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Preparation of highly filled super-paramagnetic PMMA-magnetite nano composites using the solution method

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The effect of super-paramagnetism is limited to magnetite particles at the nano scale [1–5]. Agglomerated particles exceeding a diameter of 20 nm do not show super-paramagnetism any longer. To transfer this special nano property to a bulk material it is necessary to ensure maximum dispersion of the fine particles within the polymer matrix. The focus of this paper is on the production process for super-paramagnetic magnetite PMMA nano composite material. The polymer PMMA is highly filled up to 50 mass-% with magnetite particles. The solution process uses a stabilized magnetic fluid, in which the polymer is dissolved. This solution/dispersion is atomized and dried in a spray tower to produce a fine powder of composite material. This powder is characterized (SAXS, XRD, VSM, AGM) and further processed e.g. in an injection moulding machine to manufacture structural parts. The structural parts still show super-paramagnetic properties.

1. Introduction

The preparation of nano enhanced materials is a wide field of research. A couple of new properties (mechanical, electrical, magnetic properties as well as optical properties and flame retarding effects or interacting materials for catalysis) have been mentioned until now [6–9]. The approach of polymer-particle nano composite material uses a polymer material as carrying matrix, in which the nano phase is dispersed and encapsulated. In this field as well intense research is going on. The nano phase usually consists of fine powder with particle diameter below 100 nm. One main filler material is clay. Due to its unique distribution of surface load, the interaction between the particle and the polymer chains results in a reinforced composite material, with increased mechanical stability [10].

Different approaches are used to produce polymer-particle nano composite material, which can be classified into bottom up and scale down processes. Scale down processes use a technical equipment to come to an intense mixing of the dispersed nano phase polymer melt. Bottom up processes try to encapsulate the filler before and during the synthesis of the polymer.

The main question beside the synthesis of the particles is, how to disperse the inorganic filler within the organic polymeric phase. The complexity rises with decreasing particle size. Submicron particles tend to build strong agglomerates, which are stabilized by van der Waals forces and sinter bridges. Conventional mixing strategies, which apply extruder or kneader technologies, do not achieve the high degree of mixing necessary to break submicron agglomerates. Furthermore those technologies encounter problems as they reach a high filler degree and a uniform dispersion of the filler within the polymer matrix as well in those processes. The maximum degree of filling does not exceed some mass-%, because the dry-mixing technology is not able to overcome the high surface energy of the submicron filler. The wetting of particle surface with the polymer or the polymer melt is the crucial point of dispersion.

Concerning dispersion quality, bottom up approaches have to be favoured. Starting from a stable dispersion of the filler particles the polymer can be synthesized around the particle surface. The polymerization reaction process and the dispersion have to be compatible; the formation of highly filled nanocomposite materials via direct poly-

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merization is still a challenge [11]. During polymerization, the time scale of solid formation and agglomeration is long enough to allow segregation. This results in an inhomogeneous composite material with poor encapsulation of the filler particles. Emulsion polymerization is limited to the radical polymerization mechanism. With increasing size of the micelles for reaction, the homogeneity of the material decreases. Smaller micelles consume higher energy for the emulsification process, which goes along with possible changes in the filler material. However the scale up of these lab scale processes is difficult, because dispersion of the filler, dispersion of the emulsion and polymerization have to be controlled at the same time.

The Solution process is characterized by the single-phase system of the liquid phase. The polymer is dissolved in an organic solvent. The void space between the polymer chains becomes accessible. The strategy to produce the composite material starts with a particle fluid. Actually a magnetic fluid, which contains magnetite particles with a diameter below 20 nm, is used. The detergent Oleic acid stabilizes the particle fluid. It is adsorbed onto the particle surface providing steric and osmotic repulsion forces respectively [12]. Due to the low viscosity of about 50 mPaS the magnetic fluid provides a perfect dispersion of the magnetite particles. The polymer solution and particle fluid base on the same solvent can be mixed easily. This mixing step ensures the optimum dispersion of polymer chains and particles.

The dispersion or solution is then pumped to a spray tower, where it is atomized into fine droplets. Due to its high drying velocity, the solid formation is fast enough to prevent any segregation effects. The spray drying provides a composite powder with an average diameter of 5–10 micron. The remaining solvent content is quite low and does not influence further processing.

The magnetic characterization (AGM, VSM) of the material quantifies that it is possible to transfer the nano scale property of super-paramagnetism into a 10 micron particle. X-ray methods (XRD, SAXS) prove that the magnetite particles are still de-agglomerated, when they are embedded into the polymer matrix. The analysis of the magnetite content shows that the loss of nano scale filling material depends on the concentration of the detergent Oleic acid. By keeping the amount of detergent close to a minimum, which is necessary for the stabilization of the ferrofluid, almost 96 mass-% of magnetite is encapsulated into the polymer matrix. The absolute magnetite content amounts up to 50 mass-%.

In the second step, the fine composite powder, which is definitely not the final product, is processed with an injection moulding machine. The small structural parts produced still show excellent dispersion and the super-paramagnetic properties.

2. Material and methods

2.1. Materials

PMMA granulate material is of technical quality and purchased from Rhenus AG & Co. Oleic acid, iron(II)sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) and iron(III)chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), Dichloromethane (DCM), ammonium hydroxide (26% NH_3) and petrolether are purchased from Fluka AG and used as received.

2.2. Preparation of the magnetic fluid

For the production of magnetite in a lab scale, different methods are used [13, 14]. According to [13] the magnetite nanoparticles are produced by co-precipitation of an aqueous solution of iron(III)chloride hexahydrate and iron(II)sulfate heptahydrate with a molar ratio of $Fe^{3+}/Fe^{2+} = 2:1$. The iron solution is precipitated with concentrated ammonium hydroxide in excess. The precipitation process is done with vigorous stirring in a glass beaker. Alternatively, in respect of scale up possibilities, an ultrasound flow through reactor is used [15]. By default 24.05 g $FeSO_4 \cdot 7H_2O$ and 47 g $FeCl_3 \cdot 6H_2O$ are dissolved in 1000 ml distilled water and heated to 70°C. 60 ml of ammonium hydroxide is added quickly to the resulting solution, producing deep black magnetite precipitates at once. The magnetite yield is 20 g/L. The suspension has been stirred for another 30 min at 70°C in order to evaporate any trace ammonium salts. Otherwise, the salts adsorbed after precipitation onto the particle surface and the transfer into the organic phase is obstructed.

After cooling to room temperature, the magnetite particles are transferred directly without previous drying from the aqueous phase into a mixture of Dichloromethane and Oleic acid which serves as a steric stabilizer. A minimum amount of about 0.3 $g_{OleicAc}/g_{Mag}$ is needed to transfer all the particles into the organic phase. Otherwise an intermediate phase consisting of non stabilized particles, which show a different wetting behavior, disturbs the transfer procedure. Subsequent to the transfer step a stable oil-based ferrofluid with a yield of 20 g_{Mag}/l_{DCM} is obtained. The Particle size is measured by PCS (Zetasizer Nano ZS, Malvern Inc.) to control precipitation and stabilization.

2.3. Preparation of the composite powder

After preparation of a stable ferrofluid, the polymer PMMA is directly dissolved into the magnetic fluid to minimize the amount of solvent needed. The viscosity of the suspension amounts to about 50 mPaS. It is still low enough to ensure a perfect mixture of magnetite and polymer in the molecular scale. The mass of dissolved polymer depends on the filling degree. In order to keep the amount of Oleic acid related to the mass of PMMA constant, an excess amount of acid has to be added to examine the influence of detergent on the encapsulation rate. In the present work, a ratio from 0.3 to 1.0 $g_{OleicAc}/g_{PMMA}$ is used. The composite material is synthesized in a conventional lab spray dryer (Buechi B-191). The feed flow of the spray dryer consists of dissolved polymer, steric stabilized magnetite and an excess of Oleic acid. The atomizer produces a fine spray with a small droplet size of about 20 micron, which is dried in the spray tower at 40°C. Free Oleic acid avoids the creation of a polymer skin. More detailed information about the interaction of the solvent and the polymer is given in [16] and [17] respectively. The organic and the inorganic phase do not separate during the drying process. Thus the magnetite is encapsulated and uniformly dispersed within the PMMA matrix. The product is a filled or highly filled polymer powder with a mean particle size of 2–10 micron. The nano compound is washed subsequent to its synthesis several times with petrolether to remove a film consisting of an excess of Oleic acid and non encapsulated magnetite nano particles.

2.4. Composite processing in the injection moulding machine

In order to transfer the characteristics of composite powder to larger structures of technical interest, a structural part in a form of a tensile bar has been manufactured using a micro moulding machine. The machine heats the washed powder up to the melting point of the polymer and presses the melted mass into a form applying a pressure of 690 bar. Owing to the high viscosity of the melt, the magnetite particles do not agglomerate. The dispersion of magnetite within the polymer is retained during the spray drying process. Thus the composite generation, the dispersion and de-agglomeration and the composite processing are decoupled from each other. For all processes the optimal processing parameters can be chosen, focussing the main effect of each step.

2.5. Measurement techniques

To control the particle size of magnetite in the feed flow, photon correlation spectroscopy (PCS, Malvern Instruments Nanosizer ZS) is used. The content of magnetite in the ferrofluid, in the unwashed and in the washed composite particles is quantified with a spectrophotometer (Hach Company, DR 4000) using the 1.10 Phenanthroline method.

X-ray diffraction (XRD, CrK_α radiation) and Small angle X-ray scattering (SAXS, CuK_α radiation) profiles are recorded to determine the mean particle size of magnetite inside the composite material. A transmission electron microscope (TEM) is used to observe the particle distribution and size of the filler material. Because of the high content of magnetite, ultra thin slices (60–200 nm) are prepared with the help of a Microtom. VSM and AGM measurements are carried out at room temperature to access information on the saturation magnetization and magnetic remanence of the composite powder and the tensile bars. The influence of potentially encapsulated Oleic acid on the thermal and mechanical properties of the composite material can be quantified by DSC measurements.

3. Results and discussion

3.1. Properties of the magnetic fluid

An excellent stabilization of the magnetite particles in the feed flow of the spray dryer is the basic requirement to manufacture super-paramagnetic materials. Therefore the particle size in the feed solution/dispersion is measured. Fig. 1 shows the particle size distribution in the magnetic fluid measured with PCS.

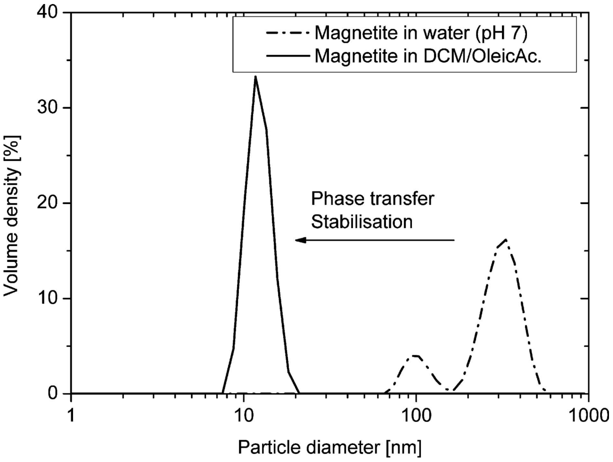


Figure 1 Particle size distribution in water (pH 7) and in dichloromethane/Oleic acid. Oleic acid in the organic phase adsorbs on the particle surface stabilizes the suspension sterically. The figure shows the primary particle size of 14 nanometers.

The electrostatic repulsion of the magnetite particles in water phase at pH 7 is too small to allow electrostatic stabilization of the dispersion. The zeta-potential of magnetite in aqueous dispersion does not exceed 30 mV in the entire pH range. The volume density distribution shows agglomerates with a mean diameter of 60–500 nanometers in aqueous surrounding. Due to the zeta-potential of about −5 mV (pH 7) [18] a strong flocculation can be expected and the super paramagnetic characteristic is lost. In contrast, the sterically stabilized particles in the organic phase show a very narrow volume density distribution. The strong repulsion forces of adsorbed Oleic acid stabilize the primary particle size of 14 nanometers even in Dichloromethane.

3.2. Structure of the nanocomposite powder material

A high filling degree is necessary for the efficient application of super-paramagnetic materials, because the saturation magnetization is directly proportional to the volumetric magnetite content. In order to control the magnetite encapsulation mechanism, the influence of Oleic acid on the encapsulation rate has been examined. After the spraying process the beads have been washed several times with petrolether to remove a film consisting of Oleic acid and non encapsulated nano particles off the polymer surface. The magnetite content of the washed and the unwashed composite particles have been compared. Fig. 2 shows the magnetite fraction in the unwashed beads depending on the magnetite content in the feed flow. The ratio of Oleic acid to polymer amounts to 0.3, 0.5 and 1.0 $g_{\mathrm{OleicAc}}/g_{\mathrm{PMMA}}$. It is obvious, that the magnetite content of the unwashed samples is independent from the

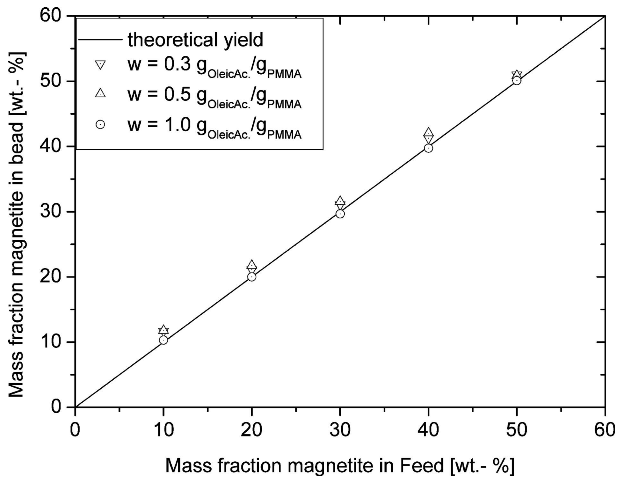
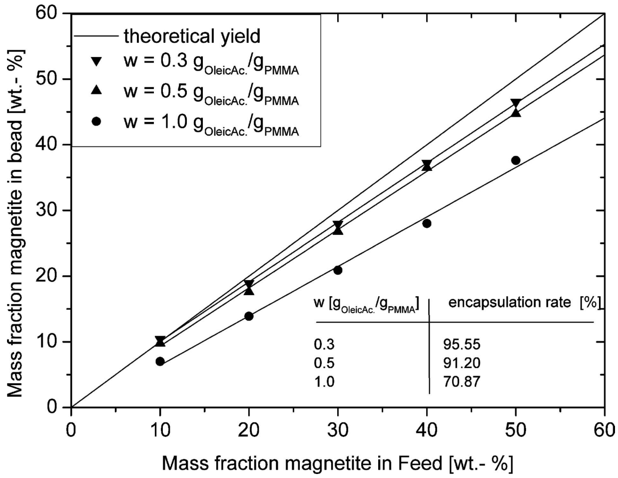


Figure 2 Magnetite content in unwashed beads versus its mass fraction in the feed flow. The results show that the filler is deposited either on the surface or inside the polymer. Nothing is lost during spray drying.

concentration of Oleic acid. The mass fraction of magnetite of the unwashed composite is approximately equivalent to the theoretical yield. It can be stated that no magnetite particles are separated from the composite powder during the spray process.

The magnetite content of the washed beads is shown in Fig. 3. It can be figured out that the filling degree, the mass fraction of magnetite in the beads respectively, is a linear function of the magnetite concentration in the feed flow. The encapsulation rate is given by the mass of magnetite in the washed beads divided by the mass of magnetite that is theoretically expected multiplied with 100%. The encapsulation rate indicates that the filling degree depends on the concentration of Oleic acid in the feed, too.

At low detergent concentration almost 96 mass-% of magnetite in the feed flow is encapsulated into the PMMA matrix. The Oleic acid, which is poorly volatile, is not evaporated at the low drying temperature of 40°C. The drying process transports the excess of Oleic acid, which is not adsorbed on the magnetite surface, to the boundary of the drop. Thus during the solidification a drag flow to drop surface occurs. This flow locally enriches the Oleic acid and therefore the surface layer also contains magnetite particles. The thicker the surface layer becomes due to a high concentration of Oleic acid, the more the encapsulation efficiency decreases. As a result, the encapsulation decreases to about 71 mass-% when the concentration of Oleic acid is increased to 1.0 $g_{OleicAc}/g_{PMMA}$. The comparison of Figs 2 and 3 indicates that the deposition of the filler material can be influenced by the concentration of Oleic acid.



w [$g_{OleicAc.}/g_{PMMA}$]	encapsulation rate [%]
0.3	95.55
0.5	91.20
1.0	70.87

Figure 3 Magnetite content in beads versus its mass fraction in the feed flow. The beads have been washed several times with petrolether to get the film consisting of Oleic acid and non encapsulated nano particles off the polymer surface.

In addition to the high filling degree, a homogeneous distribution of the magnetite particles within the polymer is essential to achieve a basic material with satisfying super-paramagnetic properties. Agglomerated magnetite particles will not show super-paramagnetism any longer. Therefore XRD and SAXS spectra have been prepared to verify the high dispersion of the filler inside the matrix. The XRD-pattern of a composite powder with 40 mass-% magnetite is shown in Fig. 4. The broad halos at 9 and 20 degrees 2-Theta correspond to a size of 1 nm and are probably from the macromolecules of the amorphous polymeric part [19]. The particle size of the nano phase is calculated from the peak broadening of the narrow reflexes. The mean crystal size is calculated to about 15 nm. This particle size within the matrix is in excellent agreement with the PCS-measurements of the particle size distribution (PSD) in the feed dispersion (Fig. 1).

The quality of the encapsulated magnetite has been verified using Mössbauer- Spectroscopy of the spray dried powder. The measurements are performed at 80 K and show the characteristic sextets [20] of magnetite. Further it can be stated from the measurements that although the particles seem to interact, they still show superparamagnetic properties.

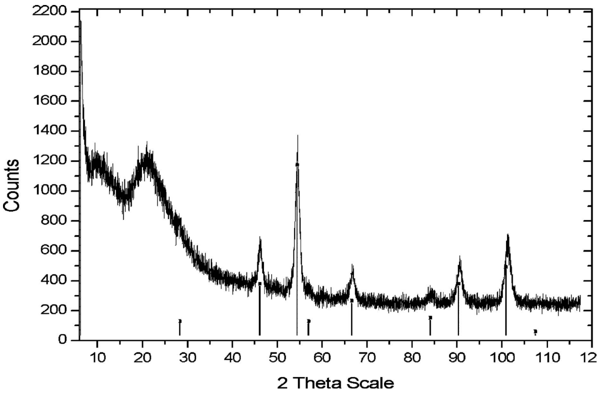


Figure 4 XRD-spectrum of highly filled PMMA. The particle size of the nano phase is calculated from the peak broadening of the narrow reflexes. The mean crystal size is 15 nm. The excellent accord with the reference peaks (International Centre for Diffraction Data, ICDD) indicates that the precipitated magnetite is very pure.

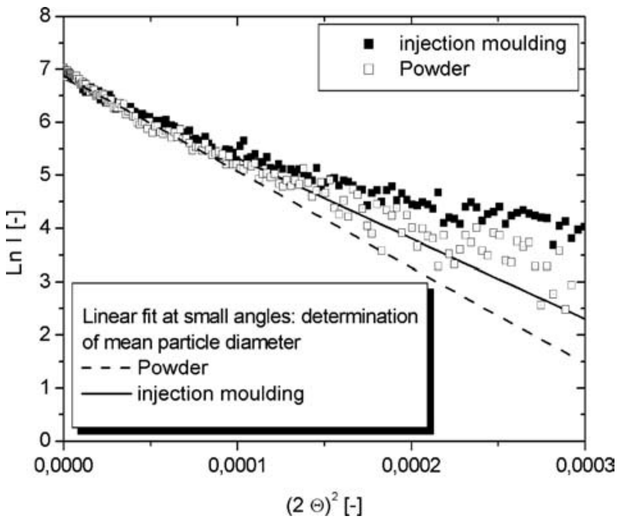


Figure 5 SAXS scattering graph of a composite before and after injection moulding. The weight fraction of magnetite is 22.8 mass-%. The measured diameters are 13.2 nm (injection moulding) and 14.5 nm (powder).

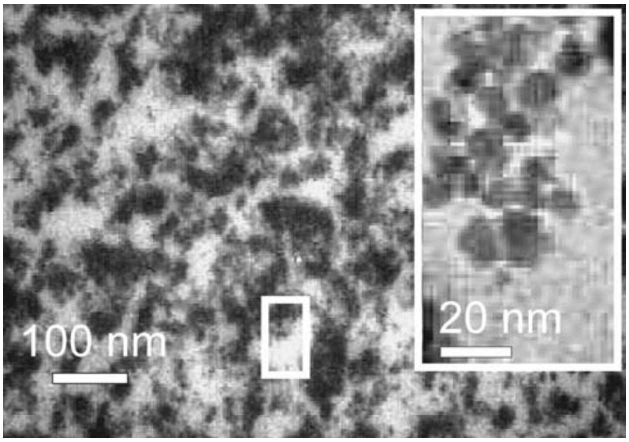


Figure 6 Transmission Electron Micrograph (TEM) for a highly filled magnetite/PMMA nanostructure. An ultra thin layer of Oleic acid keeps the nano particles at distance. This is a basic requirement for a high saturation magnetization and a low remanence.

3.3. Properties of the structural part

The reliability and resolution of the PSD measurements using SAXS is higher compared to XRD. The scattering graph of a composite powder and a tensile bar prepared by injection moulding is plotted in Fig. 5. The mean weight fraction of magnetite amounts to 22.8 mass-% for both samples. The mean particle size can be calculated from a linear fit at very small angles [21]. The result is a measured diameter of 13.2 nm (injection moulding) and of 14.5 nm (powder) after spray drying. The difference can be ascribed to the precision of measurement caused by scattering of remaining air molecules in the sample tube or of the polymer itself. The excellent aggreement between XRD, SAXS and PCS measurements indicates that the dispersion of the magnetite remains stable and constant through all processing steps: mixing, spray drying, injection moulding.

A visualization of particle distribution can be archived by TEM. Highly filled composite structures are not translucent for electron beams any longer. Therefore very thin slices of 60–200 nm (depending on the filling degree) have been prepared. Fig. 6 reveals a high structural homogeneity of magnetite in a tensile bar.

A moderate tendency of segregation which is attributed to a melt flow inside the moulding machine can be seen. The cut-out admits a more detailed view on the nano particles. It can be turned out so that even if the particles tend to agglomerate a thin layer of Oleic acid keeps them at distance. This fits with the Mössbauer results, which show a certain interaction of the magnetic fields of the magnetic particles not being strong enough to produce magnetic remanence. The distance between the particles is the is a basic requirement for a low relative remanence.

The main aim of the material and process development is excellent magnetic properties. The most important parameter is the high saturation magnetization M_s which should be close to the properties of bulk magnetite. Furthermore, a low relative saturation remanence ($m_r = M_r/M_s$) is required. The low M_r/M_s ratio signifies a reversible hysteresis loop and thus super-paramagnetic behavior. A crucial point is a possible degradation of the magnetic properties during injection moulding. Fig. 7 shows the hysteresis loop of the precursor powder and the tensile bar. In both cases the magnetite content amounts to 22.8 mass-%. The plot of both curves shows an identical progression. The relative remanence amounts to $m_r = 0.02$ in both cases, which is a very low value.

Both the polymer encapsulated particles and the constructional part are definitely super-paramagnetic. The saturation magnetization of the composite material amounts to 18.83 Am^2/kg. The corresponding value of bulk magnetite itself amounts to about $M_s = 89$ Am^2/kg [11]. Taking into account the mass fraction of 22.8 mass-%, the saturation magnetization of the magnetite within the composite material can be calculated to $M_s = 82.59$ Am^2/kg, which is fairly close to the saturation

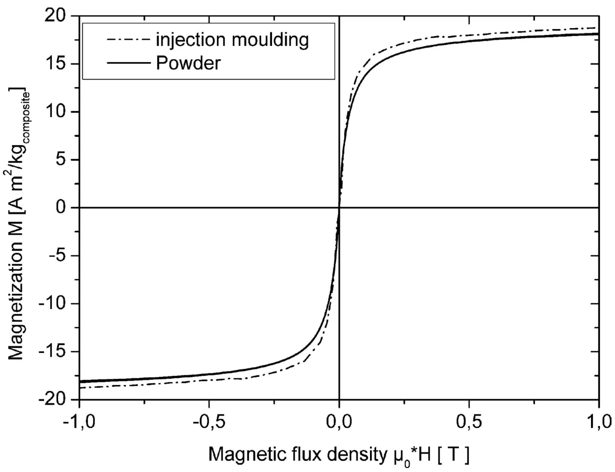


Figure 7 Magnetization curve of a nanocomposite with 22.8 mass-% magnetite before and after injection moulding. The material is definitely super-paramagnetic.

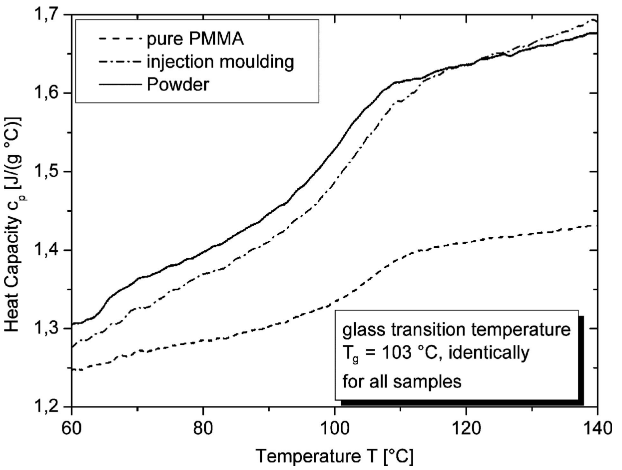


Figure 8 DSC measurements in order to determine the influence of Oleic acid on thermal stability. The glass transition temperature of $T_g = 103°C$ is constant for all samples that have been prepared. Hence the content of encapsulated Oleic acid is apparently too low to affect the thermal stability.

magnetization of bulk magnetite. The loss of magnetization is comparatively low if it is taken into consideration that the used magnetite is in the nanoscale. This indicates that the spray drying method is almost mild: No oxidizing initiator fragments that degrade the filler to non-magnetic iron oxides such as Fe_2O_3 are present within the organic magnetic fluid.

Another important question is the encapsulation of Oleic acid into the polymer matrix and its influence on the bulk properties. In order to provide a composite material with unaltered mechanical and thermal properties the amount of encapsulated surfactant should be as low as possible. Therefore differential scanning calorimetry (DSC) measurements have been performed to determine the glass transition temperature. The influence of surfactant becomes visible by comparing pure PMMA with the composite powder and injection moulded samples. The inflection point defines the glass transition temperature T_g. It is equivalent for all samples (PMMA, composite powder, tensile bar). The measurements indicate a T_g of 103°C which complies with the literature [22].

4. Conclusions

It is shown that the encapsulation up to 50 mass-% of nano scale magnetite particles into a PMMA carrier material is possible using the solution method. The material retains the super-paramagnetic properties of the filler.

The experimental set up consist of a spray dryer that processes an organic feed flow containing dissolved PMMA as a carrier material and suspended nano magnetite as dispersed phase. The crucial step is the stabilization of the ferrofluid. The feed flow is atomized into small droplets and dried within split seconds. No segregation process can be observed. The magnetite particles stay well separated from each other, kept at distance using Oleic acid as a surfactant. The process yield is a filled or highly filled composite powder with excellent magnetic properties. It can be further processed using conventional polymer processing equipment. Comparative SAXS and AGM/VSM studies point out that through further treatment the structural and magnetic properties remain constant and no quality loss occurs.

The positioning of nano particles within the composite powder material can be controlled by adjusting the concentration of Oleic acid. An excess of surfactant deposits more nano particulate filler onto the polymeric surface. This opens an additional field of application for the composite powder when using the nano particles as catalytic support.

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