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Synthesis of polyamide-imide-montmorillonite-nanocomposites via new approach of *in situ* polymerization and solvent casting

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ABSTRACT

Due to the inherent importance of nanostructuring in coatings the present article provides a new approach for exfoliation of montmorillonite via *in situ* polymerization in comparison to solvent casting method. The new *in situ* polymerization with PAI was realized by swelling MMT's intergallery with *p*-chlorphenole blocked 4,4′-methylene diphenyl diisocyanate and 1,2,4-benzenetricarboxylic acid anhydride followed by polymerization within MMT's intergalleries. XRD-measurements and SEM analysis at cross-sections revealed nanocomposites with exfoliated sheet structure up to 2.0 wt% MMT while for solvent casting 1.2 wt% was determined as limiting concentration. Therefore, this novel approach provides synthesis of higher concentrated exfoliated PAI-MMT-nanocomposites. Despite its disadvantage in lower limiting concentration, when it comes to application, the solvent casting method turned out to be superior to *in situ* polymerization as it is much faster and economically more feasible.

1. Introduction

Polymer-based nanocomposites describe a class of particle-filled polymer systems where at least one dimension of dispersed particles is in nanometer range. In nanocomposites of exfoliated layered silicate the sheets are present in range of one to a few nanometers in thickness and several nanometers to microns in lateral dimensions resulting in extraordinary large particle–polymer–surfaces [1]. In comparison to conventional micron-sized filled composites, nanocomposites of exfoliated layered silicate show extraordinary improvements. This includes a higher modulus, increased mechanical strength and heat resistance, decreased gas permeability and flammability [2–4]. Main reason for improved properties in nanocomposites is a stronger interfacial interaction between the polymer matrix and layered silicate, compared with conventional filler-reinforced systems [5]. The polymer matrix chosen for this study is polyamide-imide (PAI) which is known for its outstanding thermal performance, chemical and abrasion resistance and low coefficient of friction [6]. PAI merges both greater mechanical properties typically linked with polyamide and the high thermal stability and solvent resistance derived from polyimide. These properties enable PAI's general use as insulation coatings, for e.g. magnet wires, foils and circuit boards. Polyamide-imide can be obtained from several strategies of synthesis. The commercial routes are the acid chloride and the diisocyanate route. At the acid chloride route reaction between trimellitic acid chloride and an aromatic diamine yields in formation of a poly(amideamic acid). The formation of imide structures is obtained either due to dehydration of the acid intermediate, addition of tertiary amines or anhydrides [7–9]. The diisocyanate route used in this study based on the work of Hitachi Chemical Corp. [6] and is today most common for preparation of PAI resins. On this occasion, a polyisocyanate, preferably a diisocyanate, reacts under heat with 1,2,4-benzenetricarboxylic acid anhydride (TMA) in N-methyl pyrolidone (NMP). The synthesis is performed stepwise. At the initial reaction temperature of 80 °C 4,4′-methylene diphenyl diisocyanate (MDI) and the anhydride group of TMA form a carboxylic acid ended polyimide oligomer [10]. At the second stage around 120 °C amide groups are formed from the condensation of acid groups with the rest of MDI which combines the polyimide oligomers through the formation of amide and increases the overall molecular weight [10]. The PAI structure obtained by diisocyanate route has been characterized extensively by NMR techniques [11–13]. Statistical distributions of imide–imide, amide–imide, and amide–amide linkages were observed.

The layered material chosen for this study was 2:1 layered silicate montmorillonite (MMT). The crystal structure of MMT is defined by two tetrahedral sheets of SiO_4^{2-} and one sheet containing octahedral coordinated Al^{3+} ions. Substitution of Al^{3+} with Mg^{2+} results in overall negatively charge of the layered silicate and

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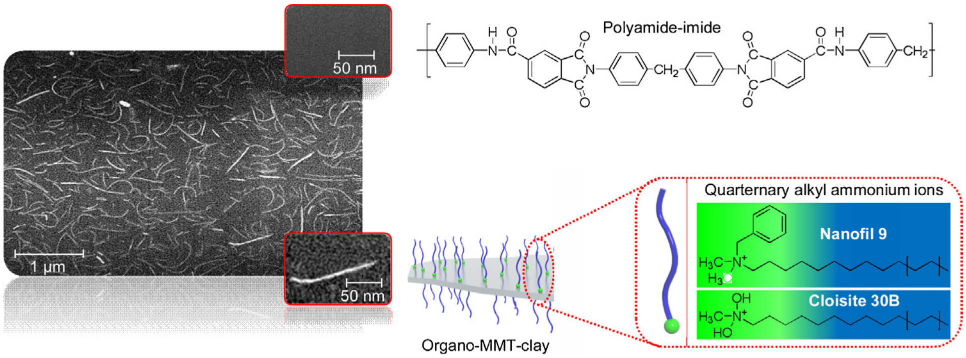

Fig. 1. SEM image of FIB prepared cross section of the PAI matrix (dark) containing exfoliated MMT sheets (white).

is counterbalanced by alkali and alkali earth cations located inside the galleries.

In this study, we focus on the synthesis of nanocomposites consisting of exfoliated montmorillonite particles in a polyamide–imide matrix (Fig. 1).

The MMT used in this study are modified by ion exchange with cationic quaternary alkyl ammonium ions in order to process these particles in organic matrices. This chemical treatment lowers MMT's surface energy and improves its wetting characteristics to the polymer matrix [5].

In order to obtain exfoliated states of particles, we focus in this article on new approaches of synthesis via *in situ* polymerization and solvent casting method.

At *in situ* polymerization the layered silicate is swollen within either a liquid monomer or a monomer solution followed by performing the polymerization within interlayer galleries of MMT. This approach is common and has been conducted for several polymer system, except for PAI [14–16]. For the diisocyanate route of PAI-polymerization there is the problem of high reactivity of the isocyanate monomer. During swelling process, it would undergo a reaction with the acid anhydride even at low temperatures. The strategy of the present work was to solve this problem by protection of the –NCO groups. The challenge for the protection agent is the requirement of a very low deblocking temperature below 80 °C in order to enable the first reaction step imide oligomer formation. Our concept to realize *in situ* polymerization via protection of MDI was inspired by works of Ho and Chen [10,17]. They investigated a PAI synthesis derived from *p*-chlorphenole-blocked MDI. This method was adapted to enable swelling MMT with MDI and TMA simultaneously and subsequent TBA catalysed polymerization within MMT intergalleries in order to achieve exfoliation of the stacked MMT structure.

The solvent casting method is based on swelling MMT intergalleries with solvent where the polymer is soluble and was first investigated by Aranda and Ruiz-Hitzky [18]. Mixing of polymer and layered silicate solutions results in intercalation of polymer chains and displace the solvent within the interlayers of silicates and is described as an entropy driven process. As it was shown by Ranade et al. exfoliated PAI-MMT-composites can be obtained via solvent casting method by premixing MMT with xylene followed by adding to a PAI solution. Exfoliated composites were obtained until a limiting MMT concentration of about 1.0 wt% [19]. The strategy of solvent casting in this study bases on the solely usage of NMP for the swelling process which is also solvent of the PAI solution.

To conclude, synthesis of exfoliated PAI-MMT-nanocomposites via *in situ* polymerization and solvent casting method was evaluated.

2. Experimental

2.1. Reagents and materials

Polyamide-imide was synthesized via diisocyanate route with 1,2,4-benzenetricarboxylic acid anhydride (TMA, 97%, obtained from Sigma-Aldrich) and 4,4′-methylene diphenyl diisocyanate (MDI, 98%, obtained from Sigma-Aldrich) in N-methyl pyrolidone (NMP) as solvent. For *in situ* polymerization MDI was blocked with *p*-chlorphenole (PCP, 98%, obtained from Merck) in toluene. Tri-*n*-butyl amine (TBA, 98.5%, obtained from Sigma-Aldrich) was used as catalyst for blocking and deblocking reaction.

Two different MMT's were chosen for synthesis of nanocomposites. These are methyl tallow bis-2-hydroxyethyl ammonium (Cloisite 30B, C30B, Byk Chemie, obtained from Nordmann, Rassmann GmbH) and dimethyl-benzylhydrogenated tallow quaternary ammonium (Nanofil 9, NF9, Byk Chemie, obtained from Nordmann, Rassman GmbH).

HDG zinc-coated steel was obtained from Voestalpine. The reagents and materials used in this study were applied without further purification.

3. Synthesis of PAI

TMA (327.98 g, 1.71 mol) and NMP (741.50 g) were added to a 2 L four-necked glass reactor under purging nitrogen gas and heated to 60 °C. The mixture was stirred until TMA was completely dissolved. Then the mixture was cooled down to 40 °C followed by addition of excess MDI (430.08 g, 1.72 mol). The reaction temperature was increased stepwise from 40 to 65, 75, 95 and finally to 130 °C and was kept for 30 min at every step. During the reaction from 80 to 130 °C large amounts of CO_2 development were observed. A highly viscous dark red to brown solution of PAI was obtained. The reaction scheme for this synthesis is provided in Fig. 2.

4. In situ polymerization

4.1. Blocking of MDI

The blocking reaction of MDI with PCP was performed according to Chen and Ho [17]. MDI (60 g, 0.24 mol) was dissolved in 500 mL toluene at room temperature. Excess PCP (46.23 g, $n(\mathrm{PCP}){:}n(\mathrm{MDI}) = 1.5$) was added and stirred until it was completely dissolved. After addition of 10 drops of TBA, the formed b-MDI started to precipitate. Subsequently, the temperature was increased to 40 °C and kept for 24 h. The product was filtered and washed with toluene followed by drying at 120 °C for 12 h. The dry *b*-MDI (Fig. 3) was processed via mortar in order to obtain a powder.