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Chemical Engineering Research and Design

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# Effect of solvent exchange on the stability of sterically functionalized magnetite nanoparticles in poly(methyl methacrylate) solutions and resulting spray dried composites

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## ABSTRACT

In this study highly filled nanoparticle–polymer composites consisting of the polymer poly(methyl methacrylate) and magnetite nanoparticles are synthesized via the solution and spray drying method. The synthesis process is carried out for two different solvents, dichloromethane and ethyl acetate, and the resulting suspensions and composites are compared to each other. The preparation of the composites consists of the following steps: First the magnetite nanoparticles are precipitated in an aqueous phase. In the next step the nanoparticles are coated with ricinoleic acid for stabilization and are transferred to the organic solvent dichloromethane. In a rotating evaporator the solvent dichloromethane is exchanged with ethyl acetate. Finally, the nanoparticles in the respective solvent and dissolved polymer are mixed and spray dried.

The stability of the nanoparticle suspensions is characterized using thermogravimetric and photometric analyses. The specific surface of spray-dried composites is determined via BET measurements and the distribution of the nanoparticles is assessed with BSE-SEM imaging and laser diffraction.

The stability of the nanoparticles is independent of the examined solvents. Both solvents provide a homogeneous distribution of nanoparticles in the composite at high filler concentrations.

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**Keywords:** Polymer nanocomposites; Spray drying; Magnetite nanoparticles; Solvent; Ethyl acetate; Dichloromethane

## 1. Introduction

Nanoparticle–polymer composites nowadays have a wide range of industrial applications, e.g. biomedicine, pharmacy, electronics, ceramics, etc. (Iskandar et al., 2003; Schwarzer and

Peukert, 2002; Zhou et al., 2001). These composites consist of a polymer matrix in which a nanoparticulate filler is dispersed (Banert and Peuker, 2005; Ciprari et al., 2006; Dallas et al., 2006). The presence of homogeneously distributed nanoparticles in a polymer matrix enhances certain properties of the material,

**Abbreviations:** BSE-SEM, back-scattered electrons-scanning electron microscope; EA, ethyl acetate; DCM, dichloromethane; PMMA, poly(methyl methacrylate); PSD, particle size distribution; RA, ricinoleic acid.

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Received 22 January 2013; Received in revised form 26 November 2013; Accepted 11 February 2014

<http://dx.doi.org/10.1016/j.cherd.2014.02.015>

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### Nomenclature

$a$	exponent
$\alpha$	empirical correction factor
$c_{\text{Poly}}$	concentration of polymer (g/l)
$c_{\text{Solid}}$	concentration of solids
$D_{1,2}$	solubility distance ( $\text{MPa}^{1/2}$ )
$D_{\text{RA}}$	surfactant ratio
$\Delta_{\text{RA}}$	surfactant concentration
$\delta_d$	dispersive interaction parameter ( $\text{MPa}^{1/2}$ )
$\delta_p$	polar interaction parameter ( $\text{MPa}^{1/2}$ )
$\delta_h$	hydrogen bonding interaction parameter ( $\text{MPa}^{1/2}$ )
$E_{600\text{ nm}}$	photometric extinction at 600 nm for the solution
$E_{0,600\text{ nm}}$	photometric extinction at 600 nm for the solvent
$F$	filling degree
$\eta$	solution viscosity ( $\text{m}^2/\text{s}$ )
$\eta_0$	solvent viscosity ( $\text{m}^2/\text{s}$ )
$\eta_{\text{sp}}$	specific viscosity ( $\text{m}^2/\text{s}$ )
$[\eta]$	intrinsic viscosity (l/g)
$K$	constant
$K_H$	Huggins constant
$\bar{M}_n$	number averaged molar mass (g/mol)
$\bar{M}_w$	mass averaged molar mass (g/mol)
$m_{\text{Magnetite}}$	mass of magnetite (g)
$m_{\text{polymer}}$	mass of polymer (g)
$m_{\text{RA}}$	mass of ricinoleic acid (g)
$m_{\text{Solvent}}$	mass of solvent (g)
$N_A$	Avogadro's number (1/mol)
$R$	universal gas constant (J/mol K)
$R_{\text{Coil}}$	radius of gyration of a polymer coil (nm)
$s$	span of the particle size distribution
$S_{m,\text{BET}}$	specific surface determined by BET ( $\text{m}^2/\text{g}$ )
$S_{m,\text{PSD}}$	specific surface determined by particle size distribution (PSD) ( $\text{m}^2/\text{g}$ )
$SP$	structural parameter
$T$	temperature ( $^{\circ}\text{C}$ )
$T_{\text{Evap}}$	evaporation temperature ( $^{\circ}\text{C}$ )
$T_{\text{In}}$	inlet temperature ( $^{\circ}\text{C}$ )
$V_1$	molar volume of the solvent ( $\text{cm}^3/\text{mol}$ )
$w_{a,600^{\circ}\text{C}}$	mass residue at $600^{\circ}\text{C}$ for untreated sample (g)
$w_{b,600^{\circ}\text{C}}$	mass residue at $600^{\circ}\text{C}$ for centrifuged sample (g)
$w_{\text{Primary}}$	amount of primary particles
$x_{10}$	10% quantile of the particle size distribution ( $\mu\text{m}$ )
$x_{50}$	50% quantile of the particle size distribution ( $\mu\text{m}$ )
$x_{90}$	90% quantile of the particle size distribution ( $\mu\text{m}$ )
$\chi_{1,2}$	Flory interaction parameter

such as mechanical, magnetic, electric or optical properties (Castrillo et al., 2007; Dallas et al., 2006; Gyergyek et al., 2008; Kirchberg et al., 2012; Rudolph et al., 2012b; Rudolph and Peuker, 2011). The main problem during processing is to prevent the nanoparticles from agglomeration or aggregation for the interactions between the nanoparticles are predominantly attractive and relatively strong due to their small size (Banert

and Peuker, 2006; Castrillo et al., 2007; Kirchberg et al., 2012; Rudolph et al., 2012a; Rudolph and Peuker, 2011).

Several methods for the synthesis of nanoparticle-polymer composites have been developed to avoid this problem: the nanoparticles and the polymer are synthesized separately and mixed afterwards in a melt or solution, the nanoparticles are synthesized in a polymer matrix, or the polymer is polymerized around the nanoparticles (Castrillo et al., 2007; Darwish et al., 2011; Gyergyek et al., 2008). However, many of these methods provide only an insufficient level of dispersion of the nanoparticles at high filling degrees (Banert and Peuker, 2006; Gyergyek et al., 2008; Rudolph and Peuker, 2011).

A straightforward method for the synthesis of highly filled composites is the solution and spray drying process introduced by Banert and Peuker (2005). In this method the polymer and the nanoparticles are introduced in a solvent in which the polymer is soluble and the nanoparticles can be well dispersed due to the low viscosity of the system. The aggregation of the nanoparticles is inhibited by adsorbed molecules which provide steric stabilization (Rudolph and Peuker, 2011, 2012c). The dispersed status of the nanoparticles is preserved by the fast evaporation of the solvent in a spray dryer (Gyergyek et al., 2008).

In this study nanoparticle-polymer composites consisting of the polymer poly(methyl methacrylate) (PMMA) and magnetite nanoparticles are synthesized via the solution and spray drying method. The addition of magnetite nanoparticles to a polymer provides superparamagnetic properties (Banert and Peuker, 2007; Gyergyek et al., 2008; Kirchberg et al., 2012; Rudolph et al., 2012a, 2012b). In the existing process chain dichloromethane (DCM) and ethyl acetate (EA) are used as solvents in order to generate comparable results and to test whether the less noxious EA can replace the highly volatile and hazardous DCM in the spray drying process.

The process chain for the synthesis of nanoparticle-polymer composites using the solution and spray drying method consists of the partial stages: precipitation, phase transfer, (exchange of the solvent) and spray drying (see Fig. 1).

The synthesis of the magnetite nanoparticles is achieved in a co-precipitation reaction of iron salts in an aqueous phase. Subsequently the nanoparticles are transferred from the aqueous to the organic liquid dichloromethane by liquid-liquid phase transfer and are sterically stabilized through the adsorption of ricinoleic acid at the interface (Banert and Peuker, 2006, 2007; Rudolph et al., 2012a). A new process stage is developed to exchange the solvent. It is not possible to transfer the precipitated nanoparticles directly into ethyl acetate for this solvent is slightly water soluble. Therefore, the exchange of solvents is realized in a rotating evaporator. Subsequently, the nanoparticles and the solved polymer are mixed and spray dried.

## 2. Materials and methods

### 2.1. Materials

The synthesized composites consist of poly(methyl methacrylate) (PMMA) and magnetite nanoparticles. The polymer PMMA with the trade name Diakon CLG902 is supplied by Lucite (Kirchberg, 2011; Rudolph and Peuker, 2011). The nanoparticles are synthesized by co-precipitation and stabilized by ricinoleic acid (RA) with technical quality from

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