation level during synthesis [7].

Magnetite nanoparticles surface was modified with an anionic surfactant (sodium dodecyl sulfate) in order to remove of cationic dye methyl violet from aqueous solutions [9].

Magnetite nanoparticles were synthesized and stabilized with citric acid and humic acid. The obtained nanoparticles have improved stability by the combined effect of steric and electrostatic effects [10].

Magnetite nanoparticles obtained by alkaline hydrolysis of Fe (II) and Fe (III) salts treated with humic acid, form stable colloidal dispersions. Over a wide range of pH, particle does not occur aggregation [11].

Oleic acid and amphiphilic block copolymers can be used as stabilizers to disperse the magnetite nanoparticles in water. The thermogravimetric analysis (TGA) and FTIR revealed the presence of the copolymer to the surface of the particles [12].

Magnetite nanoparticles synthesized by thermal decomposition of iron (III) acetylacetonate in triethylene glycol can be easily dispersed in water directly. Magnetite nanoparticles are found to be highly soluble in water, due to steric and electrostatic interactions between particles resulting from adsorption at surface of triethyleneglycol molecules, and respectively, associated positive charges [13].

Magnetite particles were prepared by coprecipitation in the presence of sodium oleate and sodium dodecyl benzene sulfonate as surfactants. Experimental results have shown that molecules of oleic acid sodium salt, have been linked to magnetite particles by chemical bonds and dodecyl benzene sodium sulfonate cover surface of magnetite particles linked to sodium oleate through Van der Waals bonds [14].

Cationic emulsifiers were used as coating agent in order to avoid aggregation of magnetite nanoparticles obtained by electrolysis with iron electrodes (iron purity 99.5%) in the ultrasound field. [15]

The present study aims at obtaining dispersions of nanoparticles by precipitation method in the presence of additives obtained by using the polyethylene terephthalate (PET) waste. These nanoparticles have the prospect of being used as catalytic systems in air blown bitumen.

## Experimental

The raw materials used for anticaking additives preparation were chopped PET wastes and diethyleneglycol (DEG) or diethanolamine (DEA). The reaction of condensation was carried out in three necks flask equipped with a Dean-Stark separator and a vertical condenser. Heating was performed using an electric heated mantle fitted with potentiometer to adjust the temperature. Stirring the reaction mixture was performed using a stirrer equipped with swivel blades.

The process took place in discontinuous conditions, in alkaline catalysis. The catalyst used was powdered potassium hydroxide. Catalyst concentration to the reactant mixture was 1% wt. Both

transesterification reaction of PET with diethyleneglycol and ammonolysis reaction with diethanolamine was performed at 200 to 210 ° C, with ethylene glycol elimination.

Three experiments were performed both with diethylene glycol and with diethanolamine, which differ by the ratio between the reactants as shown in Table 1.

**Table 1.** The experimental synthesis of anti-caking additives

Sample code	Reactants	PET content, %	Observations
PET 0	-	-	blank without anticaking
PET 1	DEG / PET	50	anticaking additives prepared with DEG
PET 2	DEG / PET	55	
PET 3	DEG / PET	65	
PET 4	DEA / PET	50	anticaking additives prepared with DEA
PET 5	DEA / PET	55	
PET 6	DEA / PET	65	

Characterization of reaction products was performed by determining the saponification index and hydroxyl index.

Anticaking performances were tested by use these additives in the preparation of magnetite nanoparticles according to the following recipe:

- 0.53 g  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ;
- 2 mL  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  solution 50% wt;
- 100 mL distilled water + 3mL anticaking additives;
- 4 mL NaOH solution 20% wt.

In 100 ml distilled water in a roundbottom flask were dissolved 0.53 g  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and 2 ml  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  solution 50% under inert nitrogen atmosphere. After adding 3 mL of anticaking additive the mixture was stirred. Under vigorous stirring was added NaOH solution and the mixture turned black, indicating formation of the magnetite particles.

Particle dimensions and size distribution were determined using a measurement system of particles dimensions by dynamic light scattering (DLS) with a Malvern-Zetasizer instrument NanoZS (Red Badge).

## Results and Discussions

Saponification values and hydroxyl values are shown in Figures 1 and 2. Saponification values increases with increasing PET content for additives obtained in the presence of both DEG and DEA. Hydroxyl values decreases with increasing PET content of additives obtained in the presence of both additives obtained in the presence of DEG and DEA.

Particle dimensions and size distribution of prepared particles are presented in Figures 3-9. Using DLS method for sample PET 0 the average particle size was 314.6 nm. This sample was chosen as standard because it contained no PET based additives in composition.

For samples PET1 and PET4, that were used additives composed of 50% weight PET, average particle size as determined by DLS was 167.8 nm for DEG-based additive and 177.5 nm for DEA-based additive. This shows that when PET is 50% of the sample mass, average particle size decreases to about half of the standard sample, containing no PET.

For samples PET2 and PET5, that were used additives composed of 55% weight PET, average particle size as determined by DLS was 268.1 nm for DEG-based additive and 216.1 nm for DEA-based additive. Average particle size is less than the standard sample, containing no PET.

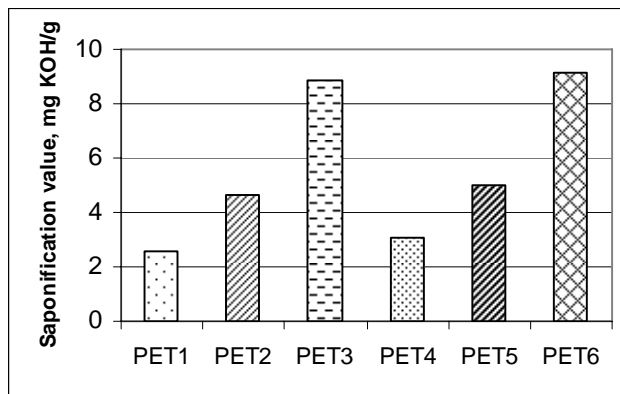


Fig. 1. Saponification values

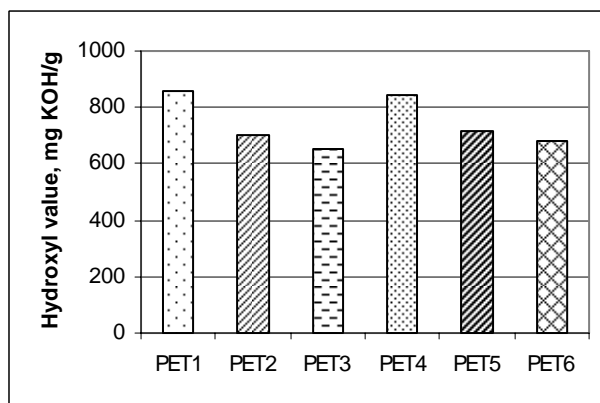


Fig. 2. Hydroxyl values

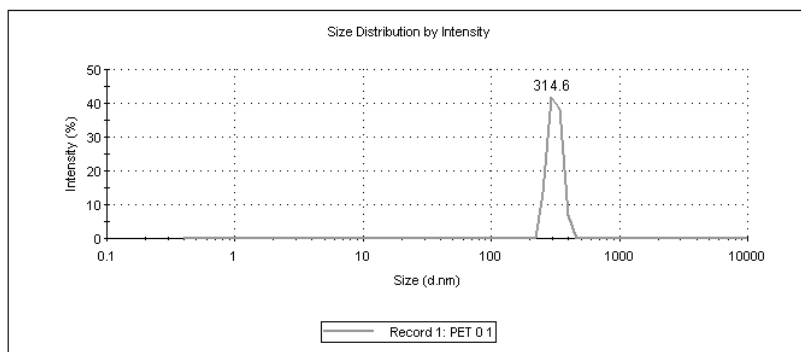


Fig. 3. DLS analysis of the sample PET 0

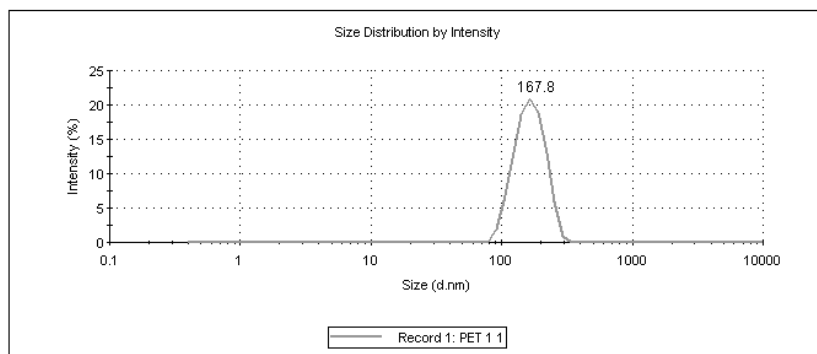
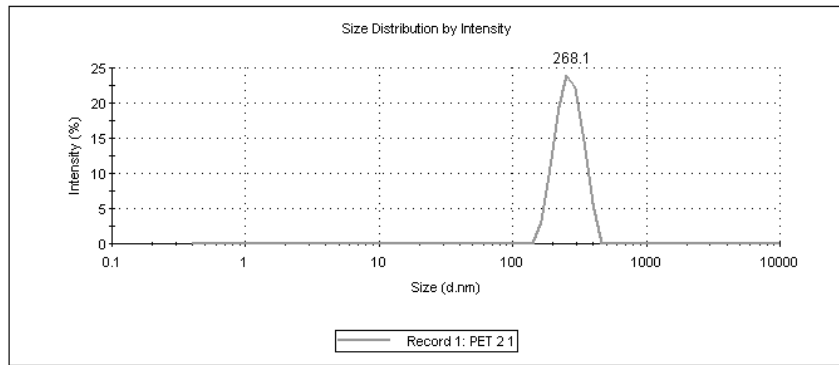
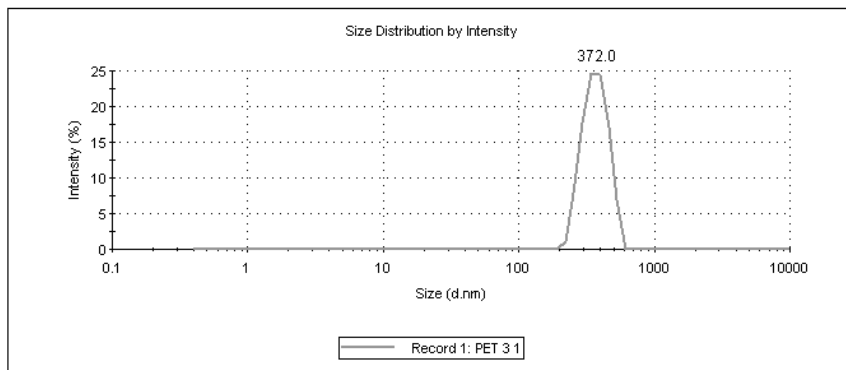
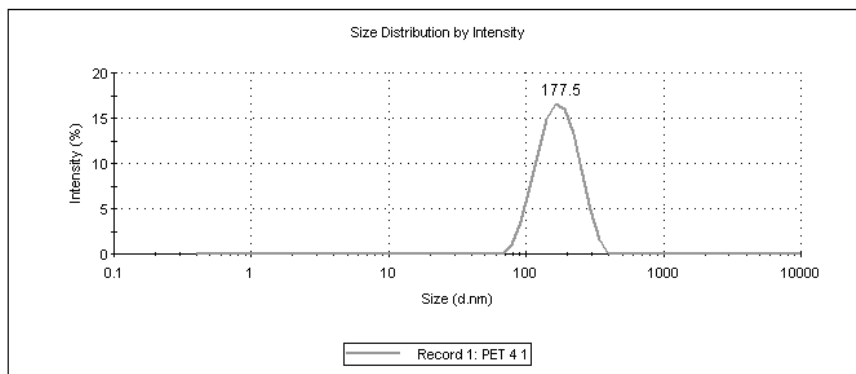
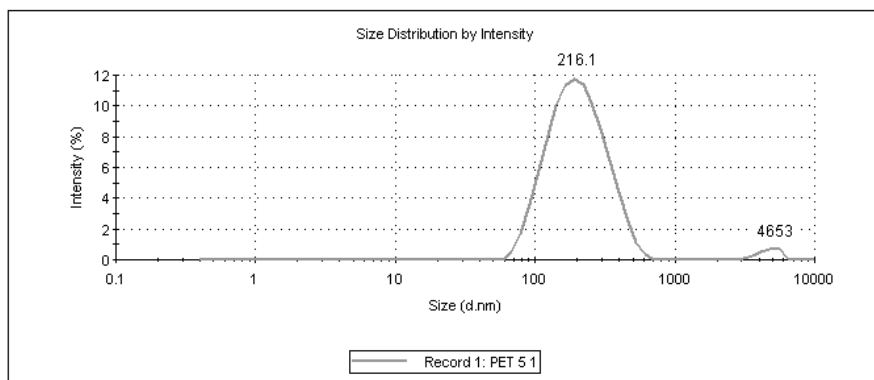
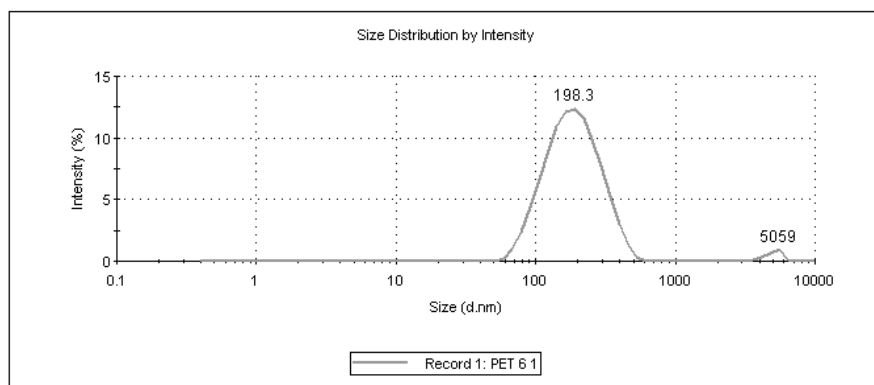


Fig. 4. DLS analysis of the sample PET 1

**Fig. 5.** DLS analysis of the sample PET 2**Fig. 6.** DLS analysis of the sample PET 3**Fig. 7.** DLS analysis of the sample PET 4**Fig. 8.** DLS analysis of the sample PET 5



**Fig. 9.** DLS analysis of the sample PET 6

For samples PET3 and PET6, that were used additives composed of 65% weight PET, average particle size as determined by DLS was 372 nm for DEG-based additive and 198.3 nm for DEA-based additive. Only in case of DEG additive average size is larger than in case of the standard sample.

The results obtained by DLS method shows that, with one exception, this admixture PET waste by making favours reducing the average size of particles, and with one exception, as the additive PET content is higher there is an increase of average particle size of the test sample.

## Conclusions

Six additives were synthesized by treating PET waste with DEG and DEA in alkaline homogeneous catalysis. Prepared additives characterization was performed by determining the saponification and hydroxyl values.

The performance of anticaking additives were evaluated by use in the preparation of magnetite nanoparticles by precipitation method.

Usually the presence of additives obtained by using the waste PET favours reducing the average size of particles, and, with one exception, while the additive content has higher PET content the average dimension of nanoparticles are increasing.

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## Obținerea de aditivi antiaglomeranți pentru sinteza nanoparticulelor pe bază de deșeuri de tip PET

### Rezumat

Utilizarea materialelor sub formă de nanoparticule prezintă avantaje datorate dimensiunilor acestora, ce conduc la o serie de proprietăți fizice remarcabile. Studiul de față are drept scop obținerea de dispersii de nanoparticule prin metoda precipitării în prezența aditivilor obținuți prin utilizarea deșeurilor de tip polietilenterestalat (PET). Au fost sintetizați șase aditivi prin tratarea deșeurilor de PET cu DEG și DEA în cataliză omogenă, alcalină. Performanțele antiaglomerante ale aditivilor au fost evaluate prin utilizarea la prepararea nanoparticulelor de magnetită prin metoda precipitării. Prezența aditivilor obținuți din deșeurile de PET favorizează reducerea dimensiunii medii a particulelor.