β-nucleation of surface modified iron oxides in isotactic polypropylene

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Master thesis

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ABSTRAKT

Cílem diplomové práce je studium β-nukleace povrchově modifikovaných oxidů železa v izotaktickém polypropylenu. Nanočástice Fe_3O_4 a částečně zoxidovaného Fe_3O_4 byly použity jako plnivo, které bylo dvěma způsoby modifikováno surfaktantem a beta nukleačním činidlem; a to precipitační a dvou stupňovou cestou. Účinnost beta nukleačního činidla na povrchu nanočástic byla studována pomocí širokoúhlého rozptylu záření X (WAXD) and DSC. Modifikace nanočástic byla studována pomocí infračervené (FTIR) a dielektrické spektroskopie stejně jako testování magnetických vlastností.

Tato práce se zabývá relativním obsahem beta krystalické fáze a krystalizační teplotou iso-propylenu plněného zoxidovanými částicemi Fe_3O_4 modifikovanými precipitační a dvou stupňovou cestou. Nanočástice oxidů železa modifikované dvou stupňovou cestou vykazují lepší nukleační účinek. Nicméně obě uvedené způsoby modifikace mohou vést do určité míry k reakci modifikátorů s nanočásticemi.

Klíčová slova: iso-polypropylen, beta nukleace, povrchová modifikace, kalcium stearát

ABSTRACT

The aim of this Master thesis is to study β-nucleation of surface modified iron oxides in isotactic polypropylene. Fe_3O_4 and partly oxidized Fe_3O_4 nanoparticles were utilized as filler which was modified with surfactant and β-nucleating agent by precipitation method and two-step method. The efficiency of β-nucleating agent modified on the surface of nanoparticles was studied by WAXD and DSC. The modification of nanoparticle was studied by FTIR spectrometry, dielectric testing and magnetic testing.

This work deals with the relative β-crystal content and crystallization temperature of iso-polypropylene filled with oxidized Fe_3O_4 nanoparticles modified by precipitation and two-step method. Iron oxide nanoparticles modified by two-step method show better nucleation effect. However, the modifiers may to some extent react with nanoparticles in both methods.

Key words: iso-polypropylene, β-nucleation, surface modification, calcium stearate

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I hereby declare that the print version of my Bachelor's/Master's thesis and the electronic version of my thesis deposited in the IS/STAG system are identical.

Zlín, 10th May 2013

Zhang Bo

CONTENTS

INTRODUCTION

In last years, there has been increased interest attributed to magnetic composites based on elastomeric or thermoplastic polymers filled with micro and nano particles, as lightweight design elements with desired mechanical, optical properties, high thermal stability and customizable electrical and magnetic properties suitable in engineering for application in electronic devices [1].

Composite based on polypropylene (PP) matrix can be divided into two types. One contains high concentration of filler (> 5 %), in which PP only acts as binder. Into this group belong polymer bonded magnets (PBSMs) for which the effect of binder on magnetic properties was widely studied [2]. The other group comprises composites with low concentration of filler (< 5 %) which can be then treated as polymer additive.

A large number of inorganic particles such as Fe_3O_4, ZnO and TiO_2 are usually used as functional fillers for iso-polypropylene (iPP). Unfortunately, addition of those fillers generally decreases the impact strength of iPP, which is attributed to the formation of α-PP due to the α-nucleation of the fillers. β-phase PP has many advantages such as higher impact strength and elongation at break, therefore β-phase PP has received more attention in terms of industrial applications. Addition of β-nucleating agent into iPP is the most effective and accessible way of obtaining β-PP. Were it possible to coat the inorganic filler with β-nucleating agent, fillers with α-nucleation could be substituted with β nucleation for iPP crystallization. Moreover, large specific surface of nanoparticles would increase the efficiency of such nucleating agents [3].

Zishou Zhang [4] studied the β-nucleation of pimelic acid coated on the CaO nanoparticle, and pointed out it was successful to obtain β-nucleating agent calcium pimelate by the reaction of pimelic acid and CaO nanoparticle. Furthermore, the large specific surface of nanoparticle improved the dispersion of calcium pimelate, resulting in high nucleating efficiency.

In this context, the purpose of presented Master thesis is to replace the CaO nano particle with calcium stearate. The highly efficient β-nucleating agent calcium pimelate was produced by the reaction of pimelic acid and calcium stearate on the particle surface. At the same time, excessive calcium stearate was also used as surfactant to alter the polar surface of nanoparticle. Fe_3O_4 and oxidized Fe_3O_4 nanoparticles were prepared as functional filler with different surface polarities. Investigation of crystallinity of composite

was carried out by using several experimental techniques, such as wide angle X-ray scattering and differential scanning calorimetry. The surface reaction and interaction between matrix and filler were studied by FTIR, dielectric spectroscopy and vibrating sample magnetometer.

I.   THEORY

1. POLYPROPYLENE

1.1 Polymerization

Polypropylene was first invented by Gulio Natta, who was following the work of Karl Ziegler. A Ziegler–Natta catalyst, named after Karl Ziegler and Giulio Natta, is a catalyst used in the synthesis of polymers of 1-alkenes (α-olefins). The monomer for PP is obtained by the cracking of petroleum products, such as natural gas or light oils. In petroleum geology and chemistry, cracking is the process whereby complex organic molecules such as kerogens or heavy hydrocarbons are broken down into simpler molecules such as light hydrocarbons, by the breaking of carbon-carbon bonds in the precursors. Polypropylene is then polymerized by using 'Ziegler type' catalysts or metallocene catalysts. A typical catalyst system may be prepared by reacting titanium trichloride with aluminium triethyl, aluminium tributyl and aluminium diethyl monochlorid in naphtha under nitrogen to form slurry consisting of about 10 % catalyst and 90 % naphtha. The properties of the polymer are influenced by the composition of catalyst and its particle shape and size [5].

1.2 Chemical structure

There are three possible sequences of non-symmetrical propylene molecule. The difference depends on the position of the methyl group: isotactic, syndiotactic and atactic, as shown in Fig.1 [6].
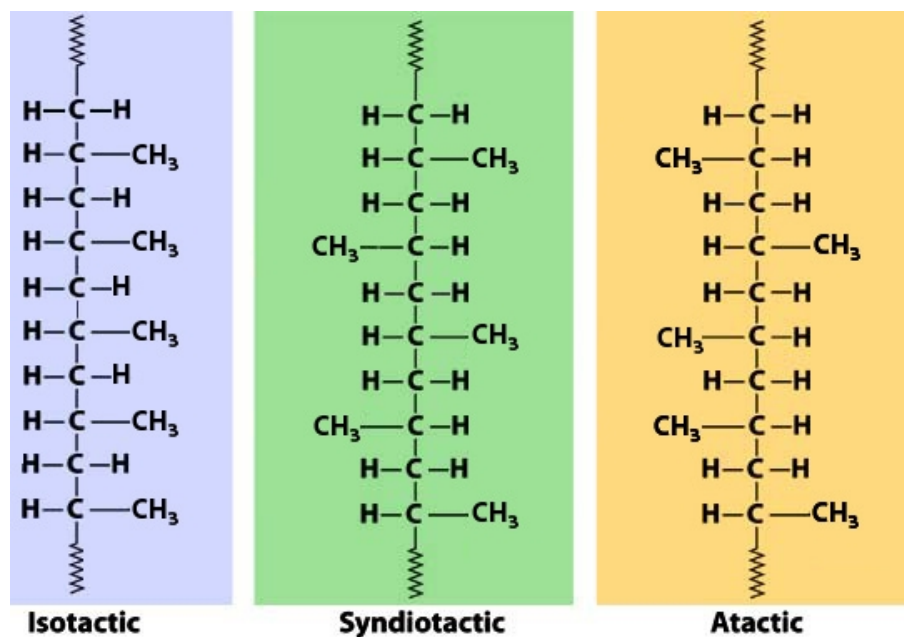

Fig.1. Three different types of polypropylene [6]

1.2.1 Isotactic polypropylene

It is the most common commercial type, pendant methyl groups are at one side of polymer chain, having the same configuration. Because of its tacticity, iPP is the most stereo-regular structured polypropylene when compared with atactic and syndiotactic polypropylenes and thus having higher degree of crystallinity [6].

1.2.2 Syndiotactic polypropylene

Syndiotactic polypropylene, with pendant methyl groups alternated on the opposite sides of polymer backbone, possesses greater toughness, clarity and heat resistance (softening point), which are all of great interest [6].

1.2.3 Atactic polypropylene

Atactic or amorphous polypropylene is characterized by a random orientation of the methyl pendant groups on the tertiary carbon atoms along the molecular chain. An atactic configuration is influenced by the random sequence of these methyl substituents. Generally the features of atactic polymers are tacky, amorphous behavior and low molecular weights [7].

On the crystal lattice level, three different morphological forms are found in isotactic polypropylene, depending on the tacticity of the polymer chain. It is influenced by the crystallization conditions, such as pressure, temperature, and cooling rate. Different forms can coexist, but one polymorphic form can switch into another under different conditions [8]. The X-ray patterns of three forms (α-form, β-form and γ-form) are shown in Fig.2.
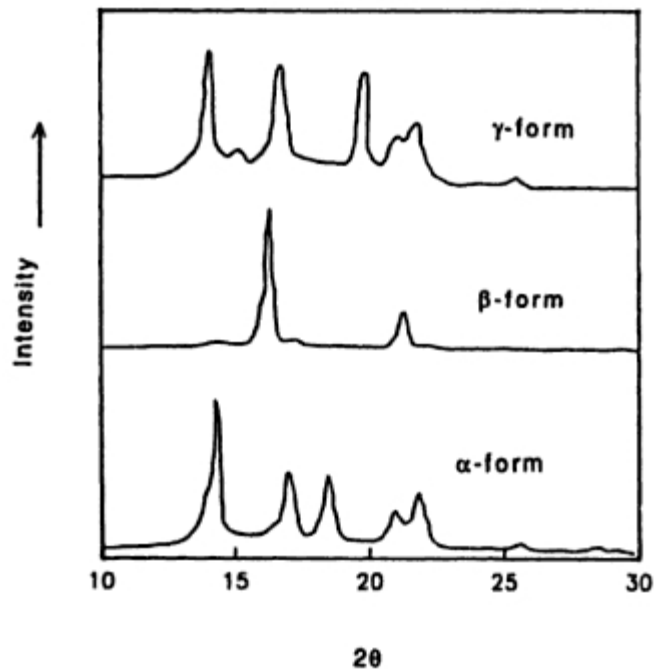
Fig.2. WAXD patterns for different forms in polypropylene crystals [8]

1.3 Crystal structure of iso-polypropylene

1.3.1 Polymorphism of isotactic polypropylene

The α-phase of polypropylene

The monoclinic α-form is predominant and the most thermodynamically stable crystalline structure in isotactic polypropylene (see Fig.3). Polymer chains in the α-form of isotactic polypropylene are folded into lamellae with thicknesses of 5-20 nm. The parameters of unit cell in α-form are shown in Fig.3 [6].
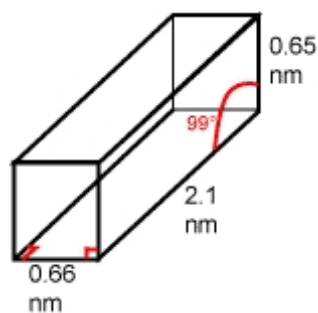

Fig.3. Crystal structure of α-form polypropylene [9]

The β-phase of polypropylene

This phase is metastable and the crystals are pseudo-hexagonal. β-phase is mainly found in block PP copolymers, which can be induced by specific nucleating agents. Padden and Keith discovered it in 1953 and it can be improved by crystallization between 130 °C and 132 °C or by orientation with shear or through mixing with specific nucleating agents [10]. Presence of beta-phase in PP homopolymer generally increases ductility in the finished parts. Maximum effect is observed at 64 % of β -phase. The unit-cell of β-phase is trigonal and lattice parameters are shown in Fig.4. The β-phase is metastable, compared with the α-phase [11].
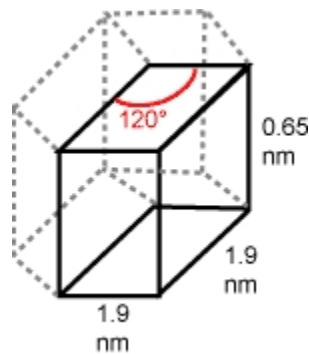

Fig.4. Unit-cell of β-form polypropylene [9]

The γ-phase of polypropylene

The crystalline structure of the γ-modification was first denoted as triclinic [12]. However, structure of γ-phase in polypropylene is orthorhombic and the parameters are shown in Fig. 5 [6].
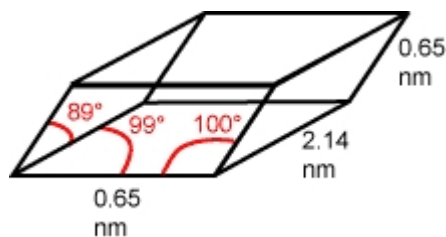

Fig.5. Crystal structure of γ-form polypropylene[9]

1.3.2 Lamellar structure

In general, thicknesses of lamellae in polypropylene can change from approximately 4 nm for the cross hatched lamellae to several tens of nanometers for primary grown lamellae. The lamellae can be isolated by amorphous layers. The thickness of the layer is usually in the order of the thickness of lamellae, as shown in Fig. 6 [13].
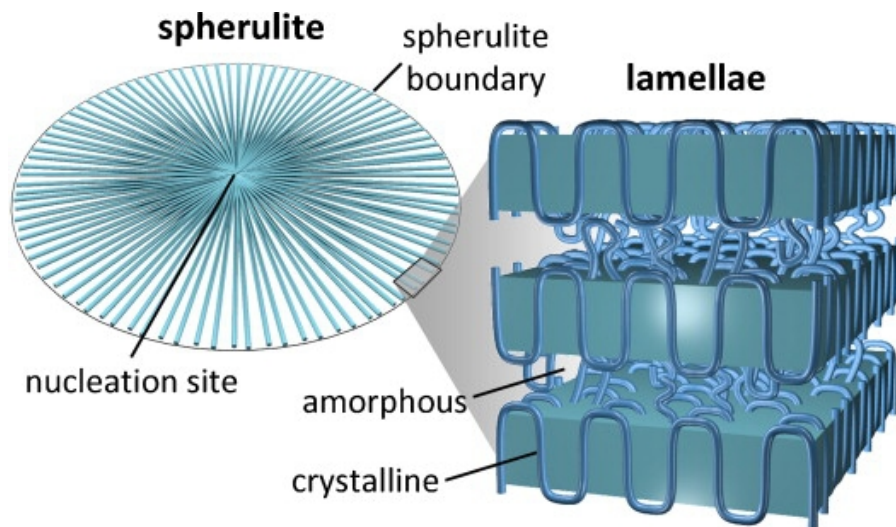

Fig.6. The spherulite and lamellae structure of polypropylene [14].

1.3.3 Spherulites

The term "spherulite" indicates an aggregate of primary crystallites of spherical shape, consisting of individual lamellae or bundles of lamellae growing from a central nucleus. Complete filling of space is formed by branching and splaying. Spherulites of iPP show the general characteristics of typical spherulitic morphologies of semi-crystalline materials, as shown in Fig. 6 [15].

1.4 Nucleating agent

1.4.1 Introduction

The addition of nucleating agents into polypropylene is usually for improving processing characteristics and clarity and changing its mechanical properties. Nucleating agents are acted as a large number of sites for the initiation of crystallization, so that spherulites formed are smaller and more numerous than in unnucleated polypropylene [16].

The crystallization temperature and the rate of crystallization can be increased by the nucleation effect; as a technological result, parts can be removed from the mold at higher temperatures, and molding cycle times are reduced, as shown in Fig.7.
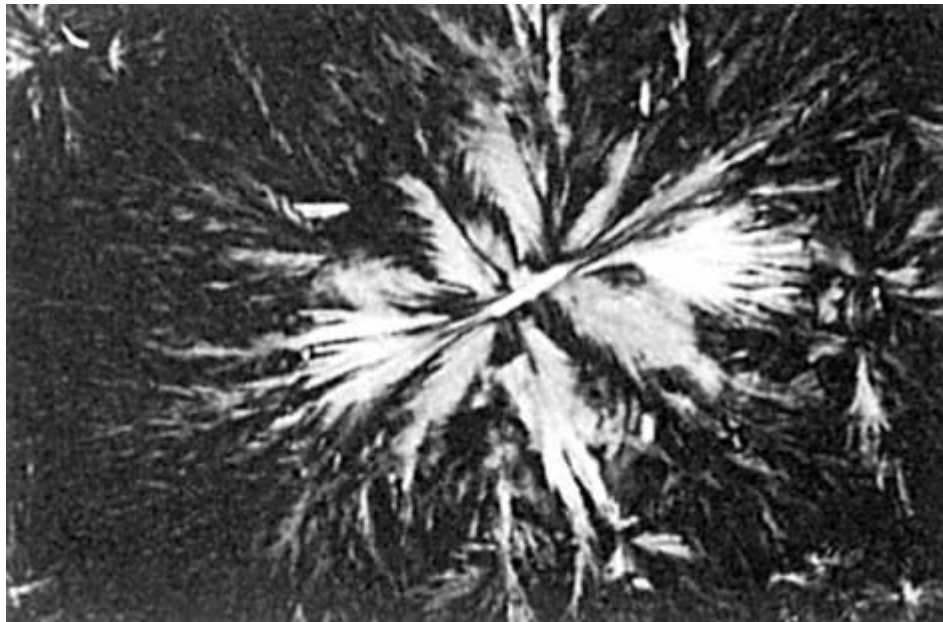

Fig.7. Micrograph of a spherulite of polypropylene formed in the presence of a nucleating agent [17]

The nucleating agent is at the center of the spherulite, suggesting that the nucleating agent initiated crystal formation. Nucleated iPP has higher tensile strength, stiffness, flexural moduli and heat deflection temperatures than unnucleated iPP, but impact strength is lower. However, high levels of crystallinity can reduce the tolerance to radiation sterilization and restrict the effectiveness of hindered amine light stabilizers and other stabilizing additives.

1.4.2 α-nucleating agents

Inorganic particles also have significant influence on the crystallization behavior of PP [18-21]. Among these inorganic particles, calcium carbonate has been one of the most commonly used inorganic filler for thermoplastics. The particle size of most commercially available $CaCO_3$ varies from 1 to 50 μ [22]. Other common α-nucleating agents are sorbitol based derivates. It has significant improvement over conventional nucleating agents both in nucleating efficiency and clarity. Unlike the dispersion type of other nucleators, they can be dissolved and dispersed uniformly in the molten iPP which is the matrix.

The most common examples of this type of nucleators are:

- 1,2,3,4-bis-dibenzylidene sorbitol (DBS);

- 1,2,3,4-bis-(p-methoxybenzylidene sorbitol) (DOS);

- 1,2,3,4-bis-(p-methylbenzylidene sorbitol) (MBDS);

- 1,3;2,4-di-(3,4-dimethylbenzylidene sorbitol) (DMDBS) [23].

And metal salts of substituted aromatic heterocyclic phosphate were investigated as very promising nucleating agents for PP matrix.

In particular, sodium 2,20-methylene-bis-(4,6-dit-butylphenylene)phosphate (NA-11) is also a powerful nucleating agent widely used in the processing of iPP [24].

1.4.3 β-nucleating agents

Under regular crystallization conditions, only a small quantity of β-phase can be generated as a supplement of α-phase. A higher concentration of β-modification can be obtained via high crystallization temperatures, high temperature gradients, rapid cooling of the melt to 130–135 °C, and from melts exposed to shear stress. There are several substances that can act as specific β-nucleators [25].

Li et al. Investigeted a series of calcium carboxylates, with different chemical structures and crystal forms as nucleators for β-PP and they were effective nucleating agents for iPP. The Ca-salt of suberic (Ca-sub) and pimelic acid (Ca-pim) possess very high β-nucleating selectivity and efficiency [26].

2. Surface modification and surface modifiers

There are mainly three reasons for surface modification:

1. Protection of the filler for storage in the end application.

2. Improved processing. Surface modification often improves compatibility between the polymer and matrix and reduces the viscosity of the mix.

3. Improved composite properties. These can include: increased strength and stiffness, better impact strength, increased abrasion resistance, reduced adsorption and less swelling in the presence of water and other fluids [27].

There are a variety of methods to accomplish surface modification of powders. These methods can be broadly classified into categories: chemical, mechanical, physiochemical methods.

The chemical method category includes all processes in which different particles are brought together and transformed by chemical reaction into new chemical compounds [28]. It is usually used for for Improving the stability of nanoparticles in liquid media. On modifying the oxide nanoparticle surface, silane was usually used as coupling agent. Metal-OH group on the particle surface is used as a reaction site [29].

In mechanical method, particle structure and surface modification are achieved on the whole by mechanical means. It usually involves hybridization system to produce functional composite powder by dry-method embedding/filming fine powder onto the surface of core powder [30].

Physiochemical modification is an umbrella term embracing aspects of both chemical and mechanical methods [28].

The most important theoretical concept in surface modification is that of the mono-layer. Theoretical mono-layer amounts can be calculated by using factors, such as the density of reactive sites and the area occupied by a molecule of coating, as shown in Fig.8.
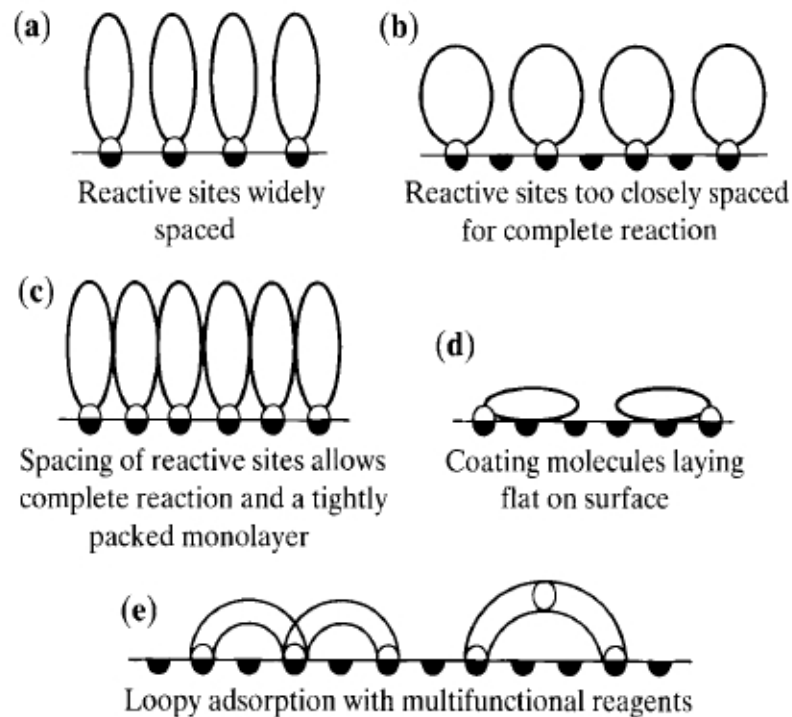
Fig.8. Different idealised structures for surface mono-layers on a filler surface [27]

A surfactant is a compound which is able to reduce surface tension in liquid, thus the contact is increased between the liquid and another substance. Some surfactants, like short-chain fatty acids, are amphiphilic or amphipathic. They have one part that has an affinity for nonpolar media and one part that has an affinity for polar media. These molecules form oriented monolayers at interfaces and show surface activity (i.e., they lower the surface or interfacial tension of the medium in which they are dissolved). In some usages, surfactants are defined as molecules capable of associating to form micelles. There are a wide variety of surfactants which can work with oil, water, and other liquids. They are also sometimes called as "wetting agents" [31].

From the chemical structure of surfactants, three main types are listed below:

I.   Anionic Surfactants are dissociated in water in an amphiphilic anion, and a cation. They are the most commonly used surfactants. Calcium stearate is non-toxic, white powdery anionic surfactants. It is a calcium salt derived from stearic acid and is widely used in cosmetics, plastics, and pharmaceuticals.

II. Nonionic Surfactants do not ionize in aqueous solution, because their hydrophilic group is in a non-dissociable type, such as alcohol, phenol, ether, ester, or amide.

III. Cationic Surfactants can be dissolved in water with an amphiphilic cation and an anion, most often the halogen type. A very large proportion of this class corresponds to the compounds such as fatty amine salts and quaternary ammoniums, with one or several long chain of the alkyl type, often coming from natural fatty acids [32].

II. EXPERIMENTAL PART

3. MATERIALS

The iPP homopolymer WG350C (Melt Flow Rate = 18 g/10 min at 230 °C/2.16 kg, mixed with antioxidant) used in the study was supplied by Borealis Company.

Fe_3O_4 nanoparticles were prepared by coprecipitation of ferrous and ferric salts in an alkaline medium (for details see a section below). Oxidized Fe_3O_4 nanoparticles were made from the Fe_3O_4 nanoparticles, which was oxidized in furnace at 300 °C for 1.5 hrs.

Chemical-grade pimelic acid and calcium stearate were obtained from Sigma-Aldrich, Inc. The ethanol and deionized water were of chemical grade.

3.1 Preparation of iron oxide magnetic nanoparticles

Magnetic particles were prepared by coprecipitation of ferrous and ferric salts in an alkaline medium. 450 ml of 1.5 M ammonium hydroxide solution, used as a precipitation agent, was mixed with a solution of ferrous chloride and ferric chloride with a molar ratio of Fe (II)/ Fe (III) = 0.5, which was used as a source of iron. This molar ratio of iron (II) to iron (III) provides the formation of stoichiometric magnetite. The reaction was performed in the argon atmosphere to prevent the oxidation of Fe^{2+} ions and to keep the iron (II) to iron (III) molar ratio constant. The temperature of the reaction mixture was maintained at 80 °C with a continuous stirring speed of 700 rpm. During the synthesis, the salts solution was added dropwise to the base solution, which provided alkaline pH of the reaction media for the whole reaction time and the immediate formation of uniform nanoparticles. The black powder of iron oxide nanoparticles formed in the reaction was separated by a permanent magnet, washed with distilled water to neutral pH and dried in air at room temperature.

3.2 Particle modification

3.2.1 Introduction of precipitation method

Calcium pimelate is usually obtained by the reaction between pimelic acid and calcium stearate, which is not easy to be mixed homogeneously with non-polar iPP. Therefore J.X.Li [33] introduced a method utilizing ethanol to dissolve pimelic acid and calcium stearate and let them precipitate onto the surface of iPP powder by evaporation of solvent. The iPP powder works as carrier, and during mixing process, two components are reacted to produce β-nucleating agent.

We apply the same method to Fe_3O_4 and oxidized Fe_3O_4 nanoparticles. However, iPP powder is inert with both pimelic acid and calcium stearate; on the other hand, Fe_3O_4 or oxidized Fe_3O_4 can react with either of them at high temperature. Thus pimelic acid might react with iron ion producing iron pimelate, and calcium stearate is able to be chemically attached to the particle surface.

Modification procedures of precipitation method (Fe_3O_4 nanoparticle)

1. 0.2 g Fe_3O_4, 0.002 g pimelic acid, 0.008 g calcium stearate and 25 ml ethanol were used during experiment.

2. Dispersing 0.2 g Fe_3O_4 into 25 ml ethanol in supersonic bath and adding the mixture of 0.008 g calcium stearate and 0.002 g pimelic acid gradually.

3. Drying in water bath at 70 °C.

4. Collecting the powder and grinding in mortar.

The procedure for oxidized Fe_3O_4 was the same.

3.2.2 Introduction of two-step method

En Hao Zhang [34] studied the surface modification of Fe_3O_4 by stearic acid, and pointed out that two types of steric acid are attached to Fe_3O_4 surface. One is absorbed by chelation reaction and thus is bonded chemically while the other is physically adsorbed, which means the surfactant is intact.

Zi Shou Zhang [4] invented a new method to obtain nucleating agents. It needs to cover the CaO nanoparticles with pimelic acid by solvent evaporation. Calcium pimelate would be produced by the reaction between CaO and pimelic acid, during the processing of iPP. The advantage of this method is quite obvious. Firstly, the calcium pimelate is homogeneously mixed by the help of nano CaO, and the efficiency of nucleating agent is greatly increased by the large specific surface of nanoparticle. The drawback is that only calcium compound can be used as filler in this method.

Two-step method is the combination of modification by surfactant and pimelic coating. The nano Fe_3O_4 particles are modified by surfactant, and subsequently coated by pimelic acid. The surfactant is not only used to avoid agglomeration, but plays a role of one of the reactants replacing CaO.

The first step is to carry out the modification of partly oxidized nanoparticles surface with surfactant. There are basically two methods of modification; dry and wet method. In our experiment, all the surface modifications were performed via wet method.

During the wet method, the selection of solvent is based on the polarity of nanoparticle and the solubility of surfactant. Generally, the polar surface of Fe_3O_4 or partly oxidized Fe_3O_4 is wetted very well with water. However, the solubility of calcium stearate in water is rather poor. Therefore, during modification process, reaction mixture has to be heated to 90 °C in order to dissolve more of surfactant.

The optimal amount of surfactant used in modification is such that would result in creation of a single layer surfactant on the particle surface. It is usually 1-2 mg of surfactant per m^2. In our case, 4 wt. % of calcium stearate from total particles weight was used for providing both surface modification and sufficient amount of reactant to produce calcium pimelate [35].

The surfactant concentration on the particle surface increases with time until the equilibrium is reached. In our case, the reaction took about 20 to 30 min.

At beginning of the process, the nanoparticles must be dispersed in the water under ultrasonic separation, while surfactant is being added gradually. After 30 min modification, the solution is filtered and dried. Dried nanoparticles and undissolved surfactant are obtained eventually.

In the second step of modification, ethanol is utilized as solvent. The unreacted pimelic acid in the first step can be dissolved again in ethanol and absorbed onto the nanoparticles. And after 30 min of dispersing at 50 °C, pimelic acid is added and attached onto the surface of nanoparticles with the evaporation of solution.

Surface of nanoparticles modified by surfactant at first step works as barrier preventing the contact between pimelic acid and nanoparticles in solution. Therefore, polarity of nanoparticle does not affect the resulting modification. In our case, only oxidized Fe_3O_4 was modified by two-step method.

Modification procedures of two-step method (oxidized Fe_3O_4 nanoparticles)

First step:surface modification by calcium stearate

1. 0.2 g oxidized Fe_3O_4 nanoparticles, 50 ml deionized water and 0.008 g calcium stearate are needed.

2. Dispersing 0.2 g of oxidized Fe_3O_4 nanoparticles into 50 ml of distilled water.

3. Heating the distilled water up to 90 °C, then adding 0.008 g calcium stearate within 5 min.

4. Sonication for 30 min at 90 °C.

5. Cooling the solvent to room temperature.

6. Filtration.

7. Drying filtrate in the oven at 100 °C to constant weight.

Second step: coating by pimelic acid

1. 0.002 g of pimelic acid, 0.2 g of modified oxidized Fe_3O_4 nanoparticles from the first step, 10 ml of acetone is needed.

2. Dissolving 0.002 g of pimelic acid into 10 ml of acetone at room temperature.

3. Dispersing 0.2 g of modified oxidized Fe_3O_4 nanoparticles from the first step with the solvent under sonication.

4. Drying it at 50 °C in water bath under sonication until it gets completely dried.

5. Grinding the powder in mortar.

Note: Only oxidized Fe_3O_4 nanoparticles were modified by two-step method.

4. SAMPLE PREPARATION

4.1 Compounding

The nano powders were mixed with iPP by HAAKE MiniLab -Compounder. The HAAKE MiniLab micro-compounder was specially developed for the compounding of small volume (7 cm^3) samples. A back flow channel in the minilab was used for recirculation of material. For our study, 5 g of iPP pellets and 1 wt. % of filler (approx. 0.05 g) were used for mixing. The powder and iPP were premixed then added gradually through the hopper of microcompounder. After 5 min, the valve was opened and mixed polypropylene collected.

4.2 Compression molding

Samples for following tests were prepared by compression molding. The solid compounded lump was cut into small pieces to fit it into the PTFE frame (4 × 4 × 0.1 cm). Samples were compression molded at 190 °C for 5 min, then transferred to the second mold at 120 °C and kept there for 30 min. All samples, including their abbreviations, used in the study are summarized in Table 1.

Table 1. Description of tested samples.

| Filler | | | Matrix | Processing conditions | Abbreviation |
Particle	Surface modifier	Method			
partly oxidized Fe_3O_4	---	---	iPP	annealed at 120°C for 0.5 hr	O_Fe_3O_4_120°C, 0.5 hr
partly oxidized Fe_3O_4	pimelic acid / calcium stearate	precipitation	iPP	annealed at 120°C for 0.5 hr	O_Fe_3O_4_(Pi+CaSt, prec.)_120°C, 0.5 hr
partly oxidized Fe_3O_4	pimelic acid / calcium stearate	two-step	iPP	annealed at 120°C for 0.5 hr	O_Fe_3O_4_(Pi+CaSt, two-step)_120°C, 0.5 hr
Fe_3O_4	---	---	iPP	annealed at 120°C for 0.5 hr	Fe_3O_4_120°C, 0.5 hr
Fe_3O_4	pimelic acid / calcium stearate	precipitation	iPP	annealed at 120°C for 0.5 hr	Fe_3O_4_(Pi+CaSt, prec.)_120°C, 0.5 hr
---	---	---	iPP	annealed at 120°C for 0.5 hr	iPP_120°C, 0.5 hr
---	---	---	iPP	fast cooled in a mold at 16°C	iPP_16°C, fast cooling
---	---	---	iPP	fast cooled in water at 8°C	iPP_8°C, fast cooling

5. EXPERIMENTAL METHODS

5.1 Fourier transform infrared spectroscopy (FTIR)

A small amount of finely ground solid sample (1-2 mg) was mixed with 100 times its weight of potassium bromide. Then the mixture was tested by Thermo Scientific Nicolet iS5 FT-IR Spectrometer.

5.2 Wide angle X-ray scattering (WAXS)

Specimens for WAXS were cut out from the central part of the prepared samples by using a rotary microtome Leica RM2255 supplied by Leica Microsystems. The specimen dimension was 20 × 20 mm.

Wide angle X-ray scattering were performed with a X'PERT PRO MPD (Multi- Purposed Diffractometer) by PANanalytical Company. Diffractometer is equipped with CuKα in reflection mode and nickel filter of thickness 0.2 mm. Radial scans of intensity vs. diffraction angle 2θ were recorded in the range of 0° to 40° by steps of 0.026°.

Relative β-phase content was determined according to the standards procedures, employing the formula

$$K_\beta = \frac{H_\beta}{H_{\alpha 1} + H_{\alpha 2} + H_{\alpha 3} + H_\beta}$$

Where $H_{\alpha 1}$, $H_{\alpha 2}$, and $H_{\alpha 3}$ are intensities of α-diffraction peaks corresponding to angles 2θ = 14.2°, 17.0° and 18.8°, respectively, and H_β is the intensity of the β- diffraction peak at 2θ = 16.2°.

5.3 Differential scanning calorimetry (DSC)

The slices were cut out from central part of a sample. The slices weighting approx. 7 mg were put into the aluminum pan by tweezers and covered with a lid. The pan and the lid were then crimped tight.

For the purpose of crystallization studies, a differential scanning calorimeter made by METLER TOLEDO was employed.

The prepared samples were heated from ambient temperature up to 210 °C with heating rate of 10 °C/min then cooled back to ambient temperature to obtain melting temperature

and crystallization temperature. The whole cycle was repeated once to account for any thermal history of the sample.

5.4 Polarized light microscopy

Samples for polarized light microscopy (PLM) were cut out by using a Leica RM2255 rotary Microtome with triming thickness of 40 μm. Slices were placed in the center of an object slide with a drop of paraffin oil and were covered with coverslip. Morphology of the crystallized samples was studied Olympus BX41.

5.5 Dielectric relaxation spectroscopy (DRS)

Dielectric properties of the samples were measured using an Impedance/Material Analyzer Agilent 4991A in the frequency range from 1 MHz to 1 GHz at measuring voltage of 100 mV on rectangular samples (20 × 20 mm) 1 mm thick. The test was conducted at ambient temperature.

5.6 Magnetic properties

Magnetization curve was determined using vibrating sample magnetometer (VSM) Lake Shore 70407 on both, filler in form of powder and compounded iPP. Powder samples were loaded into a container while compounded composites were measured on disc samples (7 mm in diameter and 1 mm thick) cut out from molded plates.

III. RESULTS AND DISCUSSION

6. FOURIER TRANSFORM INFRARED (FTIR) SPECTROMETRY

Prepared iron oxide nanoparticles were analyzed by FTIR both before and after modification. Two methods of modification and two types of nanoparticles with different surface polarities were involved.
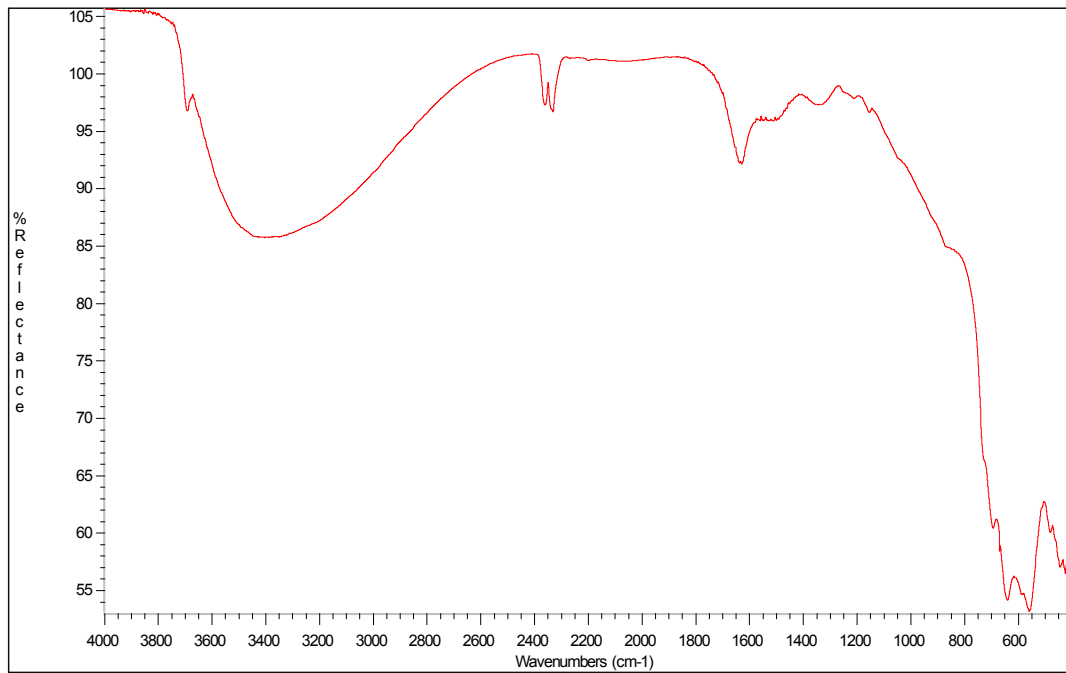
Fig.9. FTIR spectra of oxidized Fe₃O₄ nanoparticles
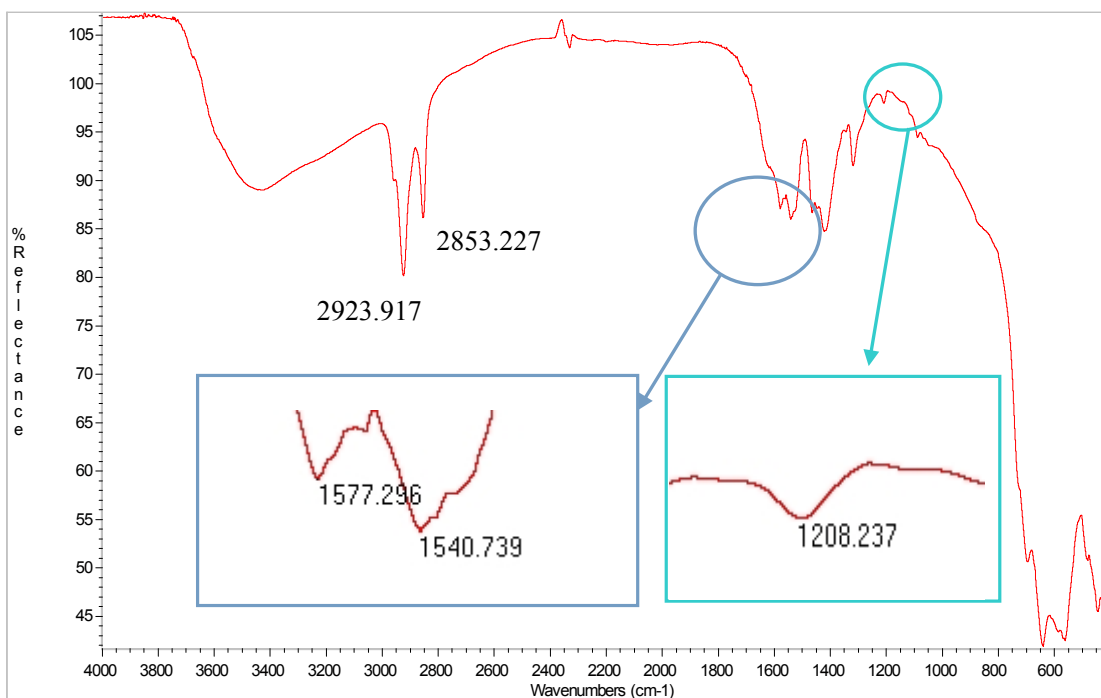
Fig.10. FTIR spectra of oxidized Fe₃O₄ nanoparticles coated with pimelic acid and calcium stearate by precipitation method

In order to compare the difference between modified and unmodified nanoparticles, the IR curve of oxidized Fe_3O_4 nanoparticles without surface modification is presented in Fig.9. In Fig.10, absorption peaks at 2923.917 cm^{-1} and 2853.227 cm^{-1} represent carbon and hydrogen bond vibration of aliphatic series indicating organic compound on the surface of nanoparticles. The absorption peaks of calcium pimelate formed on the nanoparticle surface are observed at 1577.296 cm^{-1} and 1540.739 cm^{-1}. These are assigned to the symmetric stretching vibration and antisymmetric stretching vibration. At 1208.237 cm^{-1}, the absorption peak of -COO-Fe stretching can be observed, which indicates the reaction between calcium stearate and nanoparticles.
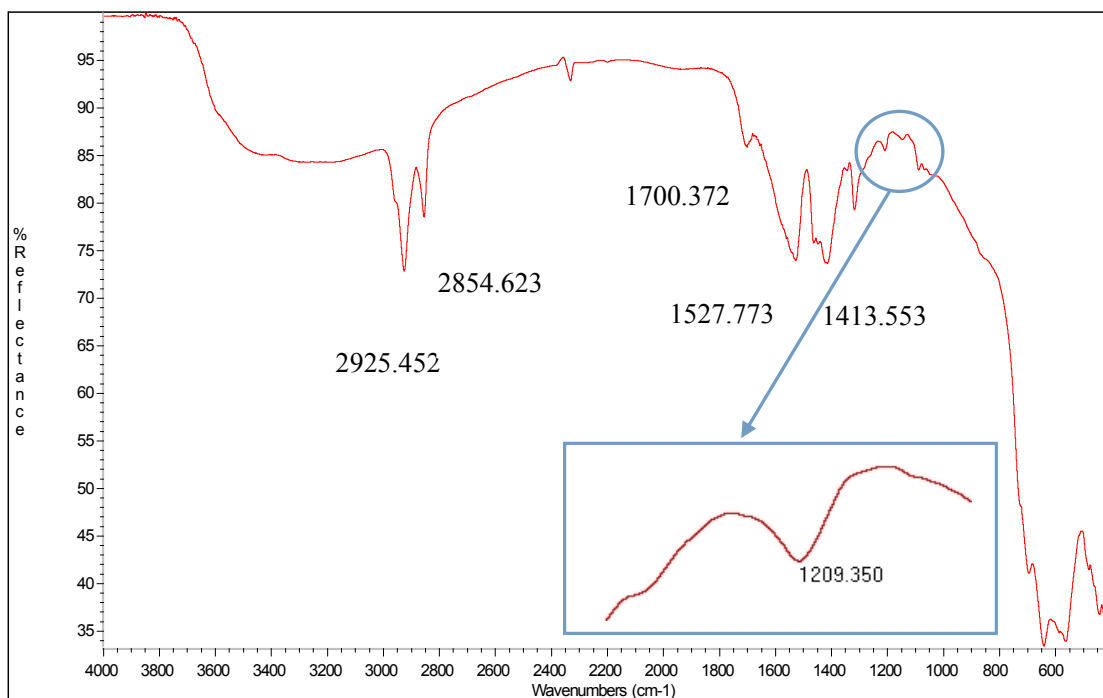
Fig.11. FTIR spectra of oxidized Fe₃O₄ nanoparticles coated with pimelic acid and calcium stearate by two-step method

In Fig.11, one can observe an absorption peak at 1700.372 cm^{-1} indicating the presence of saturated fatty acid which is pimelic acid on the particle surface. The peak at 1209.350 cm^{-1} hints at a chemical bond between surfactant and surface. It is important to stress that no absorption peaks of calcium pimelate can be found in Fig.11, which means no chemical reaction between pimelic acid and calcium stearate took place.
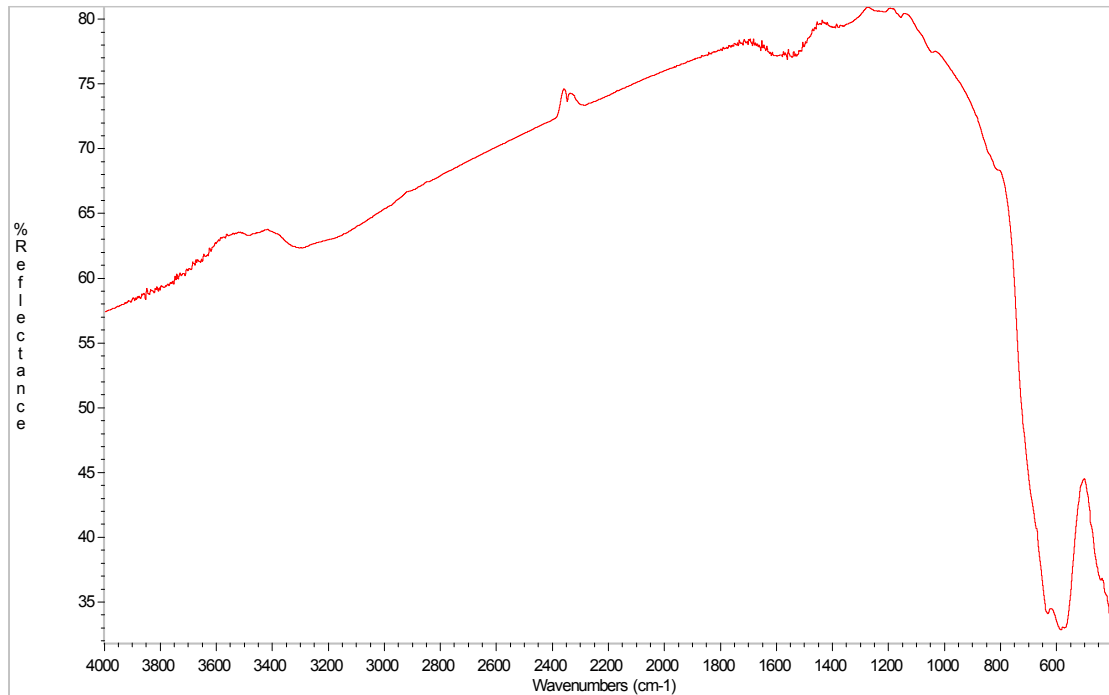
Fig.12. FTIR spectra of Fe₃O₄ nanoparticles
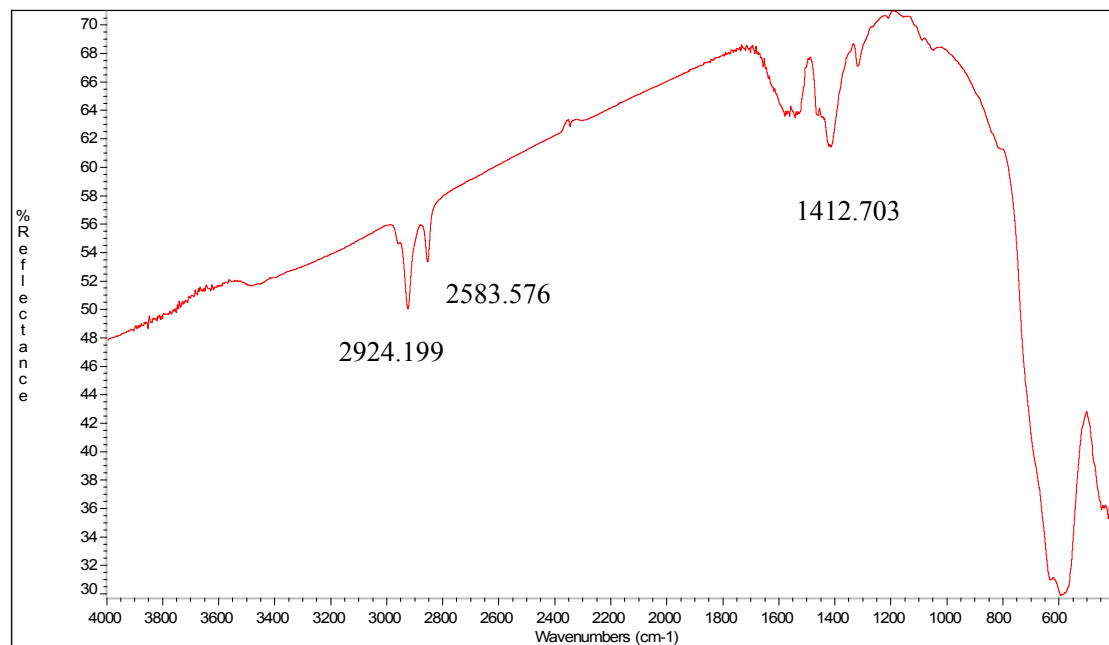
Fig.13. FTIR spectra of Fe₃O₄ nanoparticles coated with pimelic acid and calcium

stearate by precipitation method

Iron oxides coated with pimelic acid and calcium stearate by precipitation (Fig.13) show no absorption peak around 1208 cm^{-1}, compared with Fig.12 and Fig.11, which means there is no chemical bond between particle and surfactant. Absorption peaks of saturated fatty acid salt in the region from 1800 cm^{-1} to 1300 cm^{-1} are different from the ones from the other figures, which gives indirect proof of iron pimelate formation.

On the basis of FTIR results following conclusions can be drawn for the nanoparticles modified by precipitation method:

(1) Partly oxidized Fe_3O_4 nanoparticles: The polarity of Fe_2O_3 surface, i.e. oxidized Fe_3O_4, is much lower than that of Fe_3O_4 resulting in its lower reactivity. Moreover the solvent is heated up to 70 °C in order to be evaporated. Therefore, most of pimelic acid reacts with calcium stearate, producing calcium pimelate. Consequently the mixture with calcium pimelate and surfactant (calcium stearate) is formed on the surface of a nanoparticle, as shown in Fig.14.
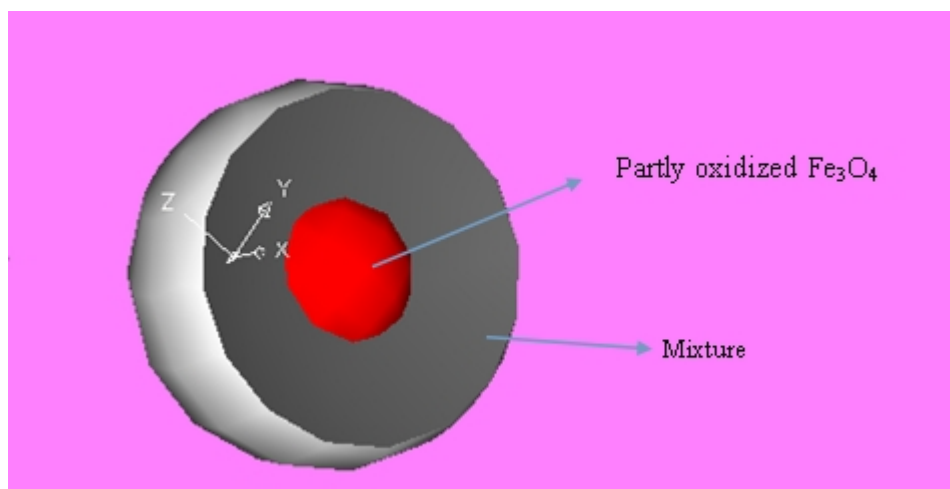
Fig.14. Morphology of partly oxidized Fe_3O_4 nano-particles modified by precipitation method

(2) Fe_3O_4 nanoparticle: Nanoparticles of Fe_3O_4 have strong surface polarity, due to high concentration of polar groups, such as hydroxyl group. Therefore Fe_3O_4 particle carries a negative charge on its surface.

During the modification process, the pimelic acid reacts first with Fe_3O_4 nanoparticle producing iron pimelate. Only then the calcium stearate gets physically bonded to the outer layer without direct contact with Fe_3O_4 surface, which explains the absence of IR spectroscopy peak related to the bond between calcium stearate and Fe_3O_4 surface, as shown in Fig. 13 and Fig. 15.
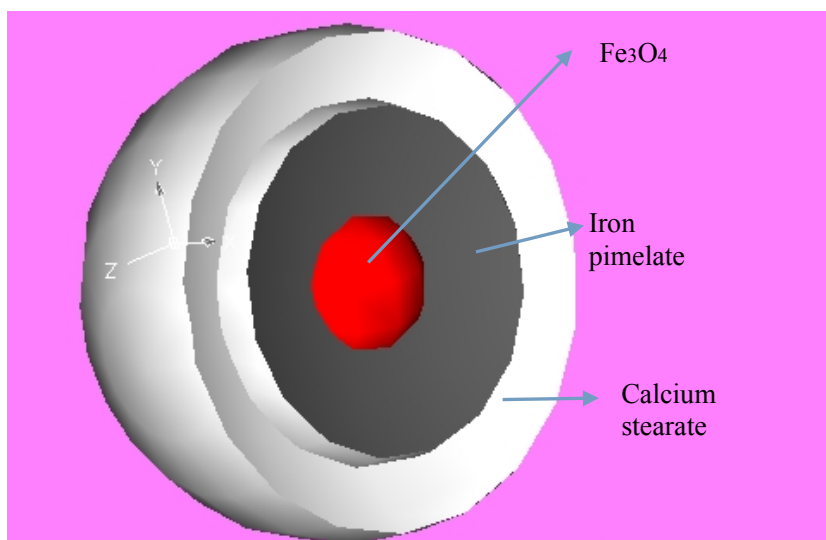

Fig.15. Morphology of Fe₃O₄ nanoparticle modified by precipitation method

7. WIDE ANGLE X-RAY SCATTERING

Wide angle X-ray scattering was employed to observe each polymorphic composition. The corresponding WAXS patterns are shown in Fig. 16. Here the typical reflections at around $2\Theta = 14.2°$, $17°$ and $18.8°$, corresponding to (110), (040) and (130) of α-form can be observed. Reflection at around $2\Theta = 16.2°$ corresponding to (300) represents β-form. The values of crystallinity samples were calculated from WAXS patterns as described earlier in the text. The results are listed in Table 2.
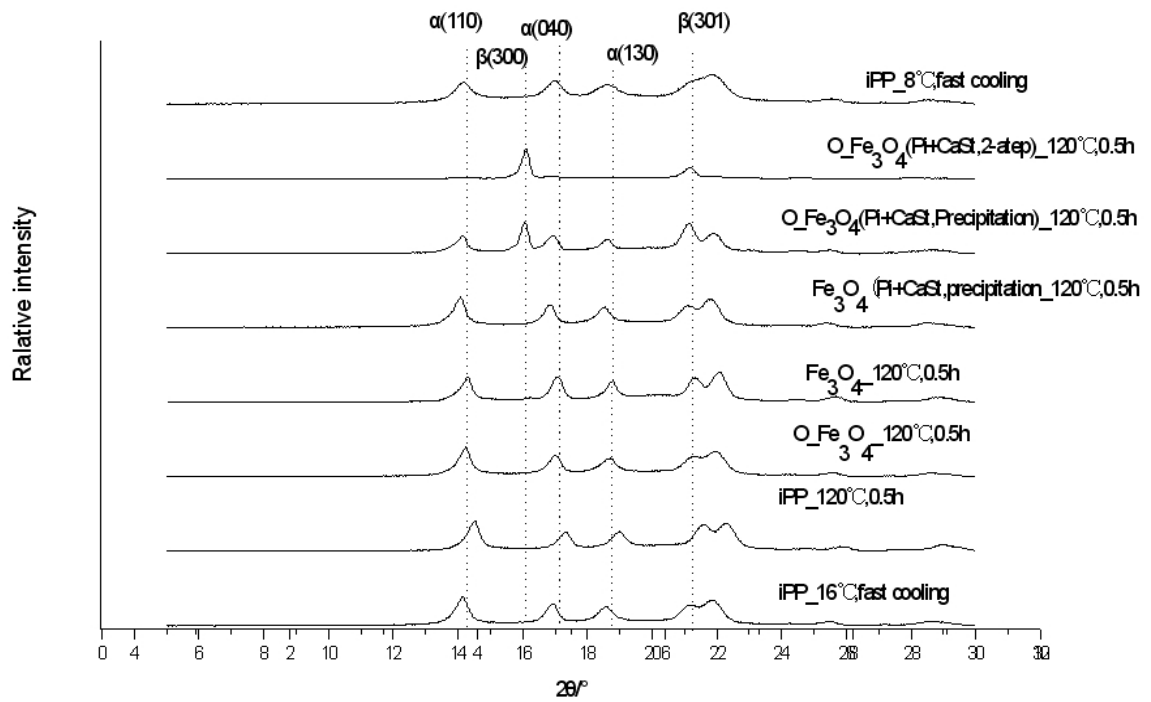
Fig.16. WAXD patterns of samples

Table 2. Crystallinity and relative β-phase content of samples

Sample abbreviation	Crystallinity (%)	K_β (%)
O_Fe$_3$O$_4$_120 °C, 0.5 hr	51	-
O_Fe$_3$O$_4$ (Pi+CaSt, prec.)_120 °C, 0.5 hr	53	39
O_Fe$_3$O$_4$ (Pi+CaSt, two-step)_120°C, 0.5 hr	52	80
Fe$_3$O$_4$_120 °C, 0.5 hr	53	-
Fe$_3$O$_4$ (Pi+CaSt, prec.)_120 °C, 0.5 hr	53	-
iPP_120 °C, 0.5 hr	56	-
iPP_16 °C, fast cooling	52	-
iPP_8 °C, fast cooling	41	-

As for the homogeneous nucleation, the crystallinity of pure iPP annealed is higher than the ones cooled in mold and water respectively due to different cooling rates. The β-phase can be only found with the oxidized Fe_3O_4 nanoparticles which were modified by two different methods. The composite filled with nanoparticles modified by two-step method has higher β-phase than that filled with nanaparticles modified by precipitation method. This is possibly determined by the uniform coating induced by two-step method.

In summary, the reaction of nanoparticles modified by two-step method can be deduced from the WAXD and IR spectroscopy. IR spectroscopy curve shows (Fig. 11) that pimelic acid did not react with calcium stearate. Yang Li [36] thought that the modification of polar nanoparticle by stearate has four different situations, as shown in Fig. 17. In two-step method, excessive amount of surfactant was dissolved twice in deionized water and ethanol respectively. Therefore, the bi-layer and multi-layer were formed.
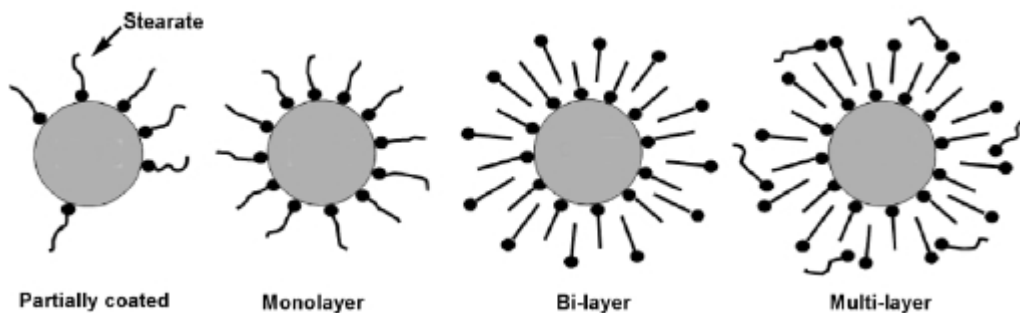
Fig.17. Schematic diagram of nanoparticles with various coverage structures

WAXD result of the sample containing partly oxidized Fe_3O_4 particles modified by two-step method exhibits 80 % of β-phase content, which indicates that the reaction took place during compounding process.

Owing to the presence of surfactant, the nanoparticles with calcium pimelate were isolated from each other resulting in large specific area, which induces high β-phase content, as shown in Fig. 18.
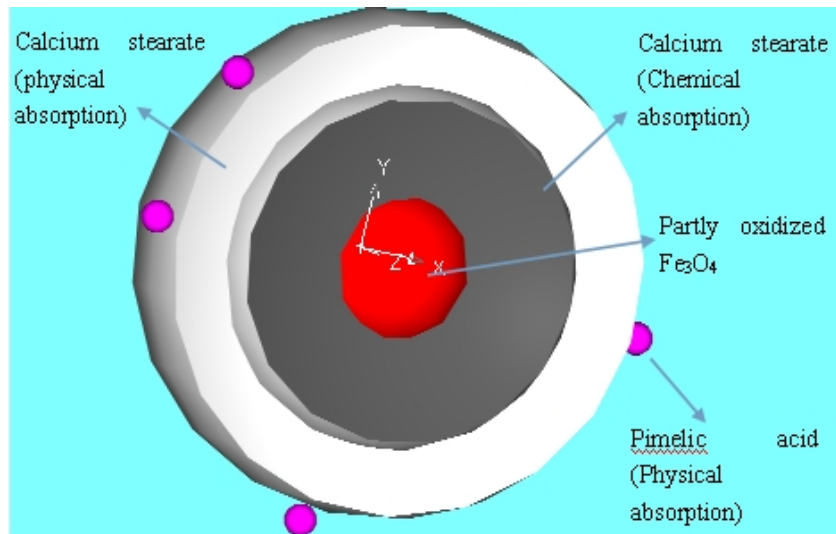
Fig.18. Morphology of partly oxidized Fe₃O₄ nanoparticle modified by the two- step process

Traditionally, the bicomponent nucleating agent is directly blended with iso-polypropylene. However, as the polar inorganic compound is difficult to be uniformly dispersed, the relative β-phase content and nucleating ability are restricted. Table 3 shows the weight percentage of each reagent and the *K* values of three composites annealed under same condition. It can be seen that two-step method consumed less expensive pimelic acid and produced higher relative β-phase content than the other two methods, which saves costs and increases *K* value.

Table 3. Comparison of nucleating agent efficiency

Method	Calcium stearate (wt. %)	Pimelic acid (wt. %)	K_β (%)
standard	0.1	0.15	40
two-step	0.04	0.01	80
precipitation	0.04	0.01	39

8. DIFFERENTIAL SCANNING CALORIMETRY

Fig. 19 and Fig. 20 show the melting and crystallization curves of samples. Temperature of crystallization peak and temperature of α and β melting peak are summarized in Table 4. It can be seen that the composites filled with oxidized Fe_3O_4 nanoparticles modified by two-step and precipitation method have two melting peaks. The lower positioned melting peak at around 150 °C is attributed to the melting of β-crystal while the melting peak at around 164 °C is assigned to melting of α-crystal.
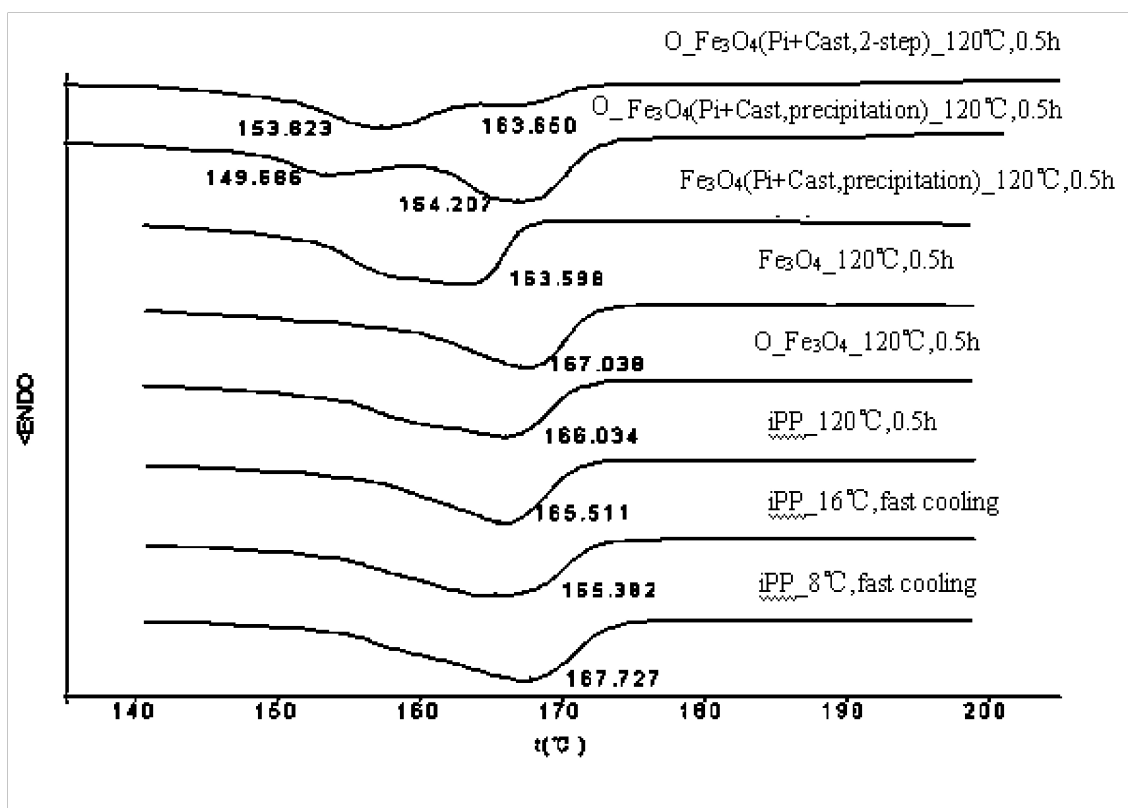
Fig.19. DSC melting curves of samples
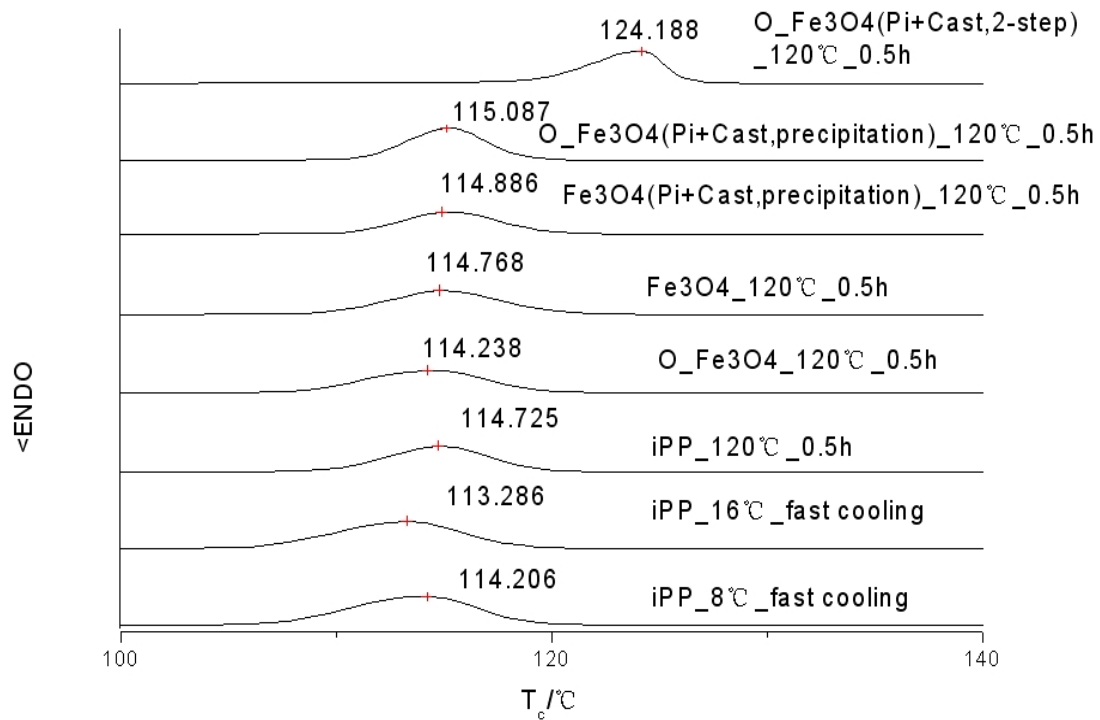
Fig.20. DSC crystallization curves of samples

From the point of crystallization temperature, Rybnikar [37] thought it is possible to evaluate the nucleating ability by the crystallization temperature difference ΔT_c between the nucleated iPP and pure iPP under same scan speed. In our case, the composites filled with Fe_3O_4 and oxidized Fe_3O_4 nanoparticles have similar T_c like the pure iPP samples under different conditions, which shows that the heterogeneous nucleation of nanoparticles without surface treatment is very weak. The composite filled with nanoparticles treated by two-step method shows T_c increase by almost 10 °C compared with pure iPP annealed at 120 °C for 0.5 hr. It clearly indicates that β-nucleating agents deposited on the surface of nanoparticles improve their nucleation ability significantly, as shown in Table 4.

Table 4. Temperature of crystallization peak and temperature of α and β melting peak measured by DSC

Sample	T_c (°C)	$T_{m\alpha}$ (°C)	$T_{m\beta}$ (°C)
O_Fe₃O₄ (Pi+CaSt, two-step)_120°C_0.5 hr	124.2	163.7	153.8
O_Fe₃O₄ (Pi+CaSt, prec.)_120°C_0.5 hr	115.1	149.7	149.6
Fe₃O₄ (Pi+CaSt, prec.)_120 °C_0.5 hr	114.9	163.6	-
Fe₃O₄_120 °C_0.5 hr	114.8	167.0	-
O_Fe₃O₄_120 °C_0.5 hr	114.2	166.0	-
iPP_120°C_0.5 hr	114.8	165.5	-
iPP_16°C_fast cooling	113.3	155.4	-
iPP_8°C_fast cooling	114.2	167.7	-

9. POLARIZED LIGHT MICROSCOPY

The morphology of the samples was observed using polarized light microscopy; corresponding micrographs are shown in Fig. 21, Fig. 22 and Fig. 23.

A)   B)   C)
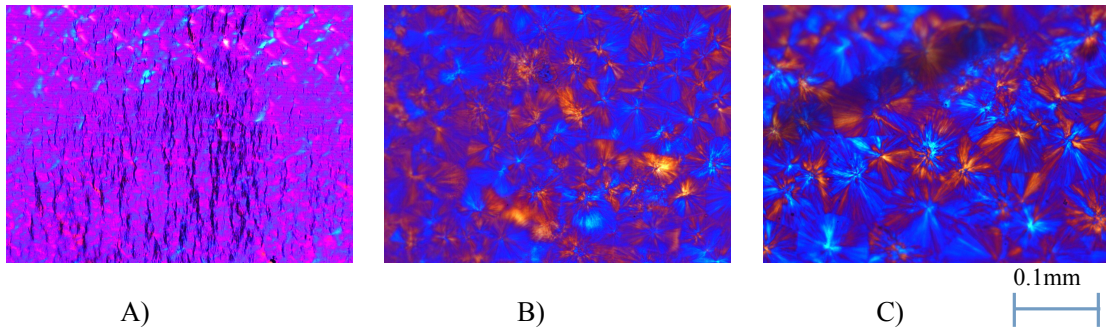
Fig.21. Polarized light micrographs of pure iso-polypropylene sample under different conditions. A) pure iso-polypropylene cooled under 8 °C in water; B) pure-iso-polypropylene cooled under 16 °C in mold; C) pure iso-polypropylene annealed under 120 °C for 0.5 hr

A)   B)   C)
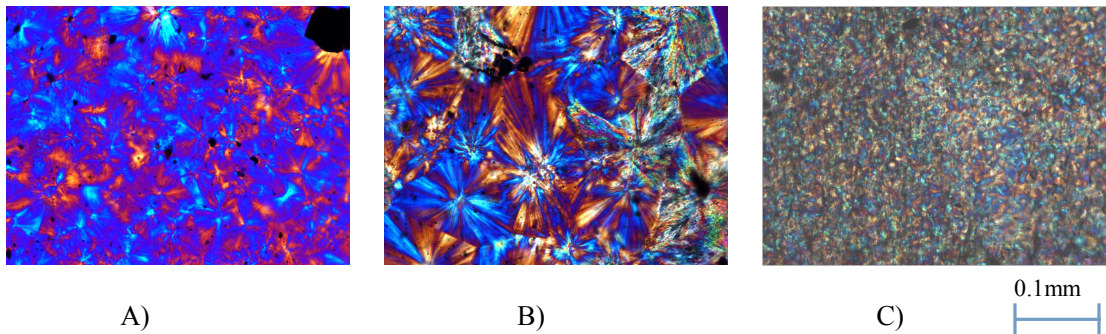
Fig.22. Polarized light micrographs for the composite containing oxidized Fe_3O_4 nanoparticles and annealed 120 °C for 0.5 hour. A) composite filled with oxidized Fe_3O_4 nanoparticles without surface treatment; B) composite filled with oxidized Fe_3O_4 nanoparticles modified by pimelic acid and calcium stearate via precipitation method; C) composite filled with oxidized Fe_3O_4 nanoparticles modified by pimelic acid and calcium stearate via two-step method

0.1mm

A) B)
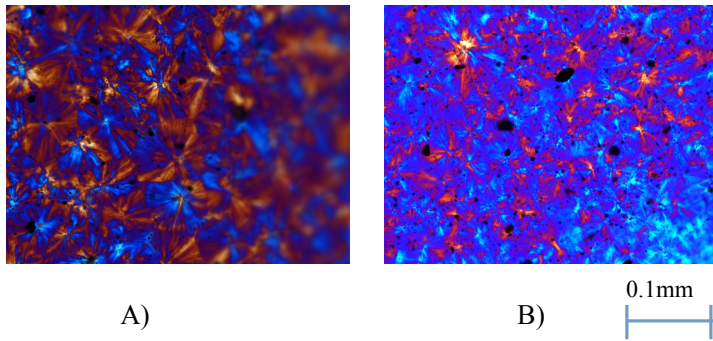
Fig.23. Polarized light micrographs for the composite containing Fe₃O₄ nanoparticles and annealed 120 °C for 0.5 hour. A) composite filled with Fe₃O₄ nanoparticles without surface treatment; B) composite filled with Fe₃O₄ nanoparticles modified by pimelic acid and calcium stearate via precipitation method

It can be seen that linear PP annealed at 120 °C for 0.5 hour shows larger spherulites with distinct boundaries than the other two fast cooled samples. Such structure was formed via homogeneous nucleation, as shown in Fig.21.

Crystallization of the composite samples, i.e. iPP filled with nanoparticles, (Fig. 22 and Fig. 23) was mainly initiated by heterogeneous nucleation. In Fig. 22B, the spherulites of the composite containing nanoparticles modified by precipitation method are more complete than that filled with nanoparticles without surface treatment (Fig. 22A). However, the spherulites induced by nanoparticles modified by two-step method are of much smaller size (Fig. 22C). This may stem from uniform coating of the particles by nucleating agent which in turn results in much better β-nucleation effect than in the composite filled with nanoparticle prepared by precipitation method.

The absence of β-nucleating agent results in no obvious difference in structure of the samples shown in Fig. 23B.

From the results of WAXD, DSC and optical microscopy, it follows that the particles modified by two-step method have stronger β-nucleating ability than those modified by precipitation method. This behavior is possibly determined by two aspects: Firstly, the nanoparticles were used as absorbent to attract free pimelic acid and calcium stearate molecules in two-step method resulting in uniform coating and reaction. Therefore, the large specific surface of nanoparticles was fully utilized. Precipitation method depends on the evaporation of solvent to achieve precipitation of substance producing film on the surface of nanoparticle. Furthermore, unlike two-step method, the nucleating agent calcium

pimelate is contained within the mixture reducing the contact area between nucleating agent and iPP matrix.

On the other hand, Chen Yan [38] studied the thermal stability of calcium pimelate and thinks the thermal degradation of calcium pimelate begins at around 150 °C. Pimelic acid and calcium stearate in two-step method react during the compounding process reducing the degradation of calcium pimelate.

10. DIELECTRIC RELAXATION SPECTROSCOPY (DRS)

Non-polar iPP does not exhibit high values of relative permittivity, with values slightly above 2 which is basically the contribution coming from deformation (i.e. atomic and electron) polarization, due to the lack of polarization processes which would enhance its dielectric constant (e.g. interface or orientation polarization). Neither the dielectric spectrum shows any strong frequency dependence at ambient temperature (Fig. 24).

No significant differences can be spotted for samples prepared at different conditions (mainly cooling rate).
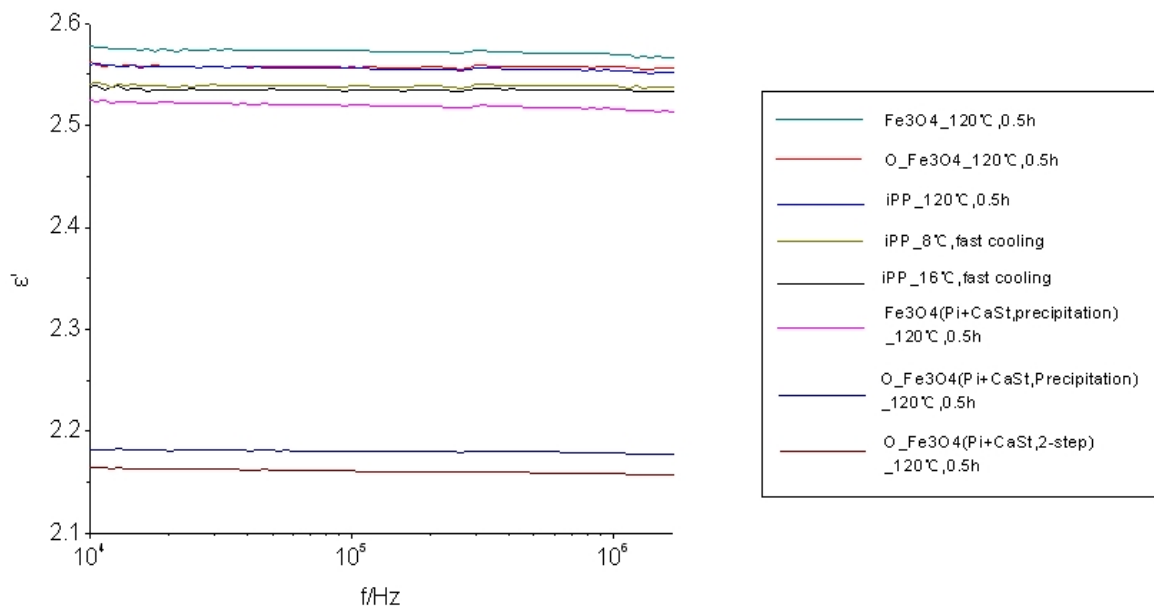
Fig.24. Real part, ε', of complex permittivity versus frequency of the samples

No considerable enhancement is seen even for composite samples. This fact can be explained by very low filler concentration (around 1 wt. %), which do not significantly alter dielectric properties of the composite as normally filler of much higher permittivity than iPP matrix would.

Filler of oxidized and non-oxidized Fe_3O_4 nanoparticle without surface treatment has polar surface which is not compatible with non-polar iso-polypropylene matrix, so the interaction between filler and matrix can be neglected.

However, the real part value of composite filled with nanoparticles coated with surfactant is lower than that of annealed iso-polypropylene in Fig. 24. That is mainly caused by two aspects. First, surfactant improves the dispersion of nanoparticles, avoiding the agglomeration. Second, the surfactant changes the surface tension of nanoparticle, which induces a better contact between particles and matrix. According to the theory of Maxwell-Garnett [39], the interaction layer may exist and affect the value of composite. Similar result was also presented between PE and Fe_3O_4 nanoparticles [40].

In our case, the composites filled with nanoparticles coated with nucleating agents have significantly lower value of real part of dielectric permittivity. That may be brought about by the polypropylene lamellae which are induced by nucleating agent on the surface of nanoparticle. The polymer chains are more compact, which may possibly improve the interaction.

11. MAGNETIC PROPERTIES

When a general magnetic (especially then ferromagnetic) material is magnetized in one direction, it will not relax back to zero magnetization when the imposed magnetizing field is removed, but will keep partial magnetization which is denoted as *remanent magnetization M_r*. It must be driven back to zero by a field in the opposite direction – coercive field or *coercivity H_c*. Magnetization of material can be increased by increasing external magnetic field up to *saturation magnetization M_S* when the total magnetic flux density levels off. If an alternating magnetic field is applied to the material, its magnetization will trace out a loop called a *hysteresis* loop. The lack of retraceability of the magnetization curve is the property called hysteresis and it is related to the existence of magnetic domains in the material (Fig. 25) [41].
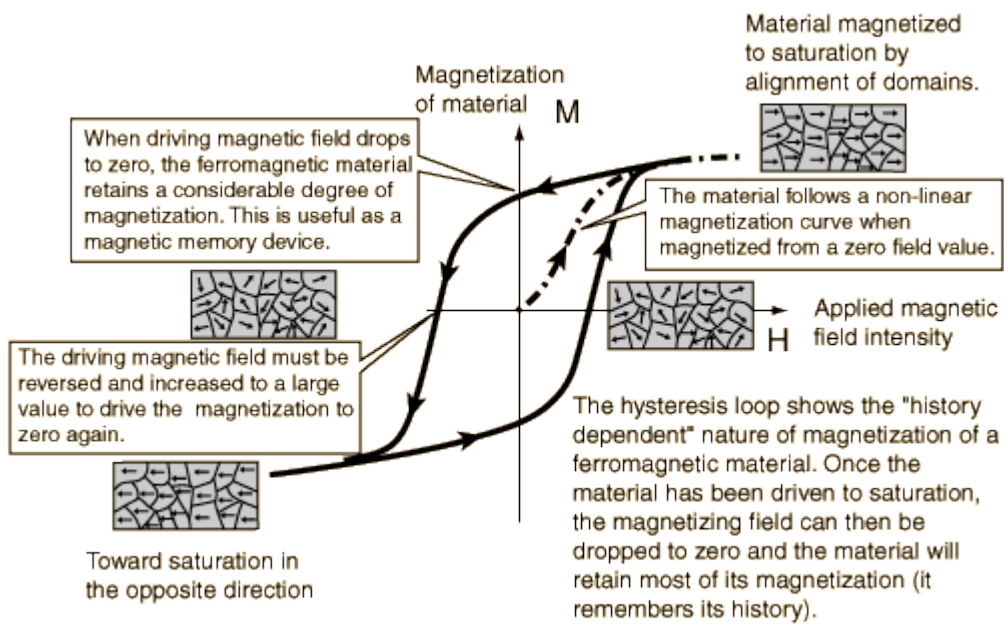
Fig.25. Hysteresis Loop [41]

Synthesized Fe_3O_4 nanoparticles are single-domain which corresponds with very low hysteresis. From Fig. 26 and Fig. 27, it can be found that the oxidation of the powder at 300 °C for 90 min do not change its magnetic properties significantly, saturation and coercivity are almost the same (Table 5).
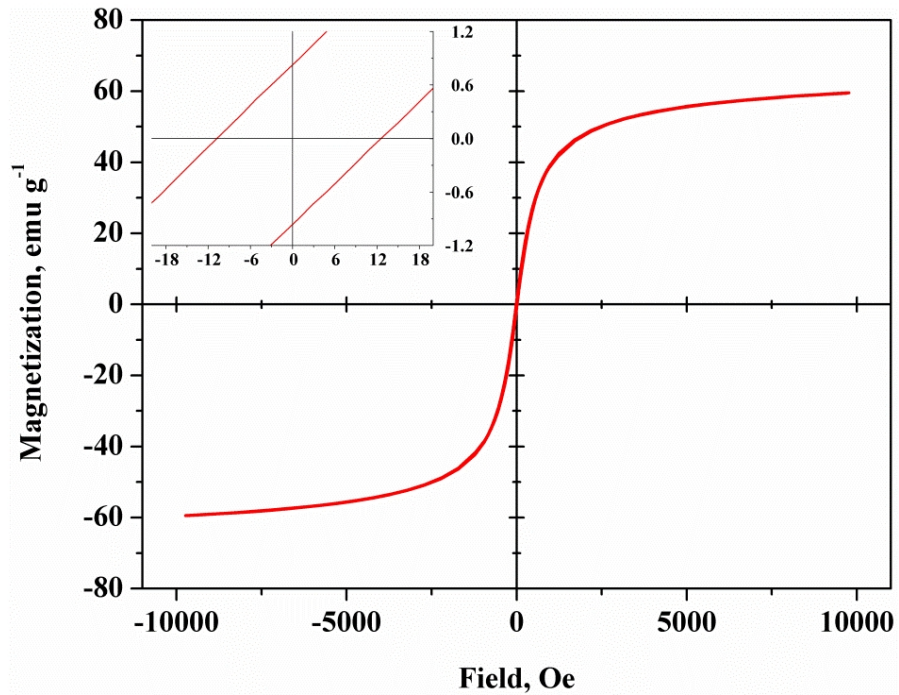
Fig.26. Magnetic hysteresis loop for Fe3O4 nanoparticles
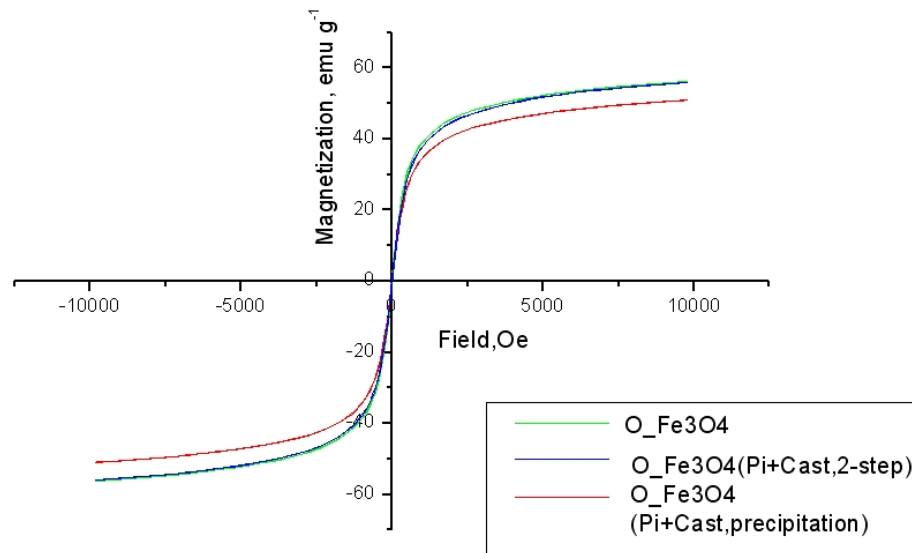
Fig.27. Magnetic hysteresis loops for nanoparticles of oxidized Fe₃O₄ and

oxidized Fe₃O₄ modified by precipitation method and two-step method

Saturation values of composites are approximately by two orders of magnitude lower than of iron oxide nanoparticles due to dilution (filler loading 1 wt. %) of sample's magnetic portion by iPP (Fig. 28) as the magnetic response of the sample was related to the mass of the whole composite not just its magnetic content.

However composites' coercivity values are not affected by this and therefore can be directly compared with iron oxide nanoparticles. Coercivity of composite samples considerably increased, namely in the case of particles modified by precipitation (38 %). This is most probably owing to the interaction between nanoparticles and polymer matrix (iPP), which induces magnetic anisotropy in nanoparticles or somehow pins free movement of magnetization vector within the particle.
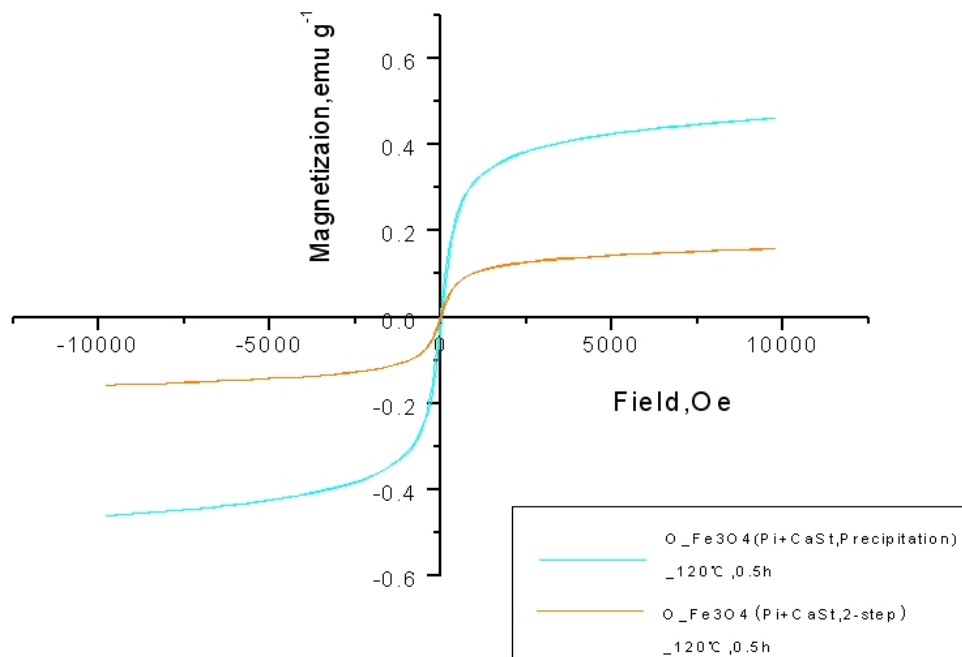
Fig.28. Magnetic hysteresis loops for composites filled with oxidized Fe$_3$O$_4$
modified by precipitation and two-step method
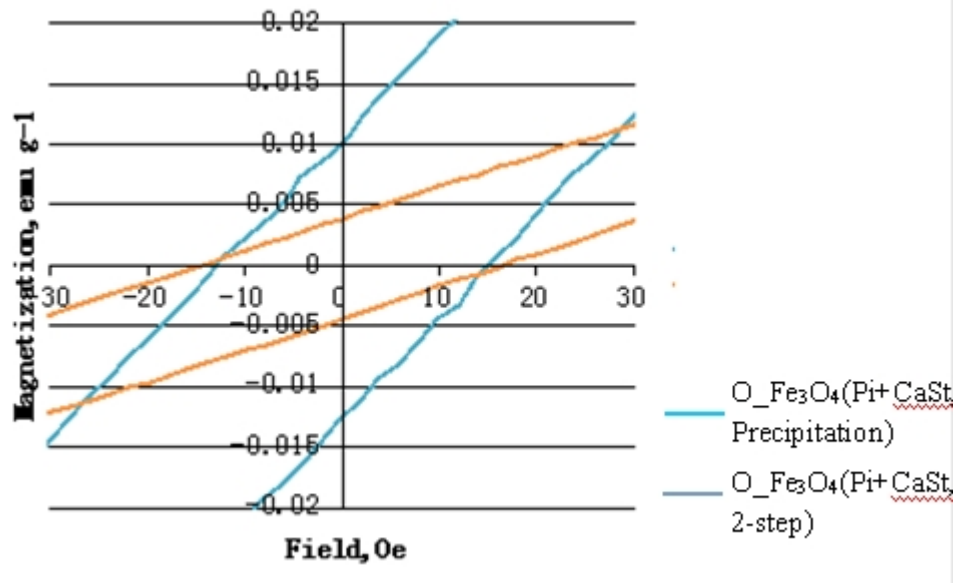
Fig.29. Detailed view of figure 28 showing coercivity and remanence of the sample

Table 5. Magnetic properties of samples

Sample / form	Saturation magnetization M_s (emu/g)	Coercivity H_c (Oe)
Fe_3O_4 / powder	60.0	13.1
$O\_Fe_3O_4$ / powder	56.0	12.4
$O\_Fe_3O_4$ (Pi+CaSt, prec.) / powder	56.2	11.2
$O\_Fe_3O_4$ (Pi+CaSt, two-step) / powder	50.9	12.1
$O\_Fe_3O_4$ (Pi+CaSt, prec.)_120°C_0.5 hr / composite	0.16	15.5
$O\_Fe_3O_4$ (Pi+CaSt, two-step)_120 °C_0.5 hr / composite	0.46	14.0

CONCLUSION

This Master thesis deals with β-nucleation of surface modified iron oxides in isotactic polypropylene. Two different methods (precipitaion method and two-step method) for modification and two different nanoparticles (Fe_3O_4 and partly oxidized Fe_3O_4 nanoparticles) with different surface polarities are involved in this study. The purpose of surface modification is to improve the dispersion of polar nanoparticles and nucleating agent in non-polar iPP matrix and also increase the relative β-phase content to change the mechanical property of composite.

The β-nucleation agent, calcium pimelate, was obtained by bicomponent reaction between pimelic acid and calcium stearate. Pimelic acid is dicarboxylic acid, which can react with the inorganic filler. Calcium stearate was also used as a surfactant to alter the surface polarity.

The precipitation method is commonly used to coat the iPP powder with calcium pimelate which is produced from pimelic acid and calcium stearate. The coating and reaction process are carried out in solution and iPP powder is inert with both pimelic acid and calcium stearate, indicating the product is only calcium pimelate. But the situation becomes complex due to presence of iron oxides in our study, which means the filler iron oxides can react with either pimelic acid or calcium stearate in solution. Both X-ray scattering and infrared spectroscopy proved that Fe_3O_4 nanoparticles firstly reacted with pimelic acid, producing iron pimelate, which did not show any β-nucleating ability. However, calcium pimelate was successfully obtained and precipitated on the surface of oxidized Fe_3O_4 nanoparticles. The difference was possibly caused by surface polarity.

Two-step method overcomes the disadvantage of selective reaction in the case of precipitation method. Regardless surface polarity, the surface is modified by surfactant firstly and coated by nucleating agent secondly as proved by FTIR spectrometry showing pimelic acid molecules physically bonded to nanoparticles. This is mainly due to the protection provided by single or possibly several layers of surfactant in solution. β-nucleating agent was predominantly formed during the compounding process.

Having compared DSC and WAXD results of different samples, two-step method shows better effect; be it the increase of crystallization temperature or the relative β-phase content. Due to the selective reaction taking place in the solution, Fe_3O_4 nanoparticles modified by precipitation method show no presence of β-phase. Nanoparticles modified by two-step

method exhibit strong nucleating capability and smaller spherulites than other samples. Pristine (unmodified) nanoparticles show no obvious nucleating effect having almost the same crystallization temperature as pure iPP sample. It is mainly due to bad compatibility between nanoparticles and matrix. Better affinity of treated nanoparticles towards the matrix was shown even in the case of the dielectric test.

It can be concluded that nucleating agents deposited onto the surface of carrier nanoparticles of iron oxide significantly increase their relative β-phase content. The deposition should follow the two-step path rather than the precipitation as it can lead to undesired competitive reactions.

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LIST OF ABBREVIATIONS

PP   Polypropylene

iPP   Isotactic polypropylene

PE   Polyethylene

α   Monoclinic crystalline form

β   Trigonal crystalline form

γ   Orthorombic crystalline form

T_c Crystallization temperature (°C)

T_m Melting temperature (°C)

T_g Glass transition temperature (°C)

$K_β$ Relative content of β-phase

WAXD Wide angle X-ray diffracting

DSC   Differential scanning calorimetry

MFI   Melt flow index

2Θ   Angle of diffraction (°)

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