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Synthesis of imidized nanoparticles containing soy oil under various reaction conditions

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ABSTRACT

The imidization of poly(styrene-*co*-maleic anhydride) nanoparticles in presence of soy oil was studied, resulting in the formation of nanoparticles with 20–80 nm diameter with a porous structure allowing to incorporate 50 wt.% soy oil. The reaction efficiency strongly depends on the amount of ammonium hydroxide as imidizing agent, which ratio was varied between 1.01 and 1.60 relatively to the maleic anhydride moieties. Finally, stable aqueous dispersions are obtained with a higher solid content and somewhat higher Zetapotential compared to purely imidized nanoparticles. There are concurring reactions between imidization and coupling of the unsaturated double bonds in soy oil to the ammonolysed maleic anhydride. Therefore, a large amount of non-embedded oil was only observed when the imidization is favoured under high concentrations of ammonium hydroxide. Using spectroscopy and thermal analysis, it is concluded that a complex organized nanostructure is formed between the poly(styrene-*co*-maleimide) and soy oil, which results in a suppression of T_g evaluated by (temperature-modulated) differential scanning calorimetry.

1. Introduction

New bio-based materials are extensively being developed as an answer to depleting fossil oil resources. Vegetable oils are favorable candidates as alternative feedstock for synthesis of renewable polymers [1]. For industrial applications, soybean oil is most abundant and cheapest in North and South America, whereas rapeseed oil is most abundant in Europe and palm oil mostly present in Asian countries. The processing of soybean oil has benefits in various industries [2]. Different criteria for selecting vegetable oil resources include their stability and reactivity. Most vegetable oils are triglycerides with several chemically active sites such as double bonds, ester bonds and allylic positions for polymerization [3]. For traditional polymer synthesis, the double bonds are used in chemical reactions such as, e.g., epoxidation and acrylation [4,5], transesterification [6], and formation of alkyd resin [7], typically used for paints and coatings that easily react further with maleic and phthalic anhydride [8]. Due to the high iodine value of soy oils (I.V. = 115–130), they have good reactivity and are classified as drying oils for the formulation of coatings polymerized by oxidation. On the other hand, their oxidative stability is inferior to more saturated oils and they should likely be protected against oxidative degradation [9]. One route providing protection lies in the encapsulation of the oil in a body with good chemical and thermal

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stability. Therefore, the encapsulating polymer is required to have good chemical resistance and high glass transition temperature to prevent weakening. In addition, for further processing of the encapsulated oil as hydrophobic agent under economic and ecological conditions, the materials should preferentially be available in stable and neutral aqueous environment without leaking.

The encapsulation of vegetable oils within a host polymer is a way for creating functional soft materials [10]: e.g., controlled release or transport of the encapsulated agents and eventually oil-soluble dyes can provide those compounds with active properties [11]. The liquid-core capsules can be formulated at the microscale by chemical processes (interfacial polycondensation, in-situ polymerization), physico-chemical routes (coacervation) or mechanical processes (droplet formation) [12]. Different polymers have been used for microencapsulation of vegetable oils, including HDPE [13], styrene–butadiene-styrene copolymers [14], polyurethane [15], ethylcellulose [16], and chitosan, starch or alginates [17–19]. However, commodity polymers and bio-based materials often have limited thermal stability. The formation of nanocapsules is often based on phase separation in mini-emulsion polymerization [20], micellar assembly of block copolymers [21], layer-by-layer adsorption of polyelectrolytes [22], polymer brush grafting [23], or dendrimer synthesis [24]. Vegetable oils have been used as core materials in cationic polymeric nanocapsules [25], but the use of appropriate surfactants remains generally required. Nanocapsules with soy oil have been alternatively formulated as stable colloids through nanoprecipitation of chloroaluminum phthalocyanine: although the encapsulation efficiency was 70%, low concentrations of soybean oil up to 2.5% (v/v) were used [26]. Otherwise, several techniques for preparing oil-in-water nano emulsions have been applied [27]. As alternative shell materials, poly(styrene-*co*-maleic anhydride) or SMA may be beneficial due to its functionality and chemical reactivity: it has a carboxyl oxygen able to interact with fatty acid groups [28], while some grades may self-organize into spherical aggregates due to their specific heterogeneous molecular structure [29]. Based on the reactivity of the fatty acids, maleination has been frequently used for the cross-linking of vegetable oils [30]. The SMA was previously used to form microcapsules from acetate or dodecanol by interfacial polyaddition with amines [31], by hydrolysis and surfactant synthesis with octadecane [32], or complex coacervation with gelatin [33]. On the other hand, the imidization of pure SMA results in nanosphere dispersions with good chemical stability and high glass transition temperatures of around 180 °C [34]. In following experiments, the imidized nanospheres could be an excellent host for protecting soy oils as encapsulating agent and simultaneously provide a flexible way to form nanocapsules.

In order to stabilize and embed soy oil with poly(styrene-*co*-maleimide) nanoparticles, insight on the influences of reaction conditions should to be obtained. In particular, the ammonium hydroxide plays a critical role in the ammonolysis of the maleic anhydride [35], while side reactions in presence of oil may dominate the synthesis. Moreover, the morphology of the obtained nanoparticles is expected to strongly alter with amount of reactant. In this work, these influences will be characterized to finally better control the formation of hybrid nanoparticles with soy oil. In later applications, we tend to use them as hydrophobic carriers, coating pigments, or nanocontainers for lubrication with controlled release.

2. Experimental details

2.1. Materials

Refined soy-oil (SO) was received from Cargill Agricola S/A (Mairinque, SP, Brazil). The oil composition and physical properties were previously characterized by spectroscopy [36], and thermal analysis [37]: it has a iodine value I.V. = 122 g(I_2)/100 g oil, peroxide value = 2.7 meq/kg, saponification value = 195 mg (KOH)/1 g oil and acid value <1. As a polyunsaturated oil, it contains 61% polyunsaturated fatty acids, 25% mono-unsaturated fatty acids and 14% saturated fatty acid.

A high-molecular weight copolymer of poly(styrene-*co*-maleic anhydride) (SMA) with molecular weight M_w = 80,000 g/mol and 26 mol-% maleic anhydride (MA) was provided by Polyscope (Geleen, The Netherlands) and used as pulverized pellets. Ammonium hydroxide was obtained from Belgocare (Niel, Belgium) as a 25% aqueous solution (0.9 g/ml).

2.2. Synthesis protocol

The hybrid nanoparticles were synthesized in a 1 l autoclave with oil-heated walls and anchor stirrer. Different reaction compositions were applied, incorporating a fixed ratio SO:MA = 1:1 (wt.%) and various concentrations of ammonium hydroxide relatively to the maleic anhydride (MA) with increasing ratios of 1.01, 1.15, 1.30, 1.50 and 1.60 NH_3:MA (wt.%) : e.g., about 212 g SMA were loaded together with 212 g soy oil and respectively different quantities of NH_3OH (25%) as follows: 37.37 g, 44.09 g, 49.88 g, 57.75 g and 61.45 g. The SMA copolymer was loaded together with an identical amount of soy oil and given amounts of ammonium hydroxide together with respective amounts of water as follows: 386.2 g, 380.9 g, 374.8 g, 365.4 g and 362.8 g. As such, the total reaction loading in the autoclave is 850 g for all reactions. A reference material with pure SMA and 1.01 NH_3:MA was also synthesized.

The reaction mixture was heated to 160 °C at a rotation speed of 300 rpm, allowing for imidisation of the SMA into poly(styrene-*co*-maleimide) or SMI and simultaneous reaction with the soy oil. After an initial temperature rise to approximately 90 °C and pressure of 1 bar, the reaction mixture was heated to the final reaction temperature of 160 °C with a parallel pressure rise to 6 bar. After 4 h, the reaction mixture was cooled to room temperature and evacuated from the reactor. During the reaction, the torque for driving the stirrer at a constant speed was recorded as a measure for the evolution of the viscosity of the reaction mixture over time: typically starting from a high viscosity, the value drops after a reaction time of 3 h as an indication