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Encapsulation of inorganic filler particles by emulsion polymerization

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Introduction

The mechanical and rheological properties of filled composites are influenced by the filler content, the filler characteristics and the chemical character of the components. The polymer/filler interaction also has a considerable effect on these properties. This interaction depends on the size of the interacting surfaces and the strength of binding. Conditions for an optimum interaction are, for instance, the homogeneous distribution of the filler in the polymer matrix, and the existence of a polymer layer on the inorganic filler particle surface with a defined thickness and structure.

It has been suggested that emulsion polymerization in the presence of inorganic particles is able to produce such an ideal polymer-filler system^{1,2,3,4,5}. The powder surface may be covered with polymer regardless of the type, shape, or size of the particles, as long as suitable reaction conditions are selected.

Hasegawa^{1,2,3} treated the inorganic particles with surfactant prior to the emulsion polymerization. When surfactant was added at a concentration below its critical micelle concentration, a large number of polymerization loci were formed on the surface of the powder. Hasegawa indicated that ionic surfactants were more effectively in covering the surface than nonionic surfactants. He also found that the encapsulation state of the powder with polymer formed, varied considerably with the initiator system used.

Hergeth^{4,5} concluded, just like Hasegawa, that the polymerization reaction took place in a surface layer around the inorganic particles. Hergeth says that this reaction locus is favoured through adsorption of monomer at the particle surface, which results in a very high monomer concentration in the vicinity of the particles compared with a limited concentration in the bulk dispersion medium.

In this work CaCO_3 particles are treated with titanates to make the surface hydrophobic and more accessible for monomer, before emulsion polymerization. Adsorption of an additional surfactant layer will create a bilayer on the surface of the CaCO_3 particles. The surfactant concentration is kept below its critical micelle concentration to minimize the possible formation of free polymer in the waterphase. If polymerization proceeds in the bilayer the CaCO_3 particles would be uniformly covered with a polymer layer.

Polymerization reactions of styrene were carried out in the presence of CaCO_3 particles modified with titanate. Electron micrographs taken from the reaction products showed that the modified particles were covered with polymer. The amount of encapsulating polymer in the isolated product was determined by Thermo Gravimetric Analysis (TGA). 80 % of the polymer in the product was extracted with toluene and its molecular weight (M_w) was determined by Gel Permeation Chromatography (GPC).

Experimental

The encapsulation process is generally performed in 2 steps. The first step involves modification of the filler in order to make the mineral surface hydrophobic. This modification is carried out with watersoluble titanates. The second step is a batch emulsion polymerization with the modified filler dispersed in the waterphase.

(1) Filler modification

The filler used so far in this work is CaCO_3 with a mean diameter of $1 \mu\text{m}$ and a specific surface of $7 \text{ m}^2/\text{g}$. CaCO_3 was dispersed in water and treated with the watersoluble alkanolamine titanate (Tilcom AT52, Tioxide chemicals). Physical adsorption was accomplished by hydrogen bonding between hydroxy groups of the titanate and hydroxy groups present on the surface of CaCO_3 . An adsorption isotherm was obtained by mixing 1 gram of CaCO_3 in 50 ml water with different concentrations of titanate. The amount of adsorbed titanate after centrifugation and drying was determined by TGA.

(2) emulsion polymerization

The polymerization reactions were carried out in a 300 ml thermostatted reactor with baffles and a gate paddle. A typical polymerization recipe with filler particles is shown in table 1

Filler (CaCO_3 , $d = 1 \mu\text{m}$)	20.0 g	(90.9 gr/l)
Monomer (Styrene)*	10.0 g	
Water	220 ml	
Titanate (AT52)	1.8 g	(7 wt% of CaCO_3)
Surfactant (Sodium dodecyl sulphate, SDS)	0.33 g	(5.2 mM)
Initiator (4,4'azo-bis-(cyanopentanoic) acid, ABCA)	0.5 g	(8.1 mM)
* monomer/water = 0.045		

Table 1: Typical polymerization recipe with filler particles

First the CaCO_3 was dispersed in the waterphase to which the titanate was added. The dispersion was thoroughly mixed by using an Ultra Turrax mixer. This dispersion was then added to the reactor and flushed with nitrogen to remove oxygen. This was followed by the addition of styrene and sodium dodecyl sulphate (SDS) as surfactant. Reaction temperature was set at 60°C and the gate paddle at a stirring speed of 250 rpm. Finally the reaction was started with the addition of 4,4'-azo-bis-(cyanopentanoic) acid as the initiator. After 7 hours of reaction time the reaction was stopped and the slurry was separated by centrifugation. After the first separation the product was washed several times with soap by repeated centrifugation steps. Finally the product was dried in a vacuum stove.

Extraction of the polymer was performed by stirring 4 grams of product in 50 ml toluene at 25°C for 24 hours. The toluene phase was separated from the solids of the dispersed phase by centrifugation. The solids were redispersed in 50 ml toluene for a second extraction step taking 48 hours.

Results and discussion

(1) Filler modification

The weight loss detected by TGA is equal to the adsorbed amount of titanate and some surface water of the CaCO_3 . A blank TGA-measurement of pure CaCO_3 gave a weight loss of 0.86 wt% due to this surface water. The blank value was therefore subtracted from the weight loss measured for the modified CaCO_3 samples. The values of adsorbed titanate were plotted versus the added amount of titanate, resulting in the adsorption curve in figure 1. The added amount of titanate is expressed in terms of weight percentages relative to the unmodified CaCO_3 . As can be seen in this figure, a plateau is reached for 20 wt% added titanate. The according amount of adsorbed titanate equals 1.35 wt%. A monolayer coverage of the titanate is probably accomplished at this value. In the polymerization reactions only 7 wt% titanate was added to the CaCO_3 , which will not have produced a monolayer on the surface of the CaCO_3 .

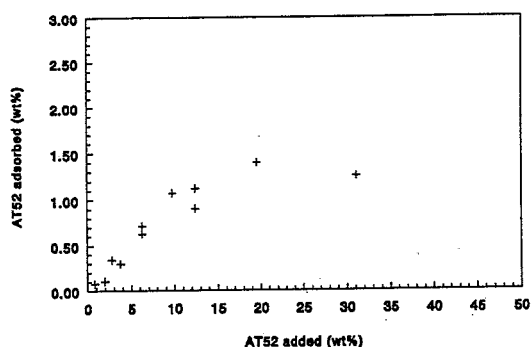


Figure 1: Adsorption isotherm for an alkanolamine titanate (ATS2) on CaCO_3

(2) Emulsion polymerization

Thermogravimetical Analysis

Figure 2 shows a TGA-plot for pure CaCO_3 (black line) and for one of the products (dotted line).

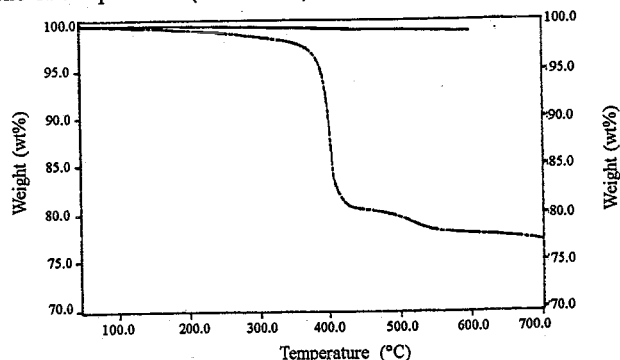


Figure 2: Thermo gravimetical analysis plot for CaCO_3 before and after polymerization

The difference between these two curves is obvious. Because decomposition of CaCO_3 does not occur below 700°C , the weight loss in the TGA plot for the product is ascribed to the formed polymer and is defined as $[\text{polymer weight (g)} / \text{product weight (g)}] * 100\%$. Unknown amounts of surfactant and titanate may be incorporated in the formed polymer. The measured weight loss in figure 2 is 22 wt%. Other polymerization reactions gave values between 20 and 30 wt% of formed polymer in the reaction product. In terms of conversion 20-30 wt% of polymer is equivalent to 60-90 % conversion. That means 60 to 90 % of the monomer is found as polymer on the surface of CaCO_3 .

Extraction of encapsulating polymer

According to the GPC results the first extraction step dissolved polymer with a molecular weight M_w of 1900 kg/mol and a dispersity M_w/M_n of 5.2. The second extraction step gave polymer with a M_w of 1780 kg/mol and a M_w/M_n of 6.7. TGA of the product after extraction revealed that polymer was still present in the product. A weight loss of 6.2 wt% was detected, which means that 80 % of the originally encapsulating polymer was removed by extraction with toluene. The remaining 20 % polymer is tightly bound to the surface of CaCO_3 .

Transmission Electron Microscopy (TEM)

Transmission electron micrographs were taken from the polymerization products. On these micrographs polymer could be seen on the surface of CaCO_3 crystals. A great part of the crystal surface was covered with a layer of polymer particles.

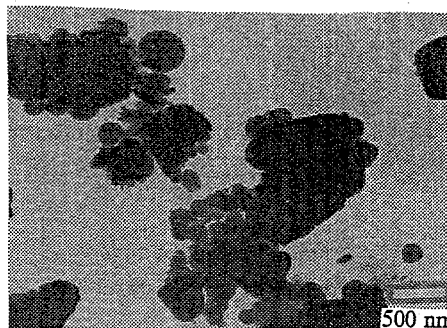


Figure 3: Electron micrograph of a polymerization reaction with modified CaCO_3 .

Also separate spherical latex particles were present free from the surface of the CaCO_3 particles. This points at free polymer formed in the waterphase during the polymerization reaction, which was not removed through centrifugation of the product. This could be due to an electrostatic interaction between the free latex particles and the CaCO_3 surface. Micrographs of products, which were polymerized with unmodified CaCO_3 clearly showed that there was far less polymer at the surface and more free polymer in the waterphase.

The bilayer formed with the titanate- and the surfactant layer promotes polymerization at the surface. As soon as primary particles are formed in the waterphase, they will be adsorbed by the CaCO_3 surface. So, in an early stage of polymerization the locus of polymerization will shift from the waterphase to the surface of CaCO_3 , resulting in a surface layer consisting of small particles.

Conclusions

The experimental results indicate that the CaCO_3 particles were covered with a polymer layer, consisting of small particles. Electron micrographs revealed that besides encapsulating polymer, free latex particles were still present in the product. A complete separation of encapsulating polymer from free polymer was therefore not achieved through centrifugation and washing with surfactant. When unmodified CaCO_3 was used in the polymerization reaction, much more free polymer was formed in the waterphase than when CaCO_3 modified with titanate was used. The existence of a bilayer of titanate and surfactant on the CaCO_3 promotes polymerization at the surface. In an early stage of the reaction the locus of polymerization will shift from the waterphase to the surface of CaCO_3 .

Extraction of the polymer in the product with toluene in 2 steps, removed 80 % of the encapsulating polymer from the surface of CaCO_3 . The remaining 20 % polymer is tightly bound to the surface of CaCO_3 . The molecular weights (M_w) of the dissolved polymer in the first and the second extraction step were about the same; 1900 kg/mol ($M_w/M_n=5.2$) and 1780 kg/mol ($M_w/M_n=6.7$) respectively.

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